No. 1 1937

THE JOURNAL
OF THE
INSTITUTE OF METALS

VOLUME LX

EDITED BY

G. SHAW SCOTT, M.Sc.

SECRETARY

LONDON
PUBLISHED BY THE INSTITUTE OF METALS
36 VICTORIA STREET, LONDON, S.W.1
1937

Form A. *(Membership Application)*

No..................

Recd................

The INSTITUTE of METALS

36 Victoria Street, London, S.W.1.

Founded 1908. *Incorporated* 1910.

To the Secretary,
The Institute of Metals.

I, the undersigned* ....

being...............years of age and desirous of becoming a †.............................. Member of the Institute of Metals, agree that if elected I will be governed by the Regulations and Bye-laws of the Institute from time to time extant and observe the obligations imposed on Members under the Articles of Association of the Institute, and that I will advance the interests of the Institute so far as may be in my power; and we, the undersigned, from our personal knowledge, do hereby recommend the said..for election.

*Name of applicant in full ....

Address..

‡Business or Profession ....

Qualification..

Degrees and/or honorific distinctions...

Dated this..........................day of.................................., 19......

....	Signatures of three Members.
....	
....	

The Council, having approved the above recommendation, declare the applicant to be duly elected as.................................. Member of the Institute of Metals.	To be filled up by the Council.
....	

36 Victoria Street,
Westminster, London, S.W.1. *Chairman.*

Dated this..........................*day of*..........................19......

† For Qualifications of Members, see Rule 6, other side.

‡ Name and address of firm (or other body) should be stated, as well as position held.

(It would be a convenience if the candidate's card were sent with this form.)

60.

EXTRACTS FROM THE RULES

(MEMORANDUM AND ARTICLES OF ASSOCIATION.)

MEMBERS AND MEMBERSHIP

Rule 5.—Members of the Institute shall be Honorary Members, Fellows, Ordinary Members or Student Members.

Rule 6.—*Ordinary Members* shall be of such age (not being less than twenty-one years) as shall be determined from time to time by the Council and/or provided in the Bye-laws. They shall be either:

(*a*) persons engaged in the manufacture, working, or use of non-ferrous metals and alloys; or

(*b*) persons of scientific, technical, or literary attainments, connected with or interested in the metal trades or with the application of non-ferrous metals and alloys, or engaged in their scientific investigations.

Student Members shall be admitted and retained as Student Members within such limits of age [17–23 years] as shall be determined from time to time by the Council and/or provided in the Bye-laws, and shall be either

(*a*) Students of Metallurgy; or

(*b*) pupils or assistants of persons qualified for ordinary membership, whether such persons are actually members of the Institute or not.

Student Members shall not be eligible for election on the Council, nor shall they be entitled to vote at the meetings of the Institute, or to nominate candidates for ordinary membership.

Rule 7.—Subject to the foregoing two clauses, and as hereinafter provided, election to membership shall be by the Council, and all applications for membership shall be in writing in the form [overleaf] marked "A," or such other form as may from time to time be authorized by the Council, and such application must be signed by the applicant and not less than three members of the Institute.

Membership shall not begin until the entrance fee and first annual subscription have been paid.

Rule 8.—Application for membership as Ordinary or Student Members shall be submitted to the Council for approval. The names of the approved applicants shall be placed on a list which shall be exhibited in the library of the Institute for at least fifteen days immediately after the Council Meeting at which such names were approved. Copies of such lists shall be supplied to the Secretaries of Local Sections of the Institute for inspection by members, and in any other manner to members as may from time to time be prescribed by the Council.

Any objection to any candidate whose name is so exhibited or notified to members shall be made in writing to the Secretary within twenty-one days of the date when the list shall first be so exhibited.

At a subsequent Council Meeting the applications for membership of persons whose names shall have been so exhibited shall be further considered, and the Council may, in their absolute discretion, elect or reject such applicants, and may refuse any application although previously approved without giving any reason for such refusal. Non-election shall not necessarily prejudice the candidate for election concerned in any future application for election.

SUBSCRIPTIONS

Rule 9.—Unless and until otherwise determined by the Council and/or provided in the Bye-laws the subscription of each Ordinary Member shall be £3 3*s.* per annum, and of each Student Member £1 1*s.* per annum. Ordinary Members shall pay an Entrance Fee of £2 2*s.* each and Student Members an Entrance Fee of £1 1*s.* each.

Rules and/or regulations may be made by the Council from time to time for the transference of Student Members from that status to that of Ordinary Members, including the fixing of an entrance fee to be payable on any such transfer of such a sum as the Council may from time to time prescribe, and/or the waiver of any such.

The Council may, in fixing such sum, take into consideration the prior payment of entrance fees by Student Members.

Subscriptions shall be payable on election and subsequently in advance on July 1st in each year, or otherwise as shall be determined from time to time by the Council and/or provided in the Bye-laws.

DUTIES AND OBLIGATIONS OF MEMBERS

Rule 12.—Every member shall be bound:

(*a*) To further to the best of his ability and judgment the objects, purposes, interests, and influence of the Institute.

(*b*) To observe the provisions of the Memorandum of Association of the Institute, the Articles, and the Bye-laws.

(*c*) To pay at all times, and in the manner prescribed, such entrance fees on election, such fees on transference from one class of membership to another, and such annual subscriptions as shall for the time being be prescribed.

(*d*) To pay and make good to the Institute any loss or damage to the property of the Institute caused by his wilful act or default.

Rule 13.—Every member, in all his professional relations, shall be guided by the highest principles of honour, and uphold the dignity of his profession and the reputation of the Institute.

[*Lafayette.*

PROFESSOR E. N. DA C. ANDRADE, F.R.S.
May Lecturer, 1937.

[*Frontispiece.*

Past-Presidents.

Sir WILLIAM HENRY WHITE, K.C.B., LL.D., D.Eng., Sc.D., F.R.S., 1908–1910 (*deceased*).

Sir GERARD ALBERT MUNTZ, Bart., 1910–1912 (*deceased*).

Professor WILLIAM GOWLAND, A.R.S.M., F.R.S., 1912–1913 (*deceased*).

Professor ALFRED KIRBY HUNTINGTON, A.R.S.M., 1913–1914 (*deceased*).

Engineer Vice-Admiral Sir HENRY JOHN ORAM, K.C.B., F.Inst.Met., F.R.S., 1914–1916.

Sir GEORGE THOMAS BEILBY, LL.D., D.Sc., F.R.S., 1916–1918 (*deceased*).

Professor Sir (HENRY CORT) HAROLD CARPENTER, M.A., Ph.D., A.R.S.M., F.Inst.Met., F.R.S., 1918–1920.

Engineer Vice-Admiral Sir GEORGE GOODWIN GOODWIN, K.C.B., LL.D., F.Inst.Met., 1920–1922.

LEONARD SUMNER, O.B.E., M.Sc., F.Inst.Met., 1922–1924.

Professor-Emeritus THOMAS TURNER, M.Sc., A.R.S.M., F.Inst.Met., 1924–1926.

Sir JOHN DEWRANCE, G.B.E., F.Inst.Met., 1926–1928.

WALTER ROSENHAIN, D.Sc., F.Inst.Met., F.R.S., 1928–1930 (*deceased*).

RICHARD SELIGMAN, Ph.nat.D., F.Inst.Met., 1930–1932.

Sir HENRY FOWLER, K.B.E., LL.D., D.Sc., 1932–1934.

HAROLD MOORE, C.B.E., D.Sc., Ph.D., F.Inst.Met., 1934–1936.

THE INSTITUTE OF METALS

OFFICERS AND COUNCIL,

1937–1938

PRESIDENT:

W. R. BARCLAY, O.B.E.

PAST-PRESIDENTS:

HAROLD MOORE, C.B.E., D.Sc., Ph.D.
RICHARD SELIGMAN, Ph.nat.D.
PROFESSOR-EMERITUS THOMAS TURNER, M.Sc., A.R.S.M.

VICE-PRESIDENTS:

H. W. BROWNSDON, M.Sc., Ph.D.
C. H. DESCH, D.Sc., Ph.D., F.R.S.
ENGINEER VICE-ADMIRAL SIR ROBERT DIXON, K.C.B., D.Eng.
PROFESSOR D. HANSON, D.Sc.
E. L. MORCOM, M.A.
LIEUTENANT-COLONEL THE HON. R. M. PRESTON, D.S.O.

HONORARY TREASURER:

JOHN FRY.

ORDINARY MEMBERS OF COUNCIL:

PROFESSOR J. H. ANDREW, D.Sc.
LIEUTENANT-GENERAL SIR RONALD CHARLES, K.C.B., C.M.G., D.S.O.
HORACE W. CLARKE.
S. F. DOREY, D.Sc., Wh.Ex.
R. GENDERS, M.B.E., D.Met.
KENNETH GRAY.
LIEUTENANT-COLONEL J. H. M. GREENLY, C.B.E., M.A.
W. T. GRIFFITHS, M.Sc.
D. J. MACNAUGHTAN.
A. H. MUNDEY.
STANLEY ROBSON, M.Sc.
C. J. SMITHELLS, M.C., D.Sc.
A. J. G. SMOUT.
D. STOCKDALE, M.A., Ph.D.
H. B. WEEKS.

EX-OFFICIO MEMBERS OF COUNCIL:

(Chairmen of Local Sections.)

W. F. BRAZENER (*Birmingham*).
H. J. GOUGH, M.B.E., D.Sc., F.R.S. (*London*).
C. E. PEARSON, M.Met. (*North-East Coast*).
H. BROWN (*Scottish*).
PROFESSOR J. H. ANDREW, D.Sc. (*Sheffield*).
HARRY DAVIES (*Swansea*).

SECRETARY:

G. SHAW SCOTT, M.Sc., F.C.I.S.

ASSISTANT SECRETARY:

S. C. GUILLAN.

TELEGRAPHIC ADDRESS:
VICTORIA 2320, LONDON.

TELEPHONE:
VICTORIA 2320.

CORRESPONDING MEMBERS TO THE COUNCIL.

Australia.

Professor J. N. Greenwood, D.Sc.,
Department of Metallurgy, The University, Melbourne, Victoria.

Canada.

Professor A. Stansfield, D.Sc., A.R.S.M., F.R.S.C.,
Chemistry Building, McGill University, Montreal.

Egypt.

H. Norman Bassett, Egyptian State Railways, Bulak, Cairo.

France.

Professor P. A. J. Chevenard,
Aciéries d'Imphy, Imphy (Nièvre).

Germany.

Dr.-Ing. Max Haas, Waltraudstr. 1, Berlin-Zehlendorf-Mitte.

Holland.

J. Hamburger, J.Azn, Maliebaan 5, Utrecht.

India.

R. Mather, B.Met., Tata Iron and Steel Company,
24 Bruce Street, Fort, Bombay.

Italy.

Dott. C. Sonnino, Corso Italia 68, Milano.

Japan.

Professor K. Tawara, D.Eng., 232 Kagomachi, Koishikawa, Tokyo.

South Africa.

Professor G. H. Stanley, D.Sc., A.R.S.M.,
University of the Witwatersrand,
P.O. Box 1176, Johannesburg, Transvaal.

Sweden.

Professor Dr. C. A. F. Benedicks, Metallografiska Institutet,
Drottninggatan 95 B., Stockholm.

Switzerland.

Professor Dr.-Ing. E. Honegger, 85 Susenbergstr., Zürich 7.

United States of America.

W. M. Corse, S.B.,
810 18th Street N.W.1, Washington, D.C.

CHAIRMEN AND HONORARY SECRETARIES OF THE LOCAL SECTIONS.

Birmingham.

Chairman : W. F. Brazener, The Mint (Birmingham), Ltd., Birmingham.

Hon. Secretary : J. W. Jenkin, B.Sc., Ph.D., Bromford Tube Co., Ltd., Erdington, Birmingham, 6.

London.

Chairman : H. J. Gough, M.B.E., D.Sc., F.R.S., Superintendent, Engineering Department, National Physical Laboratory, Teddington.

Hon. Secretary : S. V. Williams, B.Sc., Research Laboratories, The General Electric Co., Ltd., Wembley.

North-East Coast.

Chairman : C. E. Pearson, M.Met., Armstrong College, Newcastle-upon-Tyne, 2.

Hon. Secretary : O. Kennedy, Brass Department, Vickers-Armstrongs, Ltd., Elswick Works, Newcastle-upon-Tyne.

Scottish.

Chairman : H. Brown, Alexander Brown & Co., 113 West Regent Street, Glasgow, C.2.

Hon. Secretary : H. Bull, Messrs. Bull's Metal and Melloid Co., Ltd., Yoker, nr. Glasgow.

Sheffield.

Chairman : Professor J. H. Andrew, D.Sc., Department of Metallurgy, The University, St. George's Square, Sheffield, 1.

Hon. Secretary : Herbert P. Gadsby, Assoc.Met., 193 Sandford Grove Road, Sheffield, 7.

Swansea.

Chairman : Harry Davies, I.C.I. Metals, Ltd., Landore, Swansea.

Hon. Secretary : K. M. Spring, 36 Beechwood Road, Uplands, Swansea.

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CORRIGENDUM

Journal, 1931, vol. XLVI.

Page 163, line 10 from bottom. *For* "(No. 8 in the paper)" *read* "(No. 12 in the paper)."

THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS.

ANNUAL GENERAL MEETING.

The Twenty-Ninth Annual General Meeting of the Institute was held in the House of the Institution of Mechanical Engineers, Storey's Gate, Westminster, London, S.W.1, on Wednesday and Thursday, March 10 and 11, 1937, the President, Mr. W. R. Barclay, O.B.E., occupying the Chair.

Wednesday, March 10.

The Minutes of the Annual Autumn Meeting held in Paris from September 14 to 18, 1936, were taken as read, and signed by the Chairman.

The President read several letters and telegrams of apologies for absence from members of the Institute prevented from attending the meeting because of illness.

The President welcomed to the meeting members attending from overseas.

Autumn Meeting, 1938. Invitation from United States of America.

The President: Five minutes before the Council met this morning, a letter was received from America, signed by the Presidents of the American Institute of Mining and Metallurgical Engineers and the American Iron and Steel Institute. It reads:

"The American Institute of Mining and Metallurgical Engineers had occasion to extend an invitation to the Institute of Metals to hold its Autumn Meeting in the United States during the year 1932. Circumstances arising subsequent to the issue of this invitation caused a series of postponements. The American Iron and Steel Institute and the American Institute of Mining and Metallurgical Engineers are now joining in extending an invitation, in the hope that your body may find it convenient to arrange for the visit to take place during the year 1938, at such time as may accord with your custom in such matters. The month of October is suggested as favourable from the point of view of weather conditions making for comfort during the inspection of industrial establishments.

"We look forward with pleasant anticipation to your acceptance of this invitation and to the opportunities thus afforded for the establishment of personal contacts which we feel sure will inure to the benefit of our respective memberships and add to the existing cordial relations both in our common technical activities as well as in the broader field of international co-operation."

Your Council was advised by cablegram at its last meeting that this invitation was forthcoming, and unanimously agreed to accept it. I have much pleasure, therefore, in announcing that the Autumn Meeting in 1938 will take place in the United States. A similar invitation has been addressed to, and accepted by, the Iron and Steel Institute.

CO-OPERATION WITH THE IRON AND STEEL INSTITUTE AND AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS.

The PRESIDENT: At the last Annual General Meeting my predecessor announced that a discussion had just commenced with the Iron and Steel Institute, with the object of formulating a scheme of co-operation between the two bodies. I am very glad to announce that these negotiations are now completed, and that an official announcement on the subject will be issued to-day. I will not read that announcement now, but there are one or two points in it which I should like to emphasize.

The Councils of the two Institutes have agreed to a scheme for joint membership of the Institutes, not as a completed, rounded-off scheme but as a first stage in what it is hoped will be very much closer co-operation in the future. This first stage consists of an arrangement for joint membership at a reduced subscription. Members of our Institute will from now be eligible to join the Iron and Steel Institute, without any formality other than proof of membership of this Institute, at a combined subscription of £5 5*s*., to be divided between the two bodies in equal proportions. New members may benefit from this scheme if they announce their desire to do so within 12 months of election, and there will be a reduced entrance fee. An applicant may thus join both Institutes at a first outlay of £7 7*s*., including entrance fees, instead of £10 10*s*. as formerly. These privileges are also extended to Student Members of the Institute of Metals and Associate Members of the Iron and Steel Institute, but a difficulty arose here because of the different age limits in the two Institutes. Our age limit for Student Members, who must be *bona fide* students, is 26 years. The Iron and Steel Institute accepts Associate Members up to 30 years of age. Your Council does not see its way yet to alter the age limit for Student Members, but it has been agreed that each Institute is at liberty to make its own age limit for Student or Associate Members. I should like to read the penultimate paragraph of the statement to which I have referred; it reads:

> "The present scheme of co-operation follows one recently completed by the two Institutes with the American Institute of Mining and Metallurgical Engineers whereby members, associates, and student members of the British Institutes may, if under the age of 33, become Junior Foreign Affiliates of the American Institute of Mining and Metallurgical Engineers on specially favourable terms, the arrangement being reciprocal in the case of members of the American Society."

That leads me to point out that during the year we have been able to take what we consider to be very important steps to bring together in particular the younger metallurgists in the English-speaking countries, and also in both branches of metallurgy. It is hoped that this will prove in future to have been an important stage in almost obliterating, if it is possible to do so, the line of demarcation between ferrous and non-ferrous metallurgy, and it will, we hope, enable metallurgists to come into much closer contact and to share not only each other's problems but to some extent each other's successes.

The SECRETARY read in abstract the Report of Council, which had previously been circulated to members in the *Monthly Journal*.

REPORT OF COUNCIL

for the Year ended December 31, 1936.

The Council has pleasure in submitting its Annual Report covering the twenty-ninth year of the existence of the Institute of Metals. Although it is, unfortunately, not yet possible to record such a decided upward trend of membership as was hoped for on emergence from the recent period of industrial depression, it is satisfactory that our membership roll shows an increase over last year, and the financial position of the Institute is undoubtedly healthier than for some considerable time past. It is a matter for congratulation that this improvement in the finances has been achieved in spite of a membership, which is still considerably less than in the peak year of 1931.

Since industry now appears to have entered upon a period of prosperity it is to be hoped that our membership will steadily increase and so enable the Institute to render still greater service to the industry it represents.

The year has been a notable one in many ways, particularly in that the constitution and method of election of the Council has been revised and rendered potentially more fully representative of the members, and that a scheme of active co-operation with the American Institution of Mining and Metallurgical Engineers has been successfully negotiated. Another event calling for special note is the holding of the first meeting of the Institute in France. These and other matters are dealt with in detail later in this report.

Roll of the Institute.

The number of members on the Roll of the Institute on December 31 in the past five years is shown in the following table:

	Dec. 31, 1932.	Dec. 31, 1933.	Dec. 31, 1934.	Dec. 31, 1935.	Dec. 31, 1936.
Honorary Members	5	5	5	4	3
Fellows . .	8	8	7	7	8
Ordinary Members	2073	2038	1992	1987	2009
Student Members .	79	80	85	69	64
Associate Members	...	...	...	...	7
Total . .	2165	2131	2089	2067	2091

Professor R. S. Hutton, M.A., D.Sc., was appointed a Fellow of the Institute on termination of his Council membership in March after serving continuously on the Council since the Institute's foundation in 1908.

The Council is gratified that, for the first time since 1931, it is possible to record an increase in the membership. The growth in the past year—from 2067 to 2091—is slight; but there is reason to hope that, as a result both of improved industrial conditions and of certain steps taken to develop the membership, the increase will be greater during 1937.

The decrease in the number of student members is regretted. The Council attaches great importance to the steady influx of young men into the Institute's membership and is taking steps to ascertain how this flow can be made more considerable.

Obituary.

It is with much regret that the Council records the deaths of the following members: A. V. Atley; Professor Dr.-Ing. E.h. O. Bauer; R. Berrier;

Professor W. Campbell; S. Cholewiński; J. A. Crabtree; S. Fujii; L. G. Jannin; Principal C. A. King; F. G. Martin; C. W. Murray; Sir Joseph Petavel; J. Ponisovsky; C. Schwier; and A. R. Stewart.

In addition the Council record with regret the death of Professor H. Le Chatelier an Original Member of the Institute, and one of its few Honorary Members, a distinction that he held since 1912. He served for over ten years as Honorary Corresponding Member to the Council for France.

CONSTITUTION OF THE COUNCIL.

The scheme that was approved last March for the limitation of the maximum period of continuous service on the Council became operative during the past year. As a result, several members who had served on the Council for many years retired, and the vacancies thus created were filled by new members whose fresh outlook has been stimulating and helpful. The presence on the Council of the Chairmen of the Local Sections has been particularly valuable.

CO-OPERATION WITH OTHER INSTITUTES.

A scheme of co-operation with the American Institute of Mining and Metallurgical Engineers was completed in accordance with which members or student members of the Institute of Metals under the age of 33 years became eligible for election as Junior Foreign Affiliates of the American Institute, whilst members of the American body not over that age can become associated with the Institute of Metals—each on payment of an annual subscription of 21*s*. Several enrolments on both sides have been effected.

The general principles of a scheme of co-operation with the Iron and Steel Institute have been agreed, and it is hoped that a full announcement on the subject will be possible at an early date. It is the earnest belief of the Council that the proposals, when carried into effect, will have the result of increasing the influence and membership of both bodies.

MEETINGS OF THE INSTITUTE.

The Annual General Meeting was held in London on March 11 and 12, being preceded on March 10 by a Joint Meeting with several other institutions to discuss the subject of "Metallic Wear." The Annual Dinner was held on March 11. During the meeting visits were paid to the British Broadcasting Corporation, Greenwich Observatory, Greenwich Fuel Research Station, and to Fleet Street newspaper offices.

The May Lecture was delivered in London on May 6 by Mr. C. C. Paterson, O.B.E., on "The Escape of Electricity from Metals: Its Practical Consequences."

The first gathering of members to take place in France was held in Paris, from September 14 to 18, the occasion being the 28th Autumn Meeting. The Institute is greatly indebted to its Paris friends for the admirable arrangements made for the visiting members' entertainment and enjoyment.

The meeting opened with the delivery, by Professor P. A. J. Chevenard, of the Autumn Lecture on "The Scientific Organization of Works." After the discussion of papers at two morning sessions, visits were paid to works and other places of interest in and around Paris, Rouen, and Havre. The meeting was well attended by members from fourteen countries.

PUBLICATIONS.

The various changes in the form and variety of the Institute's publications to which reference was made in the Report for 1935 have, it is believed, fully justified themselves, and there can be no doubt that the influence of the Institute, particularly through its *Monthly Journal*, is steadily increasing.

Three bound volumes—two of the *Journal* and one of *Metallurgical Abstracts*—were issued during 1936. The *Monthly Journal* also appeared regularly. Work on the Decennial Index continued; it is hoped to issue the "Names" Volume in 1937. The delay in publication, which has been unavoidable, is regretted.

A new publication, being the first of a "Monograph and Report series," was issued. This is a book of 120 pages by Dr. W. Hume-Rothery entitled "The Structure of Metals and Alloys." Copies were distributed free to members who asked for them; a large number of others were sold at 3*s.* 6*d.* each. The demand for the book and the appreciative nature of the many reviews of it that have appeared in the technical press at home and abroad, indicate that there was a distinct need for an up-to-date publication of this character.

A List of Members was published after a lapse of several years. It is hoped in future to issue the List yearly, or at least once every two years. The new list reveals the large number of the Institute's members resident outside the British Isles—approximately 800 out of a total of 2091. The United States membership is the biggest overseas at 267; that of Germany totals 103, Australia 54, Japan 46, France 43, and U.S.S.R. 26. In all, 42 countries are represented in the list of members.

LOCAL SECTIONS.

The activities of the six Local Sections—and of the associated Manchester Metallurgical Society—have been effectively continued throughout the past session. Their requirements and interests have been kept fully before the notice of the Council as a result of the new arrangement whereby each Local Section Chairman has a seat on the Council; also as a result of a round of visits paid to the Local Sections by the President who was thus enabled more fully to appreciate the excellent work of the various local committees. A notable feature of the programmes of the sections has been the number of meetings arranged jointly with other bodies, including the Iron and Steel Institute, the Institute of British Foundrymen, the Society of Chemical Industry, the Institution of Automobile Engineers, and the Institution of Engineers and Shipbuilders in Scotland. Visits to works and to the National Physical Laboratory were arranged.

LIBRARY.

Books added to the Library during the past year totalled 107; the number of periodicals now regularly received is 502. The number of books and periodicals issued on loan was 3689 as compared with 2000 in the previous year. Members have made increasing use of the service by which books and periodicals can be loaned to them through the medium of the post.

Following the appearance of each issue of the *Monthly Journal* many requests are received from members for the loan of publications mentioned in the *Metallurgical Abstracts* section. These can generally be supplied either from the Institute Library or from the Science Library at South Kensington. The willing assistance of the officials of that Library in helping the Institute to meet the requirements of its members is gratefully acknowledged.

EDUCATIONAL TOURS.

Owing to the official visit of the Institute to France for its Autumn Meeting, no students' tour was arranged for 1936. The Meetings Committee has, however, a scheme under consideration for the continuance of these educational visits which have proved so valuable a feature of the Institute's work in previous years.

COMMITTEES.

The following Committees were appointed for the year 1936–1937 :

Finance and General Purposes Committee.

Charles, Lieut.-General Sir Ronald.
Clarke, H. W.
Dixon, Engineer Vice-Admiral Sir Robert (*Chair*).
Greenly, Lieut.-Colonel J. H. M.
Morcom, E. L. (*Vice-Chairman*).
Mundey, A. H.
Preston, The Hon. R. M.
Seligman, Dr. R.
Turner, Professor T.

Ex-officio :

The President.
Immediate Past-President.
Hon. Treasurer.
Chairman, Publication Committee.

Local Sections Committee.

Andrew, Professor J. H.
Brownsdon, Dr. H. W.
Gray, Kenneth.
Greer, H. H. A.
Griffiths, W. T.
Hanson, Professor D. (*Chair*).
Haughton, Dr. J. L.
Mundey, A. H.
Thompson, Professor F. C.

Ex-officio :

The President.
Immediate Past-President.
Hon. Treasurer.
Local Reception Committee's Representative.
Chairman and Secretary of :
  Birmingham Local Section.
  London Local Section.
  North-East Coast Local Section.
  Scottish Local Section.
  Sheffield Local Section.
  Swansea Local Section.

Meetings Committee.

Andrew, Professor J. H.
Brazener, W. F.
Brownsdon, Dr. H. W. (*Chair*).
Dorey, Dr. S. F.
Gwyer, Dr. A. G. C.
Hanson, Professor D.
Haughton, Dr. J. L.
Weeks, H. B.

Ex-officio :

The President.
Immediate Past-President.
Chairman, Membership Committee.
Chairman, Publication Committee.
Local Sections Committee's Representative.
Local Reception Committee's Representative.

Membership Committee.

Andrew, Professor J. H.
Charles, Lieut.-General Sir Ronald.
Genders, Dr. R.
Gray, Kenneth (*Chair*).
Macnaughtan, D. J.
Morcom, E. L.
Mundey, A. H.
Seligman, Dr. R.
Weeks, H. B.

Ex-officio :

The President.
Immediate Past-President.
Local Sections Committee's Representative.

Publication Committee.

Brownsdon, Dr. H. W.
Desch, Dr. C. H.
Dorey, Dr. S. F.
Genders, Dr. R.
Gwyer, Dr. A. G. C.
Hanson, Professor D.
Haughton, Dr. J. L.
Murphy, A. J.
Seligman, Dr. R.
Smith, Dr. S. W.
Smithells, Dr. C. J. (*Chair*).
Sutton, Dr. H.
Turner, Professor T.

Ex-officio :

The President.
Immediate Past-President.
Chairman, Finance and General Purposes Committee.

REPRESENTATIVES.

The following representatives of the Institute were appointed by the Council :

AMERICAN SOCIETY FOR TESTING MATERIALS (Committee on Die-Cast Metals and Alloys) : Mr. A. H. Mundey.

BRITISH NON-FERROUS METALS RESEARCH ASSOCIATION SPECIAL RESEARCH SUB-COMMITTEE (Institute of Metals Corrosion Committee) : Professor Sir Harold Carpenter, Dr. Richard Seligman, and Mr. H. B. Weeks.

BRITISH STANDARDS INSTITUTION (Aircraft Technical Committee AC/16, Copper Alloys) : Mr. A. J. G. Smout.

BRITISH STANDARDS INSTITUTION (Industry Committee NF/–, Non-Ferrous Metallurgy) : Mr. W. R. Barclay, Professor R. S. Hutton, Mr. H. B. Weeks, and Mr. G. Shaw Scott.

BRITISH STANDARDS INSTITUTION (Technical Committee ME/25, Brinell Hardness Testing) : Dr. H. Moore.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/18, Cast Aluminium and Light Alloys) : Dr. L. Aitchison.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/14, Cast Copper Alloys) : Mr. H. B. Weeks (*Chairman*), Mr. A. J. G. Smout.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/12, Copper for Electrical Purposes) : Mr. A. J. G. Smout, Mr. G. Shaw Scott.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/16, Copper Alloy Rods, Bars, Sections, and Forgings) : Mr. A. J. G. Smout.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/15, Copper Alloy Strip Sheets, Plates, &c.) : Mr. A. J. G. Smout.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/17, Copper Alloy Tubes) : Mr. A. J. G. Smout.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/20, Lead and Lead Alloys for Cable-Sheathing) : Mr. H. C. Lancaster.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/11, Manufactured Copper) : Mr. H. J. Miller, Mr. A. J. G. Smout, Mr. G. Shaw Scott.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/10, Nickel and Nickel Alloys : Mr. W. R. Barclay.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/13, Raw Copper) : Mr. A. J. G. Smout, Mr. G. Shaw Scott.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/9, Solders) : Professor R. S. Hutton.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/19, Wrought Aluminium and Light Alloys) : Dr. L. Aitchison.

BRITISH STANDARDS INSTITUTION (Technical Committee NF/8, Zinc) : Professor T. Turner.

CITY AND GUILDS INSTITUTE (Advisory Committee on Metallurgy) : Professor T. Turner.

CONSTANTINE TECHNICAL COLLEGE, MIDDLESBROUGH (Foundry Advisory Committee) : Professor J. H. Andrew and Mr. G. Mortimer.

INTERNATIONAL ASSOCIATION FOR TESTING MATERIALS, 1937 (Joint Committee on Materials and Testing) : Dr. H. Moore.

INTERNATIONAL ASSOCIATION FOR TESTING MATERIALS, 1937 (Organizing and Reception Committee) : Mr. W. R. Barclay.

MANCHESTER METALLURGICAL SOCIETY : Professor F. C. Thompson.

PARLIAMENTARY SCIENCE COMMITTEE : Dr. H. Moore and Mr. G. Shaw Scott.

SIR CHARLES PARSONS MEMORIAL COMMITTEE : Mr. W. R. Barclay.

PROFESSIONAL CLASSES AID COUNCIL : Mr. H. B. Weeks.

MEETINGS OF FOREIGN SOCIETIES.

During the year the Institute has been represented by the President at a number of meetings abroad of societies and organizations having interests closely akin to our own, these meetings including:

(*a*) The Seventy-Fifth Anniversary gatherings of the Svenska Teknologföreningens, held in Stockholm, at which a congratulatory address was presented from the Institute;

(*b*) The Eightieth Anniversary meeting of the Verein Deutsche Ingenieure at Darmstadt, held in conjunction with the celebrations of the Centenary of the Darmstadt Technische Hochschule;

(*c*) The Annual Meetings of the Deutsche Gesellschaft für Metallkunde, the President of which this year is one of our own esteemed German members, Dr. W. J. P. Rohn;

(*d*) The Autumn Meetings of the American Institute of Mining and Metallurgical Engineers (which included the sectional gathering of the Institute of Metals Division) at Cleveland, Ohio, U.S.A.

CORRESPONDING MEMBERS TO THE COUNCIL.

The Council again desires to extend its thanks to the following members who have acted as Corresponding Members during the past year: Mr. H. Norman Bassett (*Egypt*); Professor Dr. C. A. F. Benedicks (*Sweden*); Professor P. A. J. Chevenard (*France*); Mr. W. M. Corse, S.B. (*United States of America*); Professor J. Neill Greenwood, D.Sc. (*Australia*); Dr.-Ing. M. Haas (*Germany*); Mr. J. Hamburger, J.Azn. (*Holland*); Professor Dr.-Ing. E. Honegger (*Switzerland*); Mr. R. Mather, B.Met. (*India*); Dott. C. Sonnino (*Italy*); Professor G. H. Stanley, D.Sc., A.R.S.M. (*South Africa*); Professor A. Stansfield, D.Sc., A.R.S.M., F.R.S.C. (*Canada*); and Professor K. Tawara, D.Eng. (*Japan*).

Signed on behalf of the Council,

W. R. BARCLAY, *President.*
C. H. DESCH, *Vice-President.*

January 14, 1937.

G. SHAW SCOTT, *Secretary and Editor.*

APPENDIX.

LOCAL SECTIONS' PROGRAMMES, 1936–1937.

BIRMINGHAM LOCAL SECTION.

Chairman : W. F. Brazener.

Hon. Secretary : J. W. Jenkin, Ph.D., B.Sc., Messrs. Bromford Tube Company, Ltd., Erdington, Birmingham.

Programme.

1936.	
Oct. 1.	G. A. V. Russell, Wh.Ex. "Strip Sheet Production." (Joint meeting with the Iron and Steel Institute.)
Oct. 22.	W. L. Govier. "Non-Ferrous Metal Tubes."
Nov. 5.	J. A. Jones, M.Sc. "Present Trend in Alloy Constructional Steels."
Dec. 3.	Howard E. Collier, M.C., M.B., Ch.B. "Some Aspects of Industrial Hygiene."
Dec. 15.	N. P. Inglis, D.Sc. "Metallurgical Problems in the Chemical Industry."
1937.	
Jan. 7.	J. C. Chaston, B.Sc., A.R.S.M. "Powder Metallurgy."
Jan. 29.	J. G. Pearce, M.Sc. "Special Cast Irons."
Feb. 19.	H. W. G. Hignett, B.Sc. "Non-Ferrous Welding."
Mar. 4.	Ulick R. Evans, D.Sc., M.A. "Corrosion."
Mar. 16.	Open Discussion : "Lubrication in the Cold-Working of Metals." Introduced by H. W. Brownsdon, Ph.D., M.Sc., and F. J. Slee, B.A., B.Sc.
Apl. 1.	B. Bagshawe. "Modern Methods of Alloy Steel Analysis."

All meetings are held in the James Watt Memorial Institute, Birmingham, at 7 p.m.

LONDON LOCAL SECTION.

Chairman : H. J. Gough, M.B.E., D.Sc., F.R.S.

Hon. Secretary : S. V. Williams, B.Sc., Research Laboratories of The General Electric Co., Ltd., Wembley, Middlesex.

Programme.

1936.	
Oct. 15.	H. J. Gough, M.B.E., D.Sc., F.R.S. Chairman's Address : "The Common Field of the Engineer and Metallurgist." (Meeting held at the National Physical Laboratory, Teddington, Middlesex.)
Nov. 12.	W. H. Hatfield, D.Met., F.R.S. "Research in the Iron and Steel Industry." (Meeting held at the Royal School of Mines, South Kensington, S.W.7, at 8 p.m.)
Nov. 25.	Supper-Dance. (Thames House, Millbank, 7.30 p.m.)
Dec. 2.	W. T. Griffiths, M.Sc. "Some Impressions of Industry in the U.S.S.R." (Joint meeting with the London Branch of the Institute of British Foundrymen, held at the Charing Cross Hotel, 8 p.m.)
1937.	
Jan. 14.	R. D. Burn, M.Sc. "Copper."
Feb. 11.	C. H. Desch, D.Sc., Ph.D., F.R.S. "The Constitution of Alloys."
Mar. 18.	J. H. Partridge, B.Sc., Ph.D. "Refractories."
Apl. 8.	Annual General Meeting and Open Discussion.

The Meetings are held in the Rooms of the Society of Motor Manufacturers and Traders, Ltd., 83 Pall Mall, London, S.W.1 (unless otherwise stated), at 7.30 p.m.

MANCHESTER METALLURGICAL SOCIETY

(in association with the Institute of Metals).

President: Professor F. C. Thompson, D.Met.

Hon. Secretary: J. A. Tod, B.Sc., Messrs. I.C.I. Metals, Ltd., Broughton Copper Works, Manchester.

Programme.

1936.
Oct. 21. Professor F. C. Thompson, D.Met. Presidential Address.
Nov. 4. Joint meeting with the Institute of Metals.
Nov. 18. Discussion on Microscopy opened by J. Dickson Hannah, M.Sc.Tech.
Dec. 2. W. Andrews, B.Met. "Modern Welding."
1937.
Jan. 20. Joint meeting with the Iron and Steel Institute.
Feb. 3. Papers by junior members.
Feb. 17. H. C. Hall, M.Met. "Metallurgy in the Automobile and Aircraft Industries."
Mar. 3. W. H. Hatfield, D.Met., F.R.S. "Corrosion."
Mar. 17. A. G. Robiette, B.Sc. "The Electric Bright-Annealing of Metals." Preceded by Annual Meeting.

The Meetings are held in the Constitutional Club, St. Ann's Street, Manchester, at 7 p.m.

NORTH-EAST COAST LOCAL SECTION.

Chairman: H. Dunford Smith, M.Sc.

Hon. Secretary: C. E. Pearson, M.Met., Armstrong College, Newcastle-upon-Tyne, 2.

Programme.

1936.
Oct. 13. H. Dunford Smith, M.Sc. Chairman's Address: "Solders."
Nov. 10. M. Milbourn, A.R.C.S., B.Sc. "Spectrographic Analysis of Metals."
Nov. 27. J. W. Mellor, D.Sc., and A. T. Green. "Refractories." (Held in the Chemical Lecture Theatre, Armstrong College. Joint meeting with the Newcastle Branch of the Society of Chemical Industry.)
Dec. 19. P. B. Robinson, M.Met. "Recent Improvements in Refractory Materials." (Joint Meeting with the Newcastle Branch of the Institute of British Foundrymen.)
1937.
Jan. 11. M. A. W. Brown, M.Sc. "Shipyard Metals." (Joint Meeting with the Newcastle Branch of the Institute of Chemistry.)
Mar. 9. J. E. Newson, M.Met. "Large Non-Ferrous Castings." Annual General Meeting.

The Meetings are held in the Electrical Engineering Lecture Theatre, Armstrong College, Newcastle-upon-Tyne (unless otherwise stated), at 7.30 p.m.

SCOTTISH LOCAL SECTION.

Chairman: J. W. Donaldson, D.Sc.

Hon. Secretary: H. Bull, Bull's Metal & Melloid Co., Ltd., Yoker, Glasgow.

Programme.

1936.
Oct. 13. Works Visit, Babcock & Wilcox, Ltd., Dumbarton.
Nov. 16. *W. R. Barclay, O.B.E. "The Nickel Industry—Some Recollections."
Dec. 14. W. E. Ballard. "Metal Spraying by the Wire Process."

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* Owing to the President's unavoidable detention in America his place was taken by Mr. J. O. Hitchcock who gave a paper on "Simple and Complex Alloys of Copper with Nickel."

1937.
Jan. 11. A. J. Murphy, M.Sc. "Magnesium Alloys."
Feb. 15. D. P. C. Neave, M.A. "Copper and Its Alloys in Automobile Design." (Joint Meeting with the Institution of Automobile Engineers, Scottish Centre.)
Mar. 9. U. R. Evans, D.Sc., M.A. "Some Aspects of Metallic Corrosion." (Joint Meeting with the Institution of Engineers and Shipbuilders in Scotland.)

All Meetings, except opening meeting, are held in the Rooms of the Institution of Engineers and Shipbuilders in Scotland, 39 Elmbank Crescent, Glasgow, at 7.30 p.m.

The Works Visit took place at 7.30 p.m.

SHEFFIELD LOCAL SECTION.

Chairman: Professor J. H. Andrew, D.Sc.

Hon. Secretary: H. P. Gadsby, Assoc.Met., 193 Sandford Grove Road, Sheffield, 7.

1936. Programme.
Oct. 9. Professor J. H. Andrew, D.Sc. Chairman's Address: "The Trend of Research in Non-Ferrous Metallurgy."
Nov. 13. L. B. Williams, B.A., B.E. "Lead Mining in Derbyshire."
Dec. 11. M. Cook, M.Sc., Ph.D. "Wrought Nickel Silver Alloys."

1937.
Jan. 14. S. Wernick, Ph.D. "Technical and Industrial Development in the Electrochemical Surface Treatment of Metals."
Feb. 12. Conjoint Meeting with the South Yorkshire Section of the Institute of Chemistry.
Mar. 12. Professor F. C. Thompson, D.Met., M.Sc. "Some Recent Researches on Wire-Drawing." Annual General Meeting.

The Meetings are held in the Non-Ferrous Section of the Applied Science Department of the University, St. George's Square, at 7.30 p.m.

SWANSEA LOCAL SECTION.

Chairman: Roosevelt Griffiths, M.Sc.

Hon. Secretary: K. M. Spring, 36 Beechwood Road, Uplands, Swansea, S. Wales.

1936. Programme.
Oct. 12. G. D. Bengough, M.A., D.Sc. "Some Objectives of Corrosion Research."
Nov. 10. C. J. Smithells, M.C., D.Sc. "Gases and Metals."
Dec. 8. Film Display of Metallurgical Interest.

1937.
Feb. 9. W. R. Barclay, O.B.E. "Strip Rolling."
Mar. 16. D. J. Macnaughtan. "Some Trends in the Use of Tin in Modern Engineering Practice."
Apl. 13. H. W. Brownsdon, M.Sc., Ph.D. "Metallic Wear." Annual General Meeting.

All Meetings are held at the Y.M.C.A., Swansea, at 6.30 p.m.

The PRESIDENT proposed, and Mr. HORACE W. CLARKE, Member (Birmingham) seconded the motion for the adoption of the report.

Mr. JOHN CARTLAND, M.C., M.Sc., Member (London), expressed the hope that the Council would not lose the benefit of the advice of two members, Dr. A. G. C. Gwyer and Dr. J. L. Haughton, who retired from the Council in accordance with the Rules.

The PRESIDENT, in reply, said that valuable though the services of past Members of Council had been, those of potential Members of Council were not less valuable. There were many members, whose names would find instant acceptance, who were waiting for seats on the Council. The advice of the retiring members would still be at the Council's disposal.

The motion for the adoption of the Report was then put to the meeting and carried unanimously.

In the absence of the Honorary Treasurer, the Chairman of the Finance Committee (Engineer Vice-Admiral Sir ROBERT DIXON, K.C.B., D.Eng.), then presented the Treasurer's Report:

REPORT OF THE HONORARY TREASURER

(MR. JOHN FRY)

For the Financial Year ended June 30, 1936.

The Institute's financial position, as revealed in the accounts herewith presented for the year ended June 30 last, is a little more encouraging than that indicated in the accounts of recent years, though there is nothing outstanding to report.

An increase of £167 in the annual subscriptions has assisted the income, though half a dozen minor increases in expenditure make the final surplus of £81 less than that of the previous twelve months. This result is due to the fact that the Council authorized additional expenditure on membership development. This special work involved extra payments under the headings of wages, stationery, and postage, which expenditure it is believed will prove of benefit to the Institute in due course.

As usual, the *Journal* Account is shown separately. It shows a slight increase in expenditure of £69 due not to the *Journal* and *Metallurgical Abstracts*—which actually cost less than usual—but primarily to the issue of special publications costing £230 (but which are expected to pay for themselves in due course). An improvement in the sales of the *Journal* (£64) and advertisements (£94) encourages us for the future. Entrance fees (£190) have been carried direct to the Balance Sheet as previously, and the Entrance Fee Fund now stands at £1961.

Other items of income and expenditure call for little comment in this Report.

The actual cash position has been considerably strengthened in the year under review. The Council feels that after the long period of the depression the corner has been turned and that the finances of the Institute are slowly mending. But the Institute requires stronger reserves behind it before it can be considered to be on a sound basis. At the moment the Council, and in particular the President, are engaged in a determined effort to strengthen the financial position of the Institute.

THE INSTITUTE OF METALS

BALANCE SHEET AS AT JUNE 30, 1936.

30.6.1935. £	£	LIABILITIES.	£	s.	d.	£	s.	d.
		Creditors :						
		Sundry Creditors for accrued Expenses,						
	111	*less* proportion in advance	91	13	10			
	790	*Journal* Accounts	730	15	0			
	797	Subscriptions paid in advance	871	0	9			
	—	Entrance Fees paid in advance	7	7	0			
1,698						1,700	16	7
	157	*Bank overdrawn.*						
	5	Less *Dep. a/c.*						
	152							
	14	Less *Cash in hand.*						
138								
		Entrance Fees Account :						
	1,538	Balance as at June 30, 1935	1,770	5	5			
	232	Amount receivable for year to June 30, 1936	190	15	0			
1,770						1,961	0	5
		Industrial Fund Subscription Account :						
21		Balance as at June 30, 1935	21	0	0			
		Contributions during year	225	15	0			
						246	15	0
		Woodhouse Fund :						
13		Balance at June 30, 1936				13	8	6
		House Fund :						
1,050		Balance at June 30, 1936				1,049	19	8
		Silver Jubilee Fund :						
672		Balance at June 30, 1936				672	5	0
		Excess of Assets over Liabilities :						
	1,448	Balance at June 30, 1935	1,613	10	9			
	166	*Add* Excess of Income over Expenditure for the year to June 30, 1936	85	9	8			
1,614						1,699	0	5
£6,976						£7,343	5	7

30.6.1935. £	£	ASSETS.	£	s.	d.	£	s.	d.
		Office Furniture :						
200		Balance at June 30, 1935				200	0	0
		Library Books, &c. :						
100		Balance at June 30, 1935				100	0	0
		Sundry Debtors :						
	17	For Entrance Fees	8	8	0			
	387	,, Subscriptions	357	6	3			
	273	,, *Journal* Accounts (Sales and Advertisements)	206	17	3			
	677		572	11	6			
	148	*Less* Reserve for Doubtful Subscriptions	138	12	0			
529						433	19	6
		Stock of Journals :						
1		At nominal Valuation				1	0	0
		Investments :						
4,411		£4,438 16*s.* 8*d.* 3½% War Loan at cost				4,410	14	10
		Woodhouse Fund :						
13		Balance at Lloyds Bank, Ltd.				13	8	6
		House Fund :						
	1,045	£1000 3½% War Loan at cost	1,044	19	1			
	5	Balance at Lloyds Bank, Ltd.	5	0	7			
1,050						1,049	19	8
		Silver Jubilee Fund :						
672		£672 5*s.* 0*d.* 3½% War Loan at cost				672	5	0
		Cash :						
		Lloyds Bank, Ltd. :						
—		Current Account	449	15	2			
—		Deposit Account	4	12	11			
—		Petty Cash in hand	7	10	0			
						461	18	1
£6,976						£7,343	5	7

W. R. BARCLAY } *Members of Council.*
JOHN FRY }
G. SHAW SCOTT, *Secretary.*

We report that we have obtained all the information and explanations we have required. In our opinion the above Balance Sheet is properly drawn up so as to exhibit a true and correct view of the state of the affairs of the Institute of Metals as on June 30, 1936, according to the best of our information and from the explanations given to us and as shown by the Books of the Institute.

POPPLETON & APPLEBY, AUDITORS,
BIRMINGHAM, LONDON, AND CARDIFF.

November 30, 1936.

THE INSTITUTE OF METALS

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR TO JUNE 30, 1936.

30.6.1935. £		£	s.	d.
2,115	To Salaries	2,125	0	0
965	,, Wages and National Insurance	1,036	4	0
1,229	,, *Journal* Account	1,298	17	3
811	,, Rent, Telephone, Lighting, and Insurance	800	13	8
154	,, Printing and Stationery	101	2	7
375	,, Postages, Travelling, and Sundry Expenses	409	15	11
68	,, Library Expenses	69	18	6
163	,, Subscriptions and Grant to Local Sections	127	10	0
92	,, Expenses of Meetings	115	1	5
20	,, Repairs and Renewals	18	9	4
8	,, Bank Charges	2	17	0
26	,, Audit Fee and Legal Charges	30	7	10
166	,, Excess of Income over Expenditure	85	9	8
£6,192		£6,311	7	2

30.6.1935. £		£	s.	d.
5,918	By Annual Subscriptions	6,085	13	11
179	,, Interest on War Loan	178	17	8
35	,, House Fund Rent	35	0	0
16	,, Sundry Donations	9	9	0
44	,, Miscellaneous Receipts	2	6	7
£6,192		£6,311	7	2

JOURNAL ACCOUNT FOR THE YEAR ENDED JUNE 30, 1936.

£	£		£	s.	d.	£	s.	d.
1		To Stock of *Journals* at June 30, 1935				1	0	0
	3,098	,, Cost of Production and Abstractors' Fees, Payments made during year	3,308	7	0			
	773	Amounts owing at June 30, 1936	697	15	2			
	3,871		4,006	2	2			
	867	*Less* owing at June 30, 1935	772	19	1			
3,004						3,233	3	1
£3,005						£3,234	3	1

£	*Advts.* £	*Sales.* £		*Sales.*			*Advertisements.*					
					s.	d.	£	s.	d.	£	s.	d.
			By Net Sales of *Journals* and Advts.:									
	676	1,063	Receipts during year	1,189	12	4	810	2	6			
	198	74	Amounts owing June 30, 1936	11	11	11	195	5	4			
	874	1,137		1,201	4	3	1,005	7	10			
	161	75	*Less* Amount owing June 30, 1935	74	6	3	198	0	0			
	713	1,062		1,126	18	0	807	7	10			
1,775										1,934	5	10
1			,, Stock of *Journals* at June 30, 1935							1	0	0
1,229			Net Cost of *Journal* for Year							1,298	17	3
£3,005										£3,234	3	1

THE INSTITUTE OF METALS

JOURNAL ACCOUNT FOR THE YEAR ENDED JUNE 30, 1936.

30.6.1935. £	£		£	s.	d.	£	s.	d.
1		To Stock of *Journals* at June 30, 1935 .				1	0	0
		,, Net Cost of Production of *Journals* for the Year to June 30, 1936 :						
	1,343	*Monthly Journal*	1,297	8	7			
	631	Half-Yearly *Volumes* . . .	611	1	4			
	306	*Metallurgical Abstracts* Volume (bound)	344	2	5			
	145	Packing and Despatch of Bound Volumes (5)	216	5	8			
	—	Special Publications . . .	230	15	9			
	16	Advance and Press Copies of Papers	17	0	1			
	26	Authors' Copies of Papers . .	22	13	1			
	482	Abstractors' and Reviewers' Fees .	450	17	10			
	19	Binding of Volumes for Sale . .	14	0	3			
	17	Rent of Stock space (at printers) .	18	1	2			
	3	Translation of Papers . .	6	14	0			
	16	Miscellaneous . . .	4	2	11			
3,004						3,233	3	1
£3,005						£3,234	3	1

30.6.1935. £		£	s.	d.
1,062	By Net Sales of Publications, &c.	1,126	18	0
713	,, Net Proceeds of Advertisements	807	7	10
1	,, Stock of *Journals*	1	0	0
1,229	,, Net Cost of *Journal* for Year transferred to Income and Expenditure Account	1,299	17	3
£3,005		£3,234	3	1

HOUSE FUND ACCOUNT FOR THE YEAR ENDED JUNE 30, 1936.

30.6.1935. £		£	s.	d.
35	To Rent paid to the Institute of Metals	35	0	0
1,050	,, Balance at June 30, 1936	1,049	19	8
£1,085		£1,084	19	8

30.6.1935. £		£	s.	d.
1,050	By Balance at June 30, 1935	1,049	19	8
35	,, Interest on War Loan	35	0	0
£1,085		£1,084	19	8

THE WOODHOUSE BENEVOLENT FUND.

£		£	s.	d.
13	By Balance at June 30, 1936	13	8	6

THE SILVER JUBILEE FUND.

£		£	s.	d.
672	By Balance at June 30, 1936	672	5	0

Engineer Vice-Admiral **Sir Robert Dixon**, K.C.B., D.Eng., Chairman of the Finance Committee (moving the adoption of the Report): The Report of the Honorary Treasurer deals in some detail with the items of expenditure, and you will notice that Mr. Fry, who is a very cautious man, agrees that the outlook is more encouraging. This is a matter of considerable interest to the Finance Committee, upon which the unpleasant duty devolves of making certain, if possible, that expenditure does not exceed income.

There are three main items of expenditure: salaries, wages, and publications. I have heard many criticisms to the effect that the expenditure on salaries and wages is high compared with that on publications. On the face of it that appears to be true, but the accounts do not properly place the situation before you. We do not have a system of costing such as would be usual in a commercial undertaking. Actually the expenditure on publications is much greater than appears from the accounts, because about one-half of the time of the staff is spent on publications, and therefore about 50 per cent. of the salary charges are really publication charges. I would stress this point in view of the many criticisms I have heard. You will agree, I am sure, that the labourer is worthy of his hire. I am convinced that the salaries of the members of the staff are by no means excessive.

Our financial position, as I have said, has much improved, and, thanks to the efforts of the President, our future outlook is very bright. As most of you know, the President has a scheme for an Endowment Fund which will make the financial position of the Institute very much better than it has ever been before.

Mr. D. P. C. **Neave**, Member (in seconding the motion): I am very impressed by the good value which we receive in return for our subscriptions. Having had something to do with the production of technical books, I am especially impressed by the economical manner in which the finances of our *Journal* are conducted.

The motion for the adoption of the Report was then put to the meeting and carried unanimously.

Endowment Fund.

The **President**: Some time during last year I had occasion to study very closely the financial position of the Institute, particularly in relation to publications. We are entering upon, and indeed have already entered upon, a period of very considerable activity, not only industrially but scientifically, in the field of non-ferrous metallurgy, and unquestionably we shall find the resources of our *Journal* strained to the utmost to give publicity to the matter which is continually being brought before us. The Publications Committee has a very high standard, but nevertheless it very often accepts papers with an uneasy feeling that it may be pulled up at any time by the Finance Committee, which has a strict budget allocation for publications. That was one point.

Another was that a study of the financial position showed very clearly that for a body which has been in existence for nearly thirty years our resources are exceedingly slender. The margin of net assets over liabilities is very small indeed. Further, we have just passed through a period of serious depression, and, although we hope that we shall not have another quite so serious, we are compelled to admit the possibility of repeated periods of depression. In a period of relative prosperity we must therefore, I think, endeavour to provide some insurance against periods of adversity. That is common sense.

The last point that I would emphasize in this connection is that in this

Institute we have never given industry a real opportunity to show its appreciation of our efforts. A large proportion—I should think well over 80 per cent.—of our members are those who are in salaried positions in industrial or academic circles. I need not emphasize that salaried positions do not as a rule carry a share of the fairly adequate profits which are being made just now in the non-ferrous metallurgical industries, so that I think that it is only right that we should give industry an opportunity to show that it appreciates the work of the Institute of Metals.

Personally, I was quite prepared to give them that opportunity, even if it meant that they would adversely criticize some of our activities. I ventured to bring this matter before the Council a few months ago, with the suggestion that they should authorize a scheme for the creation of an Endowment Fund of not less than £20,000. In doing that I had made what I felt to be a very careful estimate of what would be possible. It is not what would be ideal, because I think that the Institute of Metals is worth much more than £20,000 to industry; I should put the figure in the neighbourhood of £50,000, or even £100,000. The question is, however, what is reasonably possible, taking everything into consideration.

I had conversations at the same time with a few leaders of industry, and I should like at once to pay a very warm tribute to the kindness of those to whom I spoke and with whom I discussed the matter in those early days. I would particularly mention Sir Harry McGowan, Chairman of Imperial Chemical Industries, who showed very great sympathy with the Institute, and the President of my own Company, Mr. Stanley, both of whom gave me an appreciable amount of their time. Both these gentlemen contributed fairly substantially. I would also specially mention the kindness and sympathy shown by Mr. Horace W. Clarke, who occupies a most important position in the Trade Associations in Birmingham, and I do not forget that, in a most interesting conversation, Mr. Murray Morrison, Managing Director of The British Aluminium Company, Ltd., also gave me very great encouragement and ended the interview by saying " If you are going to do this, do it now. This is the psychological moment; if you do not do it now, you will never do it at all."

I have to ask this General Meeting to-day to accept the decision of the Council to launch an appeal to industry generally for an Endowment Fund of not less than £20,000, and in doing so I am able to announce preliminary subscriptions which amount to £13,883, details of which will be circulated to members in due course.

A formal appeal has been printed, but it is the desire of the Council, with which I cordially associate myself, that no pressure whatever shall be brought to bear on individual members of the Institute. The suggestion has been made to me that we might ask the 2000 members of the Institute to contribute an extra guinea each. The Council does not approve that suggestion, but it does, of course, welcome very heartily small subscriptions, and I should very much like to see the balance of this fund made up by a very large number of small subscriptions, which could be paid over a term of years, thus allowing us to recover income tax. I am sure that the greater the area over which the contributions are spread the greater the interest which will be aroused, and the greater the indirect support which the Institute will receive. The appeal is now available for all members, and with the appeal is a deed of covenant, which if properly filled up will enable us to recover income tax on subscriptions payable over not less than seven years.

You will ask what we are going to do with this money and how we are going to take care of it. The fund will be a Capital Endowment fund, the interest only on which will be used for the purposes of the Institute. With this extra income of £500 or £600 a year we hope to do a great many things which we are unable to do now, including the improvement and enlargement of our publication programme. The investment of the money as it is contributed is in the hands of an Investment Sub-Committee which has been appointed by the Council, consisting of Engineer Vice-Admiral Sir Robert Dixon, the Chairman of the Finance and General Purposes Committee, Lieutenant-General Sir Ronald Charles, Mr. Horace W. Clarke, Mr. E. L. Morcom, Lieut.-Colonel The Hon. R. M. Preston, and Mr. A. J. G. Smout. Investments have been made to the extent of over £5000, which are already bearing interest.

Election of Officers for 1937–1938.

The Secretary read the list of officers elected to fill the vacancies on the Council for the year 1937–1938:

President:

W. R. Barclay, O.B.E.

Vice-Presidents:

Engineer Vice-Admiral Sir Robert Dixon, K.C.B., LL.D.
Lieutenant-Colonel The Hon. R. M. Preston, D.S.O.

Members of Council:

W. T. Griffiths, M.Sc.
Stanley Robson, M.Sc.
A. J. G. Smout.
D. Stockdale, M.A., Ph.D.

Election of Members and Student Members and Associate Members.

The Secretary announced the election of the following members, student members and associate members:

Members Elected on October 29, 1936.

Barker, Stuart Netherwood	Southampton.
Billinghurst, Philip Edward	Salisbury, Southern Rhodesia.
Black, Arthur, Assoc.Met.	Southampton.
Day, William Arthur Jeffries	Pretoria, South Africa.
Edens, Leonard, Dipl.-Ing.	Berlin-Spandau, Germany.
Farr, Harry	Cardiff.
Hollings, Arthur Sidney	Birmingham.
Horley, Robert Eustace	Southampton.
Kempf, Louis Walter, M.S.	Cleveland, O., U.S.A.
Laves, Fritz, Dr.-phil.	Göttingen, Germany.
Lorentz, Marjorie Geraldine, B.A.	Bridgeville, Pa., U.S.A.
MacDonald, James	London.
Messner, Martin C.	Katowice, Poland.
Pullen, Alfred Norman Douglas	Grappenhall.
Roglin, Ernest Christie, B.S.	North Canton, O., U.S.A.
Tattersall, Cecil Owen, B.Sc., A.R.C.S.	Cawnpore, India.
White, Edwin Hillier Maurice	Birmingham.
Yates, Donald, M.C., B.E.	Port Pirie, South Australia.

Student Member Elected on October 29, 1936.

King, George Roland	Hounslow.

Members Elected on December 10, 1936.

Arguelles, Angel Severo, B.S., Ch.E.	Manila, Philippine Islands.
Baker, William Albert, B.Sc.	London.
Berger-Hainaut, Maurice Camille Ghirlain Avelin	Brussels, Belgium.
Blackwell, Harold Alexandre	Liverpool.
Broadfoot, Eric Henry	Birmingham.
Chace, Thomas B.	Chicago, Ill., U.S.A.
Craggs, Harold Brabant	Pelaw-on-Tyne.
Forrest, George, B.Sc.	Chacombe, nr. Banbury.
Hall, Edward Patterson, B.Sc.	Phillipsdale, R.I., U.S.A.
Hardy, Charles	New York City, U.S.A.
Izod, Edwin Gilbert	Addlestone.
Miller, Mike Anthony, A.B., Ph.D.	New Kensington, Pa., U.S.A.
Miramon, Pierre	Paris, France.
Parker, Henry George	London.
Parlanti, Conrad A.	Herne Bay.
Philpot, Harold Percy, B.Sc.	Benares, U.P., India.
Plutte, Frederick, Jr., B.A.	Brimsdown.
Preece, Engineer Vice-Admiral George, C.B.	London.
Rao, Emani Surya Prasada, B.Sc.	Jamshedpur, India.
Reynolds, Oswald Garnet, M.C.	Melbourne, Australia.
Rigby, Richard, B.Eng., Ph.D.	London.
Scherzer, Karl, Dr.-jur.	Kreis Monschau, Germany.
von Selve, Gustav	Thun, Switzerland.
Stephens, Charles	London.

Student Members Elected on December 10, 1936.

Andrews, Kenneth William	Manchester.
Boyle, Leonard	Tynemouth.
Davies, Dai Ashton	Billingham-on-Tees.
Hull, Charles, B.A.	Cambridge.
Parker, Rowland, B.A.	Birmingham.
Raynor, Geoffrey Vincent, B.A., B.Sc.	Oxford.
Swindells, Norman, B.A.	Cambridge.

Associate Members Elected on December 10, 1936.

Ansel, Gerhard, M.Sc.	Pittsburgh, Pa., U.S.A.
Cohen, Morris, Sc.D.	Cambridge, Mass., U.S.A.
Esarey, Bernard John, B.S., Ch.E.	Indianapolis, Ind., U.S.A.
Hentschel, Robert, A.A., Sc.D.	Bridgeport, Conn., U.S.A.
Shoemaker, John Earle, M.S.	Youngstown, O., U.S.A.
de Strycker, Professor Robert Emile	Louvain, Belgium.

Members Elected on January 14, 1937.

Baines, Arthur	Coventry.
Bearcroft, Robert Owen	Osterley.
Burns, William Lindsay	Leven, Fife.
Gandolfo, José S.	Buenos Aires, Argentine.
Giulini, Edgar, Dr.-jur.	Ludwigshafen-am-Rhein, Germany.

Gmöhling, Wilhelm	Nürnberg, Germany.
Kinnell, David Russell	Marton-in-Cleveland.
Lean, Rodney James, B.A.	Luton.
Page, Basil Lloyd	Barnet.
Prins, Jan Alingh, LL.D., M.Sc.	The Hague, Holland.
Vaughan, Noel Bodin, B.Sc.	Dudley.
Ward, Edward Denis, B.A.	London.

Student Members Elected on January 14, 1937.

Harper, Richard George, M.Sc.	London.
Lowe, William Lawson	London.
Pearson, William Kenneth Jamieson	Manchester.
Rae, John, Jr.	Birmingham.
Steward, John Charles, B.Sc.	Brentford.

Associate Members Elected on January 14, 1937.

Klippert, Donald S., M.S.	Warren, O., U.S.A.
Van Note, William G., M.S.	Raleigh, N.C., U.S.A.
Vines, Raymond Francis	Bayonne, N.J., U.S.A.

Members Elected on February 11, 1937.

Buckle, Horace Leopold	Redhill.
Farmer, John Hall	West Hartlepool.
Grisenthwaite, Arthur Turner, B.Sc.	Stockton-on-Tees.
Kobayashi, Torao	Mitakamura, Tokyo, Japan.
Mathias, Anthony Robert	London.
Pope, Sidney Barton	Beverley, South Australia.
Reynolds, Peter William, B.A., B.Sc.	Oxford.
Rogez, Henri Eugène François	Paris, France.
Thompson, John Fairfield, B.S., Ph.D.	New York City, U.S.A.
Túry, Paul, Dipl.-Ing.	Ujpest, nr. Budapest, Hungary.

Associate Members Elected on February 11, 1937.

Graham, Walter Allen, B.Sc., E.Met.	Pittsburgh, Pa., U.S.A.
Palmer, Earl W., Ch.E.	Waterbury, Conn., U.S.A.

Re-Election of Auditors.

Mr. J. Cartland, M.C., M.Sc., proposed, Mr. E. E. Eccles seconded, and it was unanimously agreed that Messrs. Poppleton and Appleby be re-elected auditors for the ensuing year.

Forthcoming Meetings.

The President announced that the May Lecture would be delivered in the Hall of the Institution of Mechanical Engineers on May 5, by Professor E. N. da C. Andrade, F.R.S., whose subject would be "The Flow of Metals," and that the Autumn Meeting would be held in Sheffield from September 6 to 10. As stated earlier in the meeting the Autumn Meeting in 1938 would be held in the United States.

The President also announced that the Council had accepted an invitation to hold the 1939 Autumn Meeting in Glasgow.

COMMUNICATIONS.

Communications by the following authors were then presented and discussed: M. L. V. Gayler (762); E. C. Rollason (760); L. Northcott (764); R. S. Hutton and R. Seligman (759); M. Cook (749); H. J. Gough and D. G. Sopwith (750); J. McKeown and O. F. Hudson (754); J. McKeown (757), and B. Jones (761). A paper by M. L. V. Gayler (763) was also presented, but there was no discussion. In each case a hearty vote of thanks to the authors was proposed by the President and carried by acclamation.

ANNUAL DINNER.

The Annual Dinner was held in the Trocadero Restaurant, Piccadilly Circus, London, W.1, and was presided over by the President. More than 300 members and guests were present.

Thursday, March 11.

COMMUNICATIONS.

On the resumption of the meeting, communications by the following authors were presented and discussed: W. Hume-Rothery and P. W. Reynolds (751); W. Hume-Rothery and E. Butchers (752); R. J. M. Payne and J. L. Haughton (753); J. L. Haughton and T. H. Schofield (756); R. A. Stephen and R. J. Barnes (755); and P. W. Reynolds and W. Hume-Rothery (758). In each case a hearty vote of thanks to the authors was proposed by the President and carried by acclamation.

VOTES OF THANKS.

The PRESIDENT moved the following resolution, which was carried by acclamation.

The members assembled at this Annual General Meeting desire to convey their warmest thanks to all the contributors to the Endowment Fund whose names are included in the preliminary list of contributors, and particularly to the Trade Associations for their generosity in heading the list with the very substantial sum of £3650.

The PRESIDENT undertook, on behalf of the members, to write to the Chairmen of the Trade Associations informing them of this resolution.

The PRESIDENT moved:

"That the thanks of the Institute be and are hereby tendered to:

(1) The Council of the Institution of Mechanical Engineers, for their courtesy in permitting the use of their rooms on this occasion.
(2) Messrs. Kodak, Limited, for permitting a party to visit their works.
(3) The General Electric Company, Limited, for their organization of a special demonstration of television.
(4) The Gramophone Company, Limited, for permitting a party to visit their works.
(5) The Associated Equipment Company, Limited, for permitting a party to visit their works.
(6) Messrs. Fry's Die-Castings, Limited, for permitting a party to visit their works.
(7) Messrs. Charrington and Company, Limited, for permitting a party to visit their brewery."

The Resolution was put to the meeting and carried with acclamation. The business meeting then terminated.

VISITS.

In the evening of Tuesday, March 9, members and their ladies attended, by invitation, a demonstration of television at the Headquarters of the General Electrical Company, Ltd. In the afternoon of Thursday, March 11, visits were made to the works of The Associated Equipment Company, Ltd., Kodak, Ltd., and Fry's Die-Castings, Ltd., and to the brewery of Charrington and Company, Ltd.

GENERAL MEETING IN BIRMINGHAM.

AT A GENERAL MEETING of the Institute held in the Chamber of Commerce Buildings, New Street, Birmingham, in the evening of March 23, 1937—Mr. W. R. Barclay, O.B.E., President, in the Chair—Dr. M. Cook, M.Sc., re-presented his paper on "Directional Properties in Rolled Brass Strip," which had previously been read at the Annual General Meeting in London on March 10, 1937.

The Minutes of the last General Meeting, held in London on March 10 and 11, 1937, were taken as read and signed by the Chairman.

THE PRESIDENT gave a brief explanation of the circumstances that had led to the present meeting, pointing out that it was hoped it would be the first of a series of such meetings held in various local section centres. The Council had on several occasions expressed the desire for the closest possible collaboration between the parent body and the local sections, and such meetings as this in which papers could be read and fully discussed at greater length than was possible in the Spring and Autumn Meetings would become, it was hoped, an important factor in the future development of the Institute.

After the discussion (a record of the discussion appears on pp. 174–185), the Chairman proposed, and there was carried with acclamation, a vote of thanks to the author of the paper.

METAL SPRAYING: PROCESSES AND SOME CHARACTERISTICS OF THE DEPOSITS.* 760

By E. C. ROLLASON,† M.Sc., Member.

Synopsis.

Spraying pistols using wire, powder, and molten metal are described, together with comparative details. The nature of the sprayed deposit is discussed. A few corrosion tests using intermittent salt-spray have been made on zinc and aluminium deposits and on painted zinc coats.

Using the three types of pistol, comparative tests of aluminized surfaces have been made and heat-treated nickel–chromium–iron coatings were found to have good resistance to oxidation at elevated temperatures. Data are also given for porosity, oxide content of sprayed copper, and hardness of sprayed metals.

Twelve years have elapsed since the last paper on metal spraying was presented to the Institute.[65] During this interval new designs of spraying apparatus have been evolved using wire, powder, and molten metal. Many new applications have also been exploited successfully, some of which are becoming of great importance to the works' engineer, as for instance in the building up of worn machinery, but apart from these metal spraying demands increasing consideration as a means of combating corrosion. The corrosion of mild steel occurs irrespective of its composition, and the austenitic stainless steels are too expensive for any but special environments where corrosion is very severe. At the present time one of the most common methods of protecting iron and steel is by painting, but research is showing that this method is only really effective when the surface of the steel is prepared or cleaned by costly treatments such as sand-blasting. This treatment is the first stage in the metal-spraying process, and, if one is prepared to do this, a coat of sprayed zinc or aluminium makes the ideal protective coating for steel which will later be exposed to the weather, and circumstances will decide as to whether or not subsequent coats of paint are sprayed on to the deposit which would act as an excellent key to the paint. Having these considerations in mind, the object of this paper is to indicate briefly the capabilities of the various processes of metal spraying and the characteristics—such as porosity, hardness, and corrosion-resistance—of the deposit.

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* Manuscript received September 2, 1936. Presented at the Annual Genera Meeting, London, March 10, 1937.

† Assistant Lecturer, Department of Metallurgy, The University, Birmingham.

APPARATUS FOR SPRAYING.

Wire-Type Pistol.

All pistols spraying metal from wire employ the same basic principles, and differ only in small details of design. The pistol consists of a small air turbine, rotating at 30–50,000 r.p.m., which drives, through the medium of reduction gears, two knurled rolls which grip the wire and feed it into the melting nozzle. Compressed coal-gas or acetylene and oxygen are supplied for the flame, whilst compressed air is used for atomizing the molten metal. An illustration of this pistol is given in Fig. 1 (Plate I). Efforts have been made to increase the amount of metal sprayed in a given time by increasing the diameter of the wire, but without greatly increasing the cost. One American pistol uses $\frac{1}{8}$ in. diameter wire, whilst the English pistol can be modified to take 2 mm. diameter wire. The nozzles of the various types vary slightly. The French * type has an extra air cap allowing the air blast to arrive at the flame zone in two stages. The gas nozzle is also set slightly in advance of the wire nozzle. The same type of nozzle is used on the powder pistol recently introduced by the French company. The English † pistol has no extra air cone and the air arrives at the flame zone at a smaller angle to the wire axis than in the case of the French pistol. The American ‡ pistol has no extra air cap and the air angle is smaller than in the English pistol.

One of the important advantages of the wire pistol over other forms is the ease with which the internal surfaces of tubes can be coated. For small diameter tubes (minimum 1·25 in.) the rotary nozzle is used, whilst for larger tubes either the extension or the deflector nozzles are suitable. A fan spray nozzle has also been recently introduced to give a smoother and more uniform deposit on large surfaces.

Molten Metal Pistol.§

The modern molten metal pistol has been developed from the type invented in 1924–1926 by C. J. Jung and H. J. Versteeg, of Amsterdam. One of the disadvantages of the early pistols was their weight, but recent modifications have reduced the size and weight without lowering the capacity. The pistol (Fig. 2, Plate I) is gravity fed with molten metal held by the container, and its temperature is maintained by the flame from the Bunsen burner beneath it. The flame also preheats the com-

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* Marketed by the Société Nouvelle de Métallisation.

† Produced by Metallization, Ltd.

‡ Marketed by the Metallizing Company.

§ Produced by Mellowes, Ltd. (British Patent 276,955–6. 349,031.)

pressed air, carried by a stainless steel pipe to the silver steel nozzle (0·035 in. diameter). The front of the pistol is enclosed in a heat-resisting steel cowl and the operator's hand is protected by an asbestos-lined steel guard.

One of the difficulties with the pistol is concerned with its maintenance, the silver steel nozzle and also the container being rapidly attacked by the molten zinc; the former has a life of 1–1½ hrs., renewable in 2–3 minutes. Refractory liners of morganite *ΔN* and fused corundum increase the life of the nozzle to about 13 hrs.' spraying time, but are naturally very expensive and frequently fail as a result of the different rates of expansion of the steel and refractory. As the nozzle wears, the spray becomes coarser and somewhat irregular owing to uneven wear. To maintain a uniform thickness, the speed of spraying is increased as the nozzle wears.

The length of projection of the nozzle from the air feeder influences the character of the spray, the fine spray being produced by the longer nozzle.

This process entails the use of a separate gas furnace for melting the zinc, usually a gas-fired furnace of 1 cwt. capacity and provided with an immersion pyrometer. The metal charge (4 lb. of zinc) in the pistol lasts about 20 minutes, but if spraying is intermittent during these periods the pistol can be rested in a suitable rack or its contents can be emptied into the furnace.

Powder Process.

Of the powder pistols invented, only the Schori * has become of any commercial importance; in common with the Mellowes instrument, it has no moving parts. The powder is sucked through an oxy-gas flame and blown on to the object. The construction of the pistol is shown in Fig. 3 (Plate II). The pistol consists essentially of two injector arrangements; one is in the handle and is similar to that found in a blow-pipe used for mixing the oxygen and acetylene or other fuel gas at the same time preventing back-firing in the pipes, while the other, similar to a filter pump, is used for aspirating the powder from a suitable container fitted with a small vibration fan. Compressed air regulated by valve *V* flows into chamber *G* where it splits, part passing into chamber *A* and through the nozzle *B* thereby creating a partial vacuum in the pipe *E* connected to the supply of powder and also to the atmosphere at *F* in the handle, which must be covered by the operator's thumb before sufficient suction is created to aspirate the powder. The metal powder passes through radial holes *D* and is carried along by the compressed

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* British Patent 432,831.

air through the central tube *K*. As it is ejected from the gun it comes into contact with the oxy-acetylene flame. A quantity of air from chamber *G* passes through orifice *H*, issues at the elliptical space, shown in section *ZZ*, surrounding the circular flame, and projects the fused particles on to the object being sprayed.

The oxygen and acetylene employed for the flame enter at the bottom of the handle and pass through needle valves which can be regulated to control the temperature. In the French Schori pistol plug valves are used. The acetylene passes through the grooves *P* and the tapered extension tube which serves as an expansion chamber. The oxygen likewise passes through chamber *R* to the central hole *O* to the tapered tube where it mixes with the combustible gas. The mixture flows through the holes *J* to the nozzle, where it is ignited.

This arrangement of parts provides a handy and well-balanced pistol.

Two difficulties are met with in the design of equipment for spraying metal powders. The first is the need for using a large diameter orifice in the nozzle to prevent the clogging of the powder, with the result that a large flame is required, and the second is the maintenance of a regular and uninterrupted supply of powder to the pistol.

Comparative details of the various pistols are given in Table I.

Electrically Heated Pistols.

Several electrically heated pistols have been patented, but few have any commercial importance at the present time. The Swiss Schoop pistol employs an arc arrangement.[31]

Patent 308,355, however, describes a novel method for spraying dental plates and depends on the formation of arcs between two rotating cylinders of metal arranged to interrupt the electric circuit. The finely powdered metal formed by the arc is projected by centrifugal forces.

Associated Plant.

Each metal-spraying process requires a compressor to supply compressed air both to the pistols and to the steel grit or sand-blast equipment. Sand-blasting produces a surface more suitable for spraying than does grit-blasting, but suitable precautions have to be taken to prevent silicosis. Excessive nozzle wear has now been reduced by the use of hard carbide materials such as boron or tungsten carbide, and Neville[69] has shown that the nozzle should be held obliquely to the work at an angle of about 30°. For the small class of work the new type of sand-blast machine employing centrifugal force instead of compressed

TABLE I.—*Comparative Details of Three Types of Pistols (Makers' Figures).*

	British Wire.	Molten Metal.	Powder.
Valves	Single-plug type inside casing	Only taps on the Bunsen burner	Finger control for powder; separate valves for the gases
Moving parts	Turbine and gears encased	None	None
Weight	3½ lb.	6½ lb.	2¾ lb.
Metal form	1, 1½, 2 mm. diameter wires	Ingots melted in furnace	Powder: zinc, 100; copper and aluminium, 150; nickel, 200 mesh per in.
Limiting melting point	1550° C.	600° C. (aluminium–silicon alloy)	1550° C. (copper highest in England)
Speed of application for zinc	5 lb./hr.; 17 ft.^{2}/hr. (0·005 in.) 11·9 lb./hr. using 2 mm. wire	16 lb./hr. including stopping	20 lb./hr.
Wastage	10–20%	10–20%	20–30%
Oxygen	30–40 ft.^{3}/hr.; 25 lb./in.^{2}	None used	50 ft.^{3}/hr.; 14–28 lb./in.^{2}
Combustible gases	Coal-gas, 45 ft.^{3}/hr.; 28 lb./in.^{2}; or acetylene 24 ft.^{3}/hr.; 10 lb./in.^{2}	Coal-gas, 40–75 ft.^{3}/hr. at town main pressure; gas for furnace 150 ft.^{3}/hr. for 3 pistols	Enriched coal-gas (ferrolene) 7 lb./in.^{2}); acetylene 43 ft.^{3}/hr.; 3 lb./in.^{2}
Air	15 ft.^{3}/minute; 45 lb./in.^{2}	15 ft.^{3}/minute; 65–75 lb./in.^{2}	15 ft.^{3}/minute; 43 lb./in.^{2}
Normal working distance	3 in.	5 in.	10–12 in.
Internal work	1–3 in. diam.-use Rotary nozzle 3–12 in. diam.-use extension and deflector nozzles	Shallow work only	Shallow work
Overhead work	No difficulty	Impossible	No difficulty

air will undoubtedly gain favour. The centrifugal effect is obtained by impellors rotating at high speed, and the power required is only 10–20 per cent. of that taken by the compressed-air equipment.

Theory of Metallizing.

Schoop states that the atomized metal solidifies during flight owing to the cooling effect of the expanding air blast. When the particles strike the surface of the article their kinetic energy is transformed into heat with the result that they become momentarily plastic and weld together, but Arnold [61] and Schenk have shown that the speeds necessary to produce the required amount of heat are in excess of any obtained in the process. In support of his theory Schoop points out that inflammable material can be sprayed, and shows that the temperature of the metal stream is only 60°–70° C. as measured by a thermometer. Thormann,[37] however, has recently shown that the temperature of sprayed iron particles at a distance of 5 in. from the nozzle is 1000° C., and it is well known that if the pistol is directed to one area at a close distance the deposit can be melted. According to Schoop's theory cold powder could be sprayed to form a coherent coating, a process known to be unsuccessful.

A second theory, favoured by Karg, Kutscher, and Reininger, assumes that cold solid particles of metal are hammered into the pores of the article by the great force behind them.

The hypothesis favoured by the present author is that the particles are melted completely or partially in the flame, depending on the spraying apparatus, and cool fairly slowly while travelling in the air stream, since there is little differential movement of the two materials. When the pistol is held close to the article (1–3 in.) the particles are still molten when they strike the surface. Splashes like fallen drops of solder are formed (Fig. 5, Plate III) and interlock together. At high magnifications the microstructures of these splashes exhibit columnar crystallization, as shown in Fig. 7 (Plate III), with discontinuous oxide films and cavities at the edges of the lamination; these crystals must have formed after the particles had struck the surface. After deposition, the particles are rapidly cooled by the air stream impinging against the surface, and since the base only conducts away a small proportion of the heat, an inflammable material is not ignited by the lower melting point metals sprayed normally. At greater distances from the nozzle the particles will be cooled below their freezing point, splashes will not form, but with sufficient kinetic energy the particles will be deformed into a laminated packing enclosing fine pores. At still greater distances the particles

PLATE I.

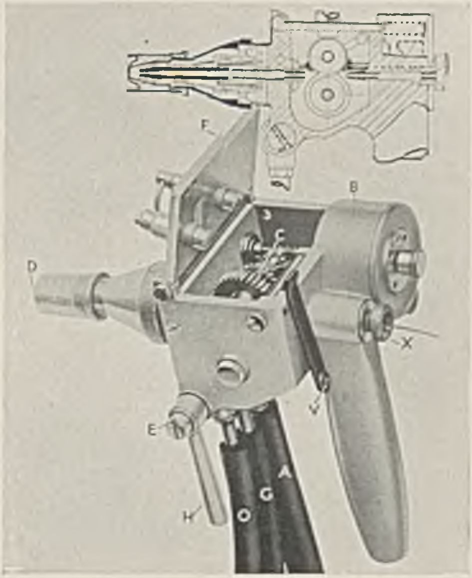


FIG. 1.—English Wire Pistol.

A Air Supply Tube.
B Turbine Chamber.
C Hinged Bracket.
D Pistol Nozzle.
E Valve Controlling Gases.
F Hinged Lid.
G Fuel Gas Supply Tube.
H Valve Handle.
O Oxygen Supply Tube.
V Spring Lever, Fastening the Lid F.
X Opening for Insertion of the Wire.

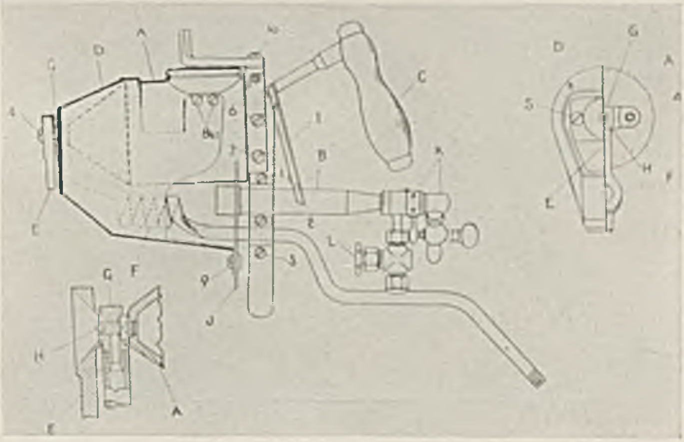


FIG. 2.—Molten Metal Pistol.

A Container.
B Burner.
C Handle.
D Cowl.
E Front Plate.
F Compressed Air.
G Air-Feeder.
H Silver Steel Nozzle.
I Hand Guard.
J Shield.
K Air and Gas Injector.
L Air Regulator.

[*To face p.* 40.

PLATE II.

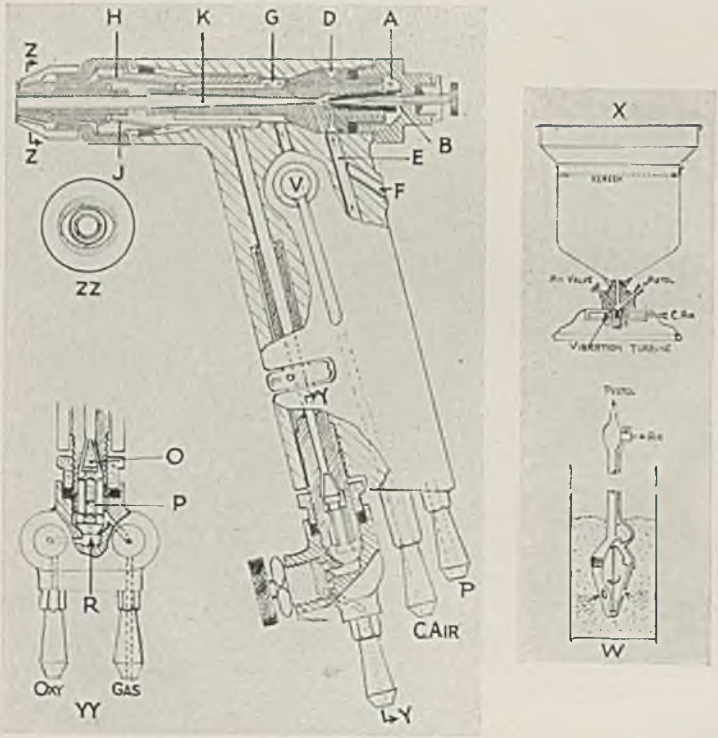
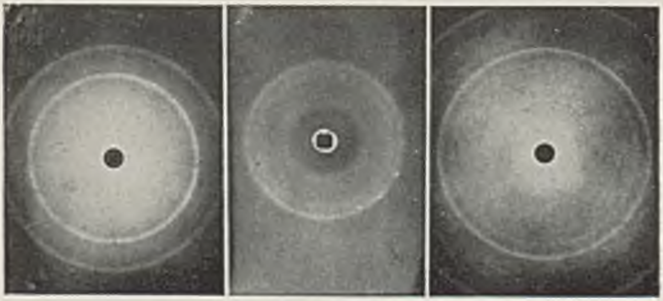


Fig. 3.—Schori Pistol and Powder Containers.

X Schori Type Container. W French Type Container.

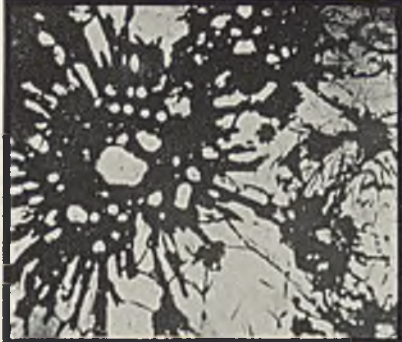


A B C

Fig. 4.—Back Reflection X-ray Photographs of Sprayed Metals: A = Copper, Wire Process; B = Aluminium, Powder Process (Note Spots on Ring); C = Zinc, Wire Process.

PLATE III.

5



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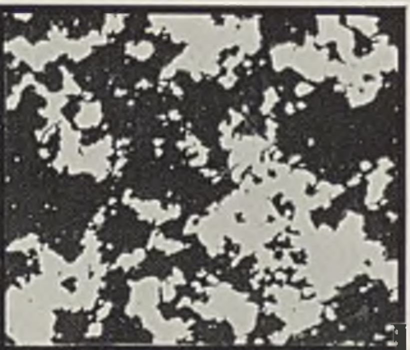

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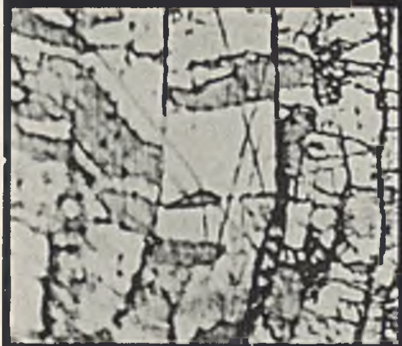

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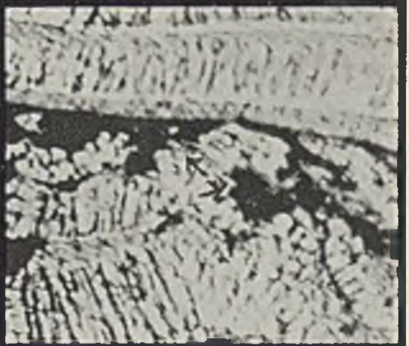

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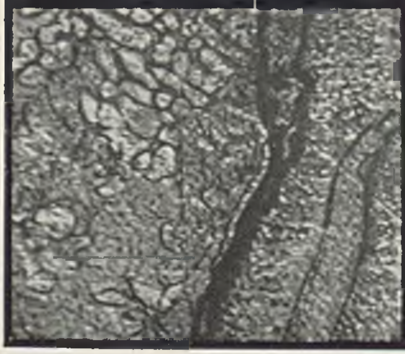

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FIG. 5.—Sprayed Copper on Glass; Wire Process; Transmission Photograph. × 50.

FIG. 6.—As Fig. 5, but Using Powder Process; No Splash Effect. × 50.

FIG. 7.—Sprayed Copper by French Wire Pistol; 1 in. Nozzle Distance; Columnar Grains across Layers, Etched. × 1000.

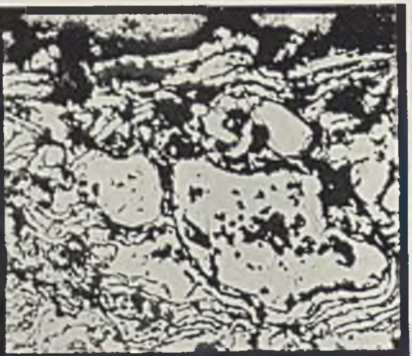
FIG. 8.—Same as Fig. 7, but 4 in. Nozzle Distance. Smaller Columnar Grains with Porosity (↑). × 1000.

FIG. 9.—Same as Fig. 7, but at 9 in. Nozzle Distance: Columnar plus Equiaxed Grains. × 1000.

FIG. 10.—Same as Fig. 7, but at 10 in. Nozzle Distance. Typical Undeformed Particle Coated with Oxide (↑).

PLATE IV.

11



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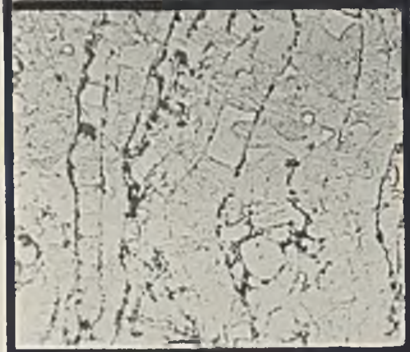

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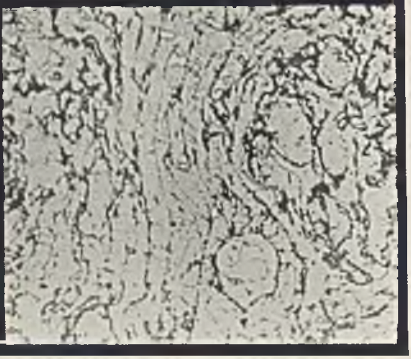

FIG. 11.—Sprayed Copper by Powder Process. Porosity = black; Cu_2O = half-tone; $O_2 = 3{\cdot}4\%$. Etched. × 400.

FIG. 12.—Sprayed Zinc by Powder Process, Normal Distance. Laminations and Round Grains. Porosity 19%. Etched. × 400.

FIG. 13.—Sprayed Zinc by English Wire Pistol; Using Acetylene, 1 in. Distance. Columnar Grains. Porosity 8·1%. Etched 2% HNO_3. × 400.

FIG. 14.—As Fig. 13, but at 10 in. Distance. Porosity 11·9%. Columnar Grains. × 400.

FIG. 15.—Sprayed Zinc by English Pistol Using Coal-Gas at 1 in. Distance. Isolated Oxide and Porosity. Porosity 1·1%. Density (Toluene) 6·56. × 400.

FIG. 16.—As Fig. 15, but at 10 in. Distance. Columnar Grains and Round Particles. Porosity 8·7%. Density (Toluene), 6·88. × 400.

17

18

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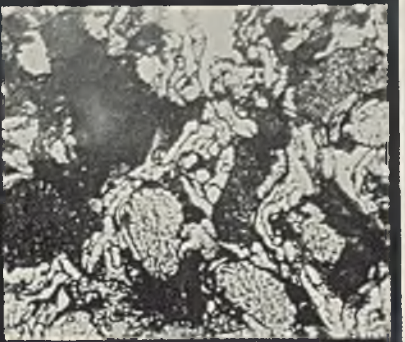

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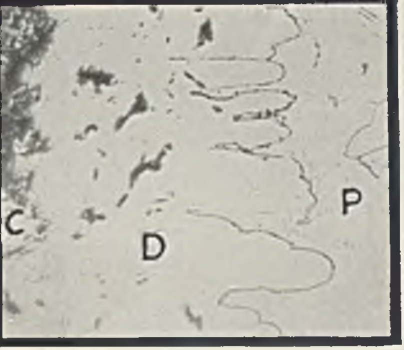

C = Sprayed Coat. D = Diffused Layer. P = Base Plate.

FIG. 17.—Zinc Sprayed at 1 in. Nozzle Distance by Molten Metal Process. Note Iron Particle (↑). Porosity 10·6%. × 400.

FIG. 18.—As Fig. 17, but at 5 in. Distance. Porosity 11·7%. × 400.

FIG. 19.—As Fig. 17, but at 11 in. Distance. "Heaped" Grain Structure. Porosity 16·5%. × 400.

FIG. 20.—Aluminium Sprayed by Powder Process. Round Particles with Cavities (Black). Porosity 34·3%. × 150.

FIG. 21.—Aluminium Sprayed by English Wire Process. Porosity 8·8%.

FIG. 22.—Sprayed Aluminium by Wire Pistol. Bitumastic Coating. Heated 780° C. for 10 Minutes. Etched in HNO_3. × 200.

PLATE VI.

23

24

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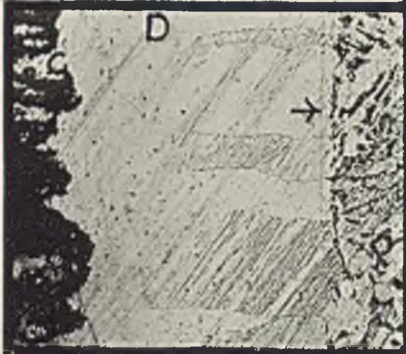

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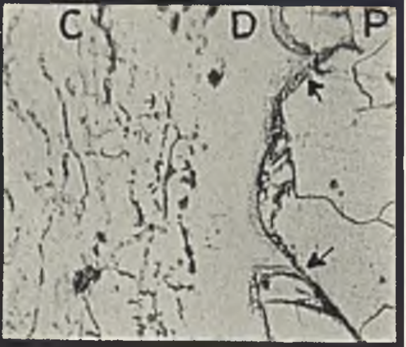

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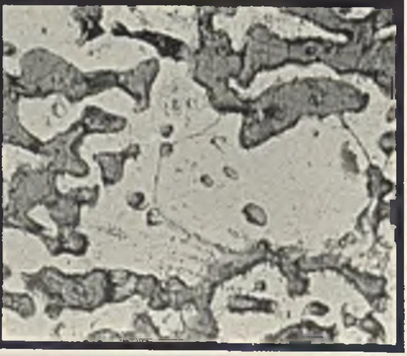

C = Sprayed Coat. D = Diffused Layer. P = Base Plate.

FIG. 23.—Sprayed Aluminium by Powder Pistol. Treated as Fig. 22. × 200.

FIG. 24.—Sprayed Aluminium-Silicon Alloy by Molten Metal Process. Treated as Fig. 22. × 200.

FIG. 25.—Sprayed Aluminium as Fig. 22 but Annealed 2 Hrs. at 1000° C. Columnar Crystals; border (↑); Concentration of Pearlite (P). × 175.

FIG. 26.—Sprayed Nickel-Chromium-Iron Alloy by Wire Process. Heated 2 Hrs. at 1100° C. Penetration along Grains (↑). × 250.

FIG. 27.—Sprayed 18 : 8 Steel by Wire Process. Heated 50 Hrs. 900° C. Note Superimposed Structure in Plate. × 200.

FIG. 28.—Sprayed Mild Steel by Wire Process, after Heating at 900° C. for $\frac{1}{2}$ Hr. Coalesced Oxide (Half-Tone). × 400

form a "heaped" sand-like mass with high porosity. This theory is substantially in agreement with that of Turner and Budgen [2] (p. 82).

STRUCTURE.

One important difference between the deposits produced by wire and powder processes is shown in Figs. 5 and 6 (Plate III) which are shadowgraphs (× 50) of copper sprayed on to glass slips. The powder process does not give the splash effect with high melting point metals to such an extent as the wire process. The true grain-size of sprayed coatings is normally very small, as is well illustrated by back-reflection X-ray photographs (Fig. 4, Plate II) which in the case of zinc, aluminium, and copper always show continuous rings, resolved doublets, and a considerable background due to slight cold-work and to oxide particles. The photomicrographs (Plates III–VI) are all taken from cross-sections through the deposit and plate.

Figs. 7–10 (Plate III) show the change in microstructure as the distance from the nozzle increases in the case of copper sprayed by the French wire pistol. A copper coating produced by the powder process is shown in Fig. 11 (Plate IV) in which the oxide masses are clearly seen; the particles have suffered but little deformation. A zinc deposit, also produced by the powder process, is shown in Fig. 12 (Plate IV); this again exhibits rounded grains associated with laminated masses. Figs. 13 and 14 (Plate IV) show zinc deposits made by the English wire process, using acetylene gas. A high flame temperature is indicated by the columnar crystallization even at a nozzle distance of 10 in. As a contrast, Figs. 15 and 16 (Plate IV) show the structure of deposits made with the same equipment using coal-gas as fuel. At a nozzle distance of 1 in. the oxide and pores are dispersed, resulting in a low permeability to liquids. At a nozzle distance of 10 in. a number of rounded particles can be seen in the structure, and the interconnected porosity has increased. This pistol is at its maximum efficiency when using coal-gas, and the flame is consequently more oxidizing than when acetylene is employed.

Figs. 17, 18, and 19 (Plate V) show the structure of zinc formed by the molten metal process. At a distance of 11 in. the structure consists essentially of "heaped" masses of particles, resulting in high porosity, whilst at 1 in. numerous unetched particles of an elongated shape are found in the structure. These are possibly iron or iron-rich material abraded from the nozzle.

The structures of aluminium deposits made by the powder and wire processes are shown in Figs. 20 and 21 (Plate V), respectively. The former consists almost entirely of rounded particles of metal each possessing a dendritic structure.

CORROSION TESTS.

Most corrosion tests on sprayed deposits have been made on samples metallized by the wire pistol. A few tests were carried out, therefore, in order to ascertain whether there is any appreciable difference between deposits made by the various processes when subjected to corrosion.

Ingot iron of known history was kindly supplied by Dr. J. C. Hudson,* the analysis being:

C	Si	S	P	Mn	Cu	O	H	N
0·018	trace	0·037	0·008	0·033	0·064	0·060	0·002	0·005

It was used in the form of 4 × 2 × ⅛ in. strips with bevelled edges and with one hole for suspension from a glass hook. After sand-blasting, the iron samples were coated by three types of metallizing processes, the amount of sprayed metal being obtained by weighing.

One set of field tests was started in the grounds of Birmingham University and another group of specimens, including Sherardized and galvanized steel, cast zinc, and a standard steel of known corrosion behaviour (*X*), was sprayed twice daily (except Sundays) with 3½ per cent. sodium chloride solution in a manner similar to that used by the Iron and Steel Institute Corrosion Committee.

Each side of the specimen was given one puff (0·03 c.c.) from a "Delta" spray at a distance of 6 in. and this was repeated at three heights, blank puffs being given at the side of the end specimens. For the first month the specimens were allowed to dry indoors, but subsequently they were placed outside so that the washing effect of the rain could be included in the tests. A number of painted specimens were also exposed to this intermittent spray test. The steel samples coated with zinc by metallizing, Sherardizing, and galvanizing processes were given a single coat of paint † of the following analysis:

	Per Cent.
Indian red	53·2
Zinc chromate	16·0
Boiled oil	13·3
Refined oil	13·3
Liquid driers	2·66
White spirit	1·52

This paint was used because its behaviour on steel was investigated by the Iron and Steel Institute Corrosion Committee, but it is quite possible that the Indian red is an unsuitable constituent in a paint to be used on zinc.

The increase in weight of the samples during the first month and the

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* Iron and Steel Institute Corrosion Committee.

† Supplied by Dr. J. C. Hudson.

time required for the first signs of rust to appear on the surface are shown in Table II. As yet the field tests have not progressed long enough to yield reliable results, but since no visible corrosion products had formed after 4 months' exposure the increase in weight of the samples (after 24 hrs. in a dessicator) is given, as a matter of interest, in Table III. It was noticed that the corrosion products on the Sherardized samples were more readily removed by the rain than in the case of the other specimens, also the samples sprayed at normal distances from the nozzle offer a greater resistance to corrosion than those sprayed either near or far from the nozzle (*e.g.* 7, 9, W7, W8). Too few experiments have been made to yield very positive conclusions, but the general trend of these results is to show that all the zinc coatings made under best commercial practice have approximately the same rate of corrosion, and this life is limited mainly by the thickness of the deposit. That the life of the sprayed samples is satisfactory was also shown by tests using 5 per cent. NaCl in a salt-spray cabinet. Samples metallized by each of the processes withstood 1000 hrs. without signs of rusting.

TABLE II.—*Accelerated Corrosion Tests.*

	Layers.	Process.	Metal.	Spraying Distance.	Oz./ft.^{2}.	Thickness, Inch.	Increase in Weight after 28 Days, Mg./cm.^{2}.	Time for First Signs of Rust, Days.
1	1	M	Zn	N	1·105	0·0022	3·32	110
5	2	M	Zn	N	1·59	0·0031	3·31	160
*7	1	M	Zn	1 in.	2·67	0·0053	4·19	220
9	1	M	Zn	11 in.	0·94	0·0018	4·54	100
11	1	M	Zn	N worn	3·19	0·0063	3·29	> 220
16	1	S	Zn	N	1·92	0·0038	4·07	240
21	2	S	Zn	N	2·61	0·0052	4·26	> 240
W1	1	W	Zn	N	1·02	0·0020	3·01	220
W5	2	W	Zn	N	1·43	0·0028	2·97	> 240
W7	1	W	Zn	1 in.	1·03	0·0020	3·18	100
W8	1	W	Zn	11 in.	0·43	0·0008	3·04	59
†X	Standard steel						13·14	3
Zn	Cast zinc						3·73	
14	Sherardized				0·84		2·09	105
15	Galvanized				1·69	0·0036	2·56	170
12	1	M	Sn	N	1·08			4
24	1	S	Al	N	0·62	0·0027	3·80	26
W9	1	W	Al	N	0·38	0·0017	0·68	170
M4	1	M	Al–Si	N	1·58	0·0072	7·14	70‡

* Specimen 7 produced no white precipitate in full immersion tests.

† X, after derusting, lost 0·165 grm./cm.^{2} in 170 days.

‡ Layer shelled off in powdery mass.

M = molten metal. S = powder. W = wire. N = normal spraying distance.

The aluminium-coated specimens, however, showed widely different characteristics. In the accelerated tests the sample sprayed by the powder process exhibited rust spots within 26 days, the surface became grey and hygroscopic, whilst in the field tests rust appeared within 7 months. The sample sprayed with aluminium–silicon alloy by the molten-metal process was soon covered with a white deposit, and at the end of 70 days' exposure to the salt-spray the coating was blistered and could be removed readily as powder. On the other hand the wire process yielded a specimen which remained unaffected and bright up to 170 days, after which period a few rust spots appeared. This is not unexpected since it is well known that the purer the aluminium the better is the resistance to corrosion.

TABLE III.—*Field Tests. Four Months (March–July).*

	Number Layers and Metal.	Process.	Spraying Distance.	Weight of Metal, Oz./ft.^{2}.	Increase in Weight, Mg./cm.^{2}.
2	1 Zinc	M	N	0·72	0·30
6	2 Zinc	M	N	1·38	0·30
8	1 Zinc	M	1 in.	2·85	0·76
10	1 Zinc	M	11 in.	1·08	0·41
17	1 Zinc	S	N	1·54	0·59
20	2 Zinc	S	N	4·43	0·57
W2	1 Zinc	W	N	1·05	0·28
W6	2 Zinc	W	N	1·64	0·24
A3	Sherardized			0·64	0·01
25	1 Aluminium	S	N	0·50	1·92
W10	1 Aluminium	W	N	0·37	0·78

M = molten metal pistol. S = powder metal pistol. W = wire metal pistol.

Painted Specimens.

The results are given in Table IV. It is clear that sprayed deposits of zinc offer excellent bonding for paint, and the greater porosity of the coating formed by the powder process is an advantage. The varnish impregnation of sprayed coating has been recently suggested by Reininger.[52]

TABLE IV.

Process.	Condition after 120 Days' Exposure to Intermittent Salt-Spray.	Effect of Rubbing Surface.
Molten, spray	Specks of white deposit	Good bond to base of paint
Powder ,,	Specks of cream deposit	Excellent ,, ,,
Wire ,,	Specks of white deposit	Good ,, ,,
Galvanized	Paint wrinkled; white deposit on bottom edge	50 per cent. paint removed
Sherardized	Crinkled paint; metal exposed in places	20 ,, ,, ,,
Paint only	50 per cent. area rusted	

RESISTANCE TO OXIDATION AT ELEVATED TEMPERATURES.

At the present time in Great Britain only the wire type of metallizing process is employed in the production of aluminized surfaces for resisting oxidation. It was decided, therefore, to find how the deposits made by the various processes compared with each other. Samples of mild steel were sprayed with known amounts of aluminium or aluminium alloy and were then subjected to four commercial preliminary treatments. The different treatments, patented in England, Germany, and France, were carried out as follows :

English : coat specimen with bitumastic paint, heat rapidly to 780° C. for 10 minutes.

German : coat specimens with waterglass, heat rapidly to 800° C. for 15 minutes.

French : coat specimens with saturated solution of borax and anneal at 600° C. for ½ hr.

English : special aluminium alloy—heat rapidly to 900° C. for 10 minutes (this alloy and its use for this purpose are the subject of British Patent 400,752).

The main object of these treatments is to prevent oxidation of the aluminium while the diffusion layer is forming. After treatment, the

TABLE V.—*Duration of Heating to Cause* 50 *Per Cent. Loss in Weight* (*Hours*).

Spray Process and Metal.	Treatment.			
	English. Coated Bitumastic Paint; Heated 780° C. for 10 minutes.	*German.* Coated Waterglass: Heated 800° C. for ½ hr.	*French.* Coated Borax: Heated 600° C. for ½ hr.	None.
Wire, aluminium	140	150	45	
Wire, cadmium–aluminium				130
Powder, aluminium	90	80	60	
Molten, aluminium–silicon	85	50	15	
Wire, 18 : 8 nickel–chromium steel				50
Wire, nickel–chromium–iron				>250
Mild steel plate 0·13 in.				7
Stainless 18 : 8 plate 0·07 in.				300
6 per cent. silicon cast iron 0·8 in diameter				100

Average weight deposited: aluminium 0·035 grm./cm.^{2}; 18 : 8 steel 0·24 grm./cm.^{2}; Ni–Cr–Fe 0·30 grm./cm.^{2}.

samples were heated for 5 hr.-periods at 900°–925° C. in a muffle, after which they were quenched in water ; this has a very drastic effect on any surface scale. The specimens were inspected and weighed periodically. For comparison, samples of mild steel, Silal, and 18 : 8 nickel–chromium steel were included, together with steel specimens coated with 18 : 8 austenitic steel and with the alloy nickel 65, chromium 15, iron 20 per cent. sprayed from wire. The two latter specimens were previously annealed at 1100° C. for 2 hrs. without protection in order to form a diffused layer. After the treatment one specimen coated with nickel–chromium showed two blisters, whilst the specimen sprayed with austenitic steel oxidized badly.

The bitumastic paint protection appears to be very successful, and the wire process yields the best results. Even after 250 hrs. under test the specimen coated with nickel–chromium–iron showed a negligible change in weight.

The structures of these samples are shown in Figs. 22–27 (Plates V–VI). In all cases the pearlite is concentrated in the front of the diffusing layer, and in the initial stage this layer occurs in the form of finger-like masses. After treatment at 900° C. this latter characteristic is lost, the diffusion layer is most frequently parallel to the surface, as shown in Fig. 25, but in one sample the aluminium had completely diffused through the specimen in isolated places with the production of large crystals. At these places oxidation occurred with the production of round shell-like masses of oxide; this is possibly due to the lower aluminium concentration in these areas. Local oxidation also occurred occasionally on the edges where either metallizing or preliminary treatment had not been perfect.

Ageew and Vher [68] have shown that the diffusion of aluminium occurs in two stages : (*a*) dissolution of the iron in the liquid aluminium, with the formation of a solution in equilibrium with the solid phase at a given temperature; (*b*) diffusion of the iron–aluminium solution into the iron. The main principle underlying the above treatments is to initiate these two reactions. Subsequently, at 900° C. the diffusion of the iron–aluminium solution into the iron occurs rapidly at first, but decreases as the concentration of aluminium is reduced. The reason for the columnar grains in the diffusion layer and the concentration of pearlite in front of them has been explained by Benedicks [67] as due to the aluminium being more soluble in the ferrite than in the austenite. With suitable concentration of aluminium, ferrite crystals (in which carbon is not appreciably soluble) are formed, and these grow slowly inwards. Bardenheuer and Müller have shown that oxides present in the sprayed coating have a harmful effect on the diffusion process, and this is possibly the cause of the difference in resistance of the samples sprayed by the powder and wire processes.

Fig. 27 also shows what appears to be two structures superimposed.

POROSITY.

The density of sprayed metal is always less than that of cast material, and this is due partly to porosity and partly to oxide particles. The porosity, consisting as it does of isolated cavities and interconnected pores, is difficult to estimate absolutely, and no values are found in the literature. The interconnected pores allow liquids or gases to penetrate to the base metal, a disadvantage in certain applications, *e.g.* when copper is used to protect steel from carburizing and also when the deposit is electropositive to the base. The interconnected porosity (or permeability) has been estimated by the following method: Built-up samples of sprayed metal ($\frac{1}{8}$–$\frac{3}{16}$ in. thick) were stripped from the base, weighed, boiled in toluene for 1 hr., and subsequently weighed suspended in toluene, the temperature being estimated to ± 0·1° C. The toluene penetrates the pores with great rapidity, and the specific gravity subsequently calculated is that of the metal, oxide, and isolated pores. The samples were then heated under reduced pressure until the original weight was obtained (in order to drive off the toluene).

The specimens were next coated with a very thin film of vaseline (0·02–0·04 grm.) and weighed suspended in distilled water. The film of grease prevented the water from penetrating the pores, and enabled consistent results to be obtained. The difference between the two calculated specific gravities has been converted to percentage (permeable) porosity as shown in Table VI. The difference between the density (in toluene) and the density of the same metal in cast form indicates the extent of isolated pores together with oxides. The results show that the powder process produces deposits with the greatest porosity, and this is undoubtedly due to the fact that the particles are cooler when they strike the base with the result that they are not closely interleaved. The English wire pistol using coal-gas produced zinc deposits with low "inter-connected" porosity, but the low density (in toluene) clearly indicates that there are an appreciable number of isolated pores. This is confirmed by reference to the microstructure shown in Fig. 15 (Plate IV). In many cases the oxides tend to fill up the pores.

In these experiments the effect of variable nozzle distance from the base was studied. At very small nozzle distances the porosity is at its minimum, but it rapidly increases as the nozzle distance increases. This result is not unexpected since at close distances to the nozzle the particles are sufficiently plastic to allow effective interleaving. At

TABLE VI.—*Porosity (Permeable) and Hardness of Sprayed Masses* ($\frac{1}{8}$–$\frac{5}{16}$ *in. Thick*).

Process.	Metal.	Spraying Distance, Inches.	Specific Gravity.		Porosity, Per Cent.	Hardness.	
			In Water.	In Toluene.		Vickers (5 kg.).	Scratch 1/*W* (150 kg. Load).
English wire	Zinc C.G.	1	6·49	6·56	1·1	37·1	5·9
,, ,,	,,	3	6·44	6·71	3·9	29·9	5·4
,, ,,	,,	5	6·45	6·76	4·5	25	5·3
,, ,,	,,	7	6·37	6·85	6·6	25	5·3
,, ,,	,,	10	6·33	6·88	8·7	22	5·3
,, ,,	Zinc Ac	1	6·32	6·88	8·1	25·3	4·9
,, ,,	,,	3	6·36	6·84	7·0	26·2	4·9
,, ,,	,,	5	6·26	6·91	9·4	21·3	5·0
,, ,,	,,	7	6·29	6·96	9·5	22·6	5·3
,, ,,	,,	10	6·22	7·07	11·9	22	5·9
American (1)	Zinc Ac	3	6·15	6·76	8·9		
Molten metal	Zinc	1	6·24	6·98	10·6	35·5	6·0
,, ,,	,,	3	6·16	6·92	10·9	35·3	7·4
,, ,,	,,	5	6·15	6·96	11·7	34·3	7·7
,, ,,	,,	7	6·05	7·05	14·3	32·1	8·0
,, ,,	,,	9	6·04	7·04	14·4	34·3	6·7
,, ,,	,,	11	5·87	7·04	16·5	37·3	15·7
Powder	,,	8	6·04	7·00	13·8	28	5·1
,,	,,	12	5·76	7·06	18·4	19	5·3
,,	,,	15	5·63	7·05	20·1	21·6	5·9
American wire	Aluminium C.G.	N	2·35	2·69	12·8	30·7	
Powder	Aluminium	8	1·86	2·76	32·7	15·6	
,,	,,	11	1·81	2·76	34·3		
,,	,,	15	1·82	2·76	34·2	13·8	
Molten	Aluminium–Silicon	N	2·47	2·55	3·3	65	
Molten	Tin	N	6·95	7·00	1·0		
English wire	Tin C.G.	1	6·85	7·08	3·3		
,, ,,	,,	3	6·59	7·07	6·8		
,, ,,	,,	5	6·53	7·03	7·0		
,, ,,	,,	7	6·53	7·09	7·9		
,, ,,	,,	9	6·51	7·12	8·6		
,, ,,	Copper C.G.	1	7·71	8·09	4·7		
,, ,,	,,	3	7·54	8·30	9·1	107	
Powder	Copper	8	6·27	7·98	21·4	66	
,,	,,	10	6·05	7·83	22·8	51·5	
,,	,,	12	6·13	7·84	21·8	5·5	
American wire	Copper	3	7·32	8·29	11·8	99	
English wire	18 : 8	N	6·50	6·92	6·1	264	
,, ,,	0·7% C Steel	N	6·33	6·55	3·4	236	
,, ,,	Mild Steel	N	6·44	6·59	2·3	309	
,, ,,	Lead	N	10·01	10·5	4·6		

C.G. = using Coal-Gas. Ac = using Acetylene. N = normal spraying distance.

great nozzle distances the particles are cooler, more rigid and have less velocity, consequently forming a loose " heaped structure."

Unfortunately, with the usual design of nozzle the difficulties of operating at close distances are great, due to overheating of the deposit and also to its unevenness. In practice wire-brushing the coating is found to be successful in closing up the surface pores.

OXIDE CONTENT OF SPRAYED COATINGS.

In the literature on this subject there are many different opinions regarding the oxide content of the sprayed deposit. Schoop,[53] Arnold,[64] Bablik [66] consider that no oxidation of the particles in flight occurs except when a highly oxidizing flame is employed. Reininger,[34] Parkes,[3] and Karg [10, 11] admit the presence of oxide in the coating, but no values are given. The estimation of oxygen in most metals offers experimental difficulties with the exception of copper. A few typical values for copper are given in Table VII.

TABLE VII.

	Nozzle Distance, Inches.	Oxygen, Per Cent.	Cu_2O, Per Cent.
Powder Pistol . . .	8	2·84	25·6
" " . . .	10	3·39	30·6
" " . . .	12	3·17	28·4
American wire . . .	3	1·72	15·4
English wire . . .	3 C.G.	1·02	9·2
" " . . .	3 Ac	0·59	5·3
French wire . . .	3 Ac	0·71	6·4

C.G. = Coal-Gas. Ac = Acetylene.

Ballard and Harris [56] in a recent paper also give results of oxygen contents for wire pistols which are particularly interesting (Table VIII).

TABLE VIII.—*Percentage of Oxygen in Copper Deposits (Ballard and Harris).*

Nozzle Distance, Inches.	Coal-Gas Fuel (450 B.T.U.).		Acetylene Fuel Gas.		
	English.	French.	English.	French	American.
1	0·79	0·35	0·32	0·33	...
2	0·80	0·40	0·56	0·46	0·74
3	0·90	0·54	0·54	0·65	0·90
4	1·10	0·60	0·61	0·76	1·03
5	1·15	0·69	0·69	0·75	1·12
6	1·08	0·66	0·66	0·72	1·04
7	0·95				1·06
8	0·91				1·27
9	0·75				

English pistol designed for coal-gas. French pistol designed for acetylene.

These investigators also show that the oxygen content of the coating is (*a*) increased as the oxygen pressure is increased, and (*b*) reduced by keeping the base metal cool. This is not unexpected, since oxidation of the metal occurs (1) in melting, (2) during flight, and (3) on the surface of the article. At close distances the particles are in a reducing zone of the flame, thereby being protected from oxidation in flight. To obtain deposits low in oxide, it would appear advisable to use a slightly reducing flame and to reduce the nozzle distance so far as it is possible without overheating the base. Unfortunately, a pistol using a reducing flame is not working at its maximum efficiency. The practice of preheating the article advocated some 10 years ago[2] (p. 56), is now seen to be undesirable.

In one German pistol[12] carbon dioxide is used for atomizing in the case of low melting point metals, and the use of nitrogen instead of air has also been suggested but not worked commercially.

HARDNESS.

The hardness of sprayed deposits is becoming more important owing to the increased use of the process in the building up of worn articles. It is greatly affected by the amount of oxide and porosity of the coat, because a material full of pores has less resistance to penetration than sound metal, consequently yielding a lower Brinell number. On the other hand, oxide particles in the same material will tend to give a high scratch hardness. In mild steel the oxide present as sprayed makes the material almost unmachinable, but annealing decreases the hardness due to agglomeration of oxide, as shown in Fig. 28 (Plate VI). A few hardness values are given in Table VI and in Fig. 29 which shows the effect of nozzle distance. Thormann,[37] and Kessner and Everts,[51] using a wire pistol found that the hardness was increased by increasing the speed of wire feed, by higher oxygen pressure and also, to a less degree, by higher hydrogen pressure, optimum values being given.

DILATION.

The dilation behaviour of a sprayed deposit is important in certain applications where heat is applied. A few curves showing the effect of annealing are given in Fig. 30, as obtained from a Gale-type dilatometer. The duration of the heating has an important influence on the results, and in these experiments the time taken to reach 1000° C. was approximately 1¼ hrs.

Copper: On the first heating normal expansion occurs up to about 600° C., followed by a gradual contraction as recrystallization occurs,

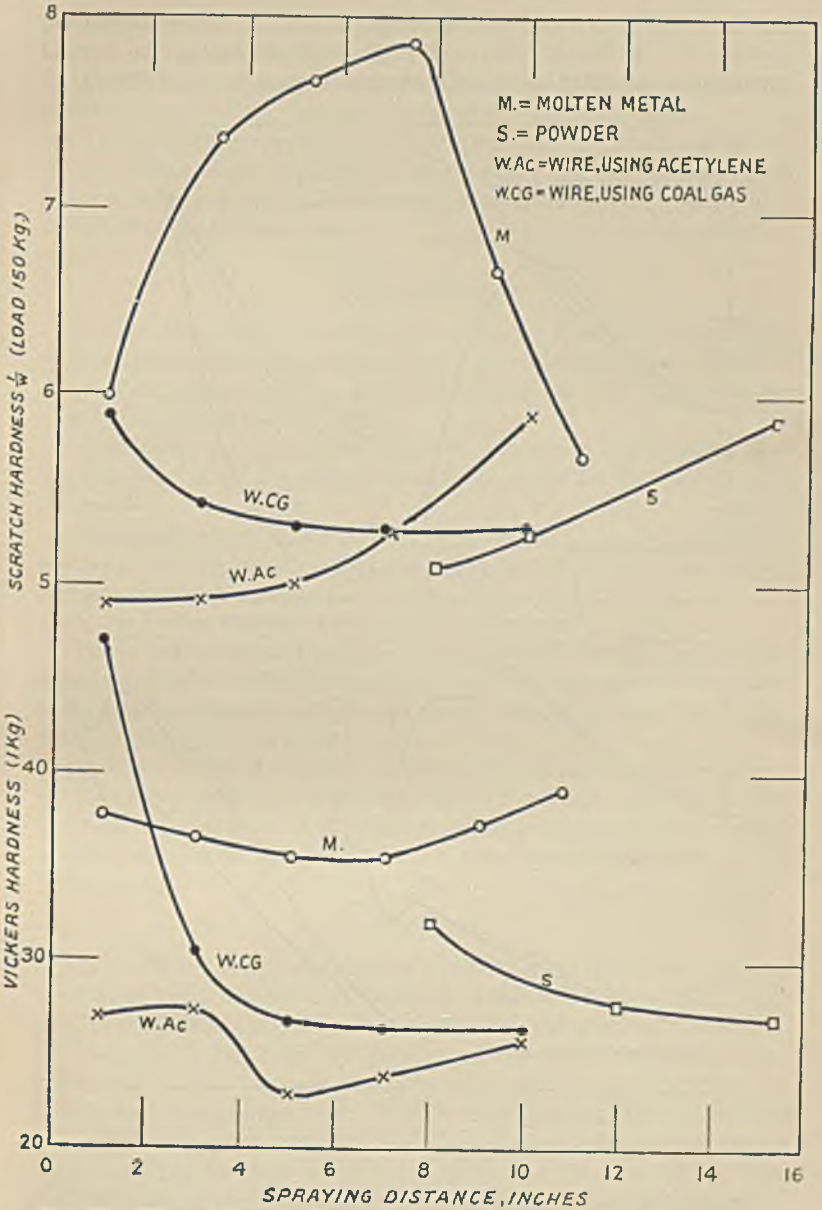

Fig. 29.—Effect of Spraying Distance on the Scratch and Vickers Hardness of Sprayed Zinc.

together with coalescence of the oxide particles. During the second heating the contraction above 600° C. counterbalances the normal expansion, but a third heating gives normal expansion up to 1000° C.

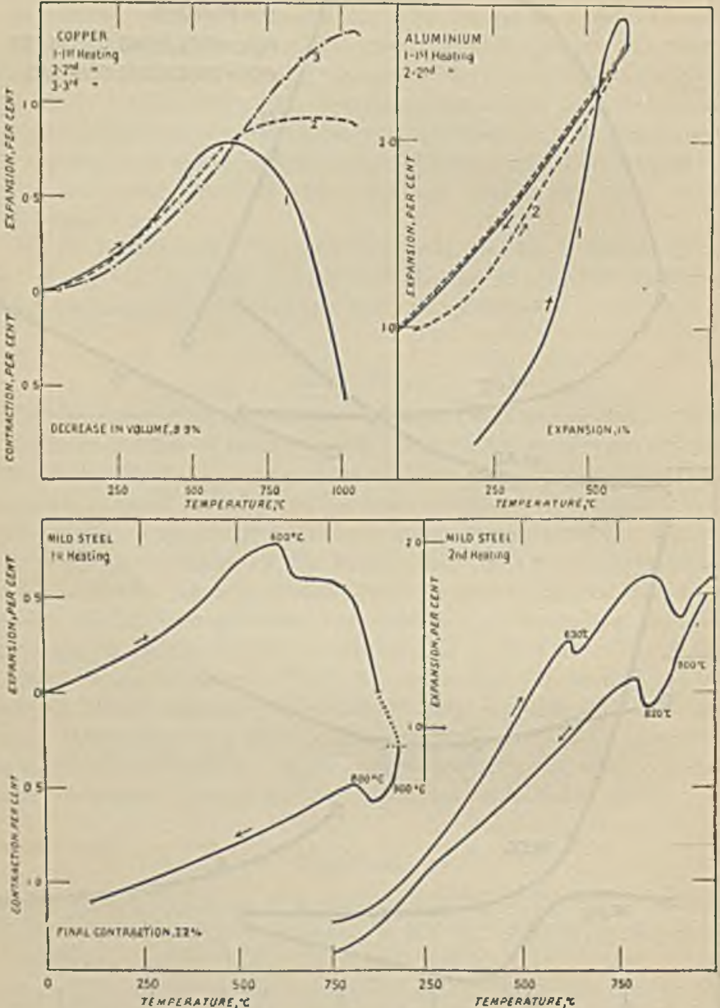

Fig. 30.—Dilation Curves of Sprayed Copper, Aluminium, and Mild Steel.

Steel: The first heating curve is similar to that of copper, except for a small modification at 700° C. due to the effects of the volume changes associated with the critical ranges in steel. These latter volume changes become normal after the second heating.

Aluminium: Whilst the other materials exhibit a permanent contraction after heating, aluminium expanded about 1 per cent.

The contraction resulting from heating causes little trouble when the coating is on a shaft, but tends to strip a lining from a hollow cylinder. The contraction is not uniform in all directions but is greater in a direction normal to the surface.

APPLICATIONS.

Zinc coatings afford excellent protection for iron and steel without danger of distortion, and are particularly useful for steel windows, light-gauge sheet metal, springs, and non-metallic articles. Zinc coatings afford an excellent base for paint.

Aluminium coatings are resistant to sulphurous atmospheres, and the very pure metal is gaining favour as a coating for the steel parts of aircraft.

Aluminizing is, of course, used to prevent scaling in furnace equipment operating at high temperatures (up to 950° C.) and to protect exhaust manifolds on aircraft.

Tin is used principally for coating food vessels.

Lead, nickel, copper, steel, and stainless steel coatings all have their uses, the harder metals particularly for building up worn machine parts and for filling blow-holes and cracks in castings where only compressive strength is required.

Among the more novel applications may be mentioned the treatment of insulators, radio apparatus, diathermic bandages, and wall paper, due to the conductive and electrical shielding properties of the coatings.

Further details will be found in the papers mentioned in the bibliography.

CONCLUSIONS.

In conclusion it appears that each of the three types of metal-spray equipment has characteristic advantages which will allow all of them to survive competition and become useful tools in the engineer's hands.

Owing to its low costs, the powder process will undoubtedly prove successful in spraying large surfaces with zinc, especially when the coat is subsequently painted. This powder-spraying pistol also offers possibilities of spraying brittle metal mixtures of glass and zinc and alloys of high melting point which could not be drawn into wire, although deposits of the higher melting point metals which have been examined are not wholly satisfactory as yet.

The molten metal instrument can produce thick coatings of the low melting point metals at a reasonable price, and should prove useful to the galvanizer doing contract work, especially as the metal in ingot form is used and neither acetylene nor oxygen is required.

The wire pistol, on the other hand, will without doubt hold the field in building up thick deposits on worn articles and also for producing heat-resisting surfaces. Even in the production of zinc coating where the cost is higher than in the case of the other processes the wire pistol offers advantages in the spraying of internal work.

Acknowledgments.

The author must thank Mr. A. E. Phipps (Mellowes, Ltd.), Mr. C. F. Lumb (Schori Metallizing Company), and Mr. W. E. Ballard (Metallization, Ltd.) for granting facilities, and for supplying the sprayed coatings, especially as it is rare to find competitive industrial organizations willing to allow independent investigators an opportunity to carry out comparative work on their respective equipment. Thanks are also due to Professor D. Hanson, D.Sc., for allowing much of this work to be carried out in his laboratories.

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DISCUSSION.

DR. T. P. HOAR (Member) summarized a contribution from Dr. U. R. Evans, who was unable to attend the meeting. This communication is included under Correspondence on p. 60.

MR. W. E. BALLARD * (Member): This paper is intensely practical and is I believe unique, because three competing firms supplied samples of their products for independent tests. If this happened more frequently the Institute would benefit by obtaining more practical papers.

I agree with the author that the paint used in his corrosion tests was not a happy choice, as paints with a zinc oxide base are better for covering zinc coatings, as would be expected from a theoretical reasoning.

The author mentions that the protection offered by zinc coatings is proportional to their thickness; I think that this is generally agreed. In commerce, coatings are usually sold according to their thickness and I think that it is fair to assume that for equal thicknesses, coatings from the wire pistol having a porosity of 5 per cent. will be better than coatings made by other processes giving a porosity in the order of 15 per cent.

On p. 45 mention is made of four types of aluminizing treatment, and it is stated that the last one is the subject of a British Patent. In order that there may be no misunderstanding, it should be stated that the three other processes also form the subject of British Patents.

I am surprised that the author did not obtain better results with the special alloy, because, commercially, we are satisfied that this usually gives the best results.

The corrosion test results are not quite in agreement with practice because the author has found that aluminium coatings are not quite so good as those of zinc. The work of U. R. Evans and of Sutton proves that aluminium coatings are better under conditions of atmospheric corrosion and even in some marine conditions.

With regard to the oxidation of the metal during the process of spraying,

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* Director, Metallization, Ltd., Dudley.

there yet appears to be much to learn. It is a complicated subject and it may be mentioned that under certain conditions it is possible to spray brass with a wire pistol and loose copper and not zinc. This is perhaps the only oxidation method used in commerce where there may be a preferential loss of copper from brass.

Mr. A. E. PHIPPS : * With reference to Fig. 17 (Plate V), the unetched particles of elongated shape found in the structure and said to be iron or iron-rich material abraded from the nozzle are more probably zinc–iron alloy, due not so much to the abrasion of the nozzle as to the solvent action of the zinc on the iron container.

With regard to the question of suitable paints for use on zinc coatings, experience has shown that zinc oxide paint is best, but red iron oxide paints have been used without ill effects. Lead-base paints have been found to be generally unsuitable.

Table II (accelerated corrosion tests) gives figures showing a very wide variation. The thickness of one layer of zinc by the molten metal method is given as 0·0022 in., and of two layers as 0·0031 in. This is quite different from the estimated figures, which are 0·004 in. for one layer and 0·007–0·008 in. for two layers. The thicknesses given for zinc sprayed by the wire method are unusual, 0·0020 in. for one layer being in accordance with the maker's figures, but 0·0028 in. for two layers being surprisingly thin. Has the author any information on that subject?

The suggestion that the life is limited mainly by the thickness of the deposit is not entirely borne out by Table II, because in several cases the life of the specimens appears to bear little relation to the thickness of the coating. For example, the coating 0·0020 in. thick apparently withstood the test for the same number of days as the coating of 0·0053 in. thick. From that it appears that accelerated corrosion tests made with so few specimens and in such a limited time are not of practical value, and I suggest that it might be of advantage if further tests were carried out on a much greater number of specimens and over a longer period.

CORRESPONDENCE.

MR. W. E. BALLARD † (Member) : In Table I figures are given for the speed of application of zinc. It should be made clear that these figures represent the rate of the flow of metal passing through the pistol nozzle. The actual amount of metal deposited with a given speed of flow will depend on a large number of factors, such as the type of process, nozzle distance, and the rate of travel over the surface sprayed. The author gives an average figure of 17 sq. ft. per hr. with a 5 lb. flow of metallic wire. This is the average over a large variety of work and this area will be exceeded on plain surfaces, but the area covered will be smaller with the same flow of metal if the surface to be covered is more unsuitable. The percentage loss with powder spraying is greater than with wire spraying.

Tables II and III give the actual thickness of the coatings and also further columns stating the "number of layers." From America has come a tendency to speak of the number of layers or coats in metal spraying, and coatings are specified as being so many coats thick. This is very much to be deprecated, as the thickness of each coating will depend on the speed of travel of the

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* Mellowes and Company, Ltd., Sheffield.

† Director, Metallization, Ltd., Dudley.

nozzle. My own firm always specifies the actual thickness applied and I believe that this is the only positive method of measurement and the only one which will assure that the customer gets what he requires. Great care is taken in checking the weight of wire used and in checking the spraying rate, so that the sprayed coatings are of the actual thickness specified. It is somewhat unfortunate, therefore, that the author has specified the number of layers as this is merely arbitrary. This point is shown well in Table II in the case of the molten metal pistol, where one layer sprayed at normal distance is found to be 0·0022 in. thick in one case and 0·0063 in. thick in another, when the nozzle is worn. As the nozzle size increases during the life of 1 hr., the number of coats loses all significance.

Table V gives results of the protection offered by heat-treated aluminium coatings from high-temperature oxidation. It will be seen that the wire process shows to advantage; experiments which I have carried out have always confirmed these results. Coatings applied by many types of powder pistol have never given satisfactory results for this class of work, and this is probably due to the high initial oxide content in the coating which causes a very low absorption rate of the aluminium into the base.

With regard to the hardness of sprayed coatings, it should be noted that this property is extremely difficult to specify. It has been found that the hardness of sprayed metal varies considerably through the coating itself, and is usually much greater on the surface than in the interior. The exact control of this property is not yet fully understood. It probably bears some relation to oxidation which, as I mentioned in the oral discussion, is a complicated study which has not been worked out to definite conclusions. I believe that the author is the first to publish dilation curves. This curious property of sprayed metal is extremely important when dealing with thick coatings used for the repair of worn parts.

In presenting his paper the author stated that the powder pistol had been improved since his samples had been prepared. It would be interesting to have some details of this improvement because I feel that it is scarcely likely that the main difficulties of the powder system will be overcome. The main difficulty with any powder system is that it is impossible to make certain that all the particles of powder attain the same temperature within the flame zone. In France a powder pistol is used to a limited extent which has a double air cap such as is found on the French wire pistol. It is claimed by this means that very much better results are obtained than with the ordinary powder nozzle, but even so the makers do not claim that the powder process approaches the wire system in technical efficiency.

Mr. J. C. Bowen * (Member): With regard to the oxide content of sprayed metal coatings and the factors influencing the percentage of oxide, it is stated that the wire pistol is not working at its maximum efficiency with a reducing flame. This is not quite true. When hydrogen is used the flame is always reducing, as there is always an excess of hydrogen over the amount required for combustion. The actual volumes consumed when spraying zinc are 72 ft.^{3} of hydrogen and 25 ft.^{3} of oxygen. The design of the pistol does not permit any great variation between the relative pressures of oxygen and hydrogen, the difference between the two pressures can only be 1 or 2 lb./in.^{2}.

When coal-gas is used with the same pistol, the orifices through which the gases enter are the same and it will be seen, therefore that as the specific gravity of coal-gas is so much greater than that of hydrogen (coal-gas, 0·42–0·49; hydrogen, 0·06958; air, 1·0), there will be a smaller excess of combustible gas and the conditions will be less reducing. There is therefore a tendency for

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* General Manager, Metal Sprayers, Ltd., London.

there yet appears to be much to learn. It is a complicated subject and it may be mentioned that under certain conditions it is possible to spray brass with a wire pistol and loose copper and not zinc. This is perhaps the only oxidation method used in commerce where there may be a preferential loss of copper from brass.

MR. A. E. PHIPPS: * With reference to Fig. 17 (Plate V), the unetched particles of elongated shape found in the structure and said to be iron or iron-rich material abraded from the nozzle are more probably zinc–iron alloy, due not so much to the abrasion of the nozzle as to the solvent action of the zinc on the iron container.

With regard to the question of suitable paints for use on zinc coatings, experience has shown that zinc oxide paint is best, but red iron oxide paints have been used without ill effects. Lead-base paints have been found to be generally unsuitable.

Table II (accelerated corrosion tests) gives figures showing a very wide variation. The thickness of one layer of zinc by the molten metal method is given as 0·0022 in., and of two layers as 0·0031 in. This is quite different from the estimated figures, which are 0·004 in. for one layer and 0·007–0·008 in. for two layers. The thicknesses given for zinc sprayed by the wire method are unusual, 0·0020 in. for one layer being in accordance with the maker's figures, but 0·0028 in. for two layers being surprisingly thin. Has the author any information on that subject?

The suggestion that the life is limited mainly by the thickness of the deposit is not entirely borne out by Table II, because in several cases the life of the specimens appears to bear little relation to the thickness of the coating. For example, the coating 0·0020 in. thick apparently withstood the test for the same number of days as the coating of 0·0053 in. thick. From that it appears that accelerated corrosion tests made with so few specimens and in such a limited time are not of practical value, and I suggest that it might be of advantage if further tests were carried out on a much greater number of specimens and over a longer period.

CORRESPONDENCE.

MR. W. E. BALLARD † (Member): In Table I figures are given for the speed of application of zinc. It should be made clear that these figures represent the rate of the flow of metal passing through the pistol nozzle. The actual amount of metal deposited with a given speed of flow will depend on a large number of factors, such as the type of process, nozzle distance, and the rate of travel over the surface sprayed. The author gives an average figure of 17 sq. ft. per hr. with a 5 lb. flow of metallic wire. This is the average over a large variety of work and this area will be exceeded on plain surfaces, but the area covered will be smaller with the same flow of metal if the surface to be covered is more unsuitable. The percentage loss with powder spraying is greater than with wire spraying.

Tables II and III give the actual thickness of the coatings and also further columns stating the "number of layers." From America has come a tendency to speak of the number of layers or coats in metal spraying, and coatings are specified as being so many coats thick. This is very much to be deprecated, as the thickness of each coating will depend on the speed of travel of the

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* Mellowes and Company, Ltd., Sheffield.

† Director, Metallization, Ltd., Dudley.

nozzle. My own firm always specifies the actual thickness applied and I believe that this is the only positive method of measurement and the only one which will assure that the customer gets what he requires. Great care is taken in checking the weight of wire used and in checking the spraying rate, so that the sprayed coatings are of the actual thickness specified. It is somewhat unfortunate, therefore, that the author has specified the number of layers as this is merely arbitrary. This point is shown well in Table II in the case of the molten metal pistol, where one layer sprayed at normal distance is found to be 0·0022 in. thick in one case and 0·0063 in. thick in another, when the nozzle is worn. As the nozzle size increases during the life of 1 hr., the number of coats loses all significance.

Table V gives results of the protection offered by heat-treated aluminium coatings from high-temperature oxidation. It will be seen that the wire process shows to advantage; experiments which I have carried out have always confirmed these results. Coatings applied by many types of powder pistol have never given satisfactory results for this class of work, and this is probably due to the high initial oxide content in the coating which causes a very low absorption rate of the aluminium into the base.

With regard to the hardness of sprayed coatings, it should be noted that this property is extremely difficult to specify. It has been found that the hardness of sprayed metal varies considerably through the coating itself, and is usually much greater on the surface than in the interior. The exact control of this property is not yet fully understood. It probably bears some relation to oxidation which, as I mentioned in the oral discussion, is a complicated study which has not been worked out to definite conclusions. I believe that the author is the first to publish dilation curves. This curious property of sprayed metal is extremely important when dealing with thick coatings used for the repair of worn parts.

In presenting his paper the author stated that the powder pistol had been improved since his samples had been prepared. It would be interesting to have some details of this improvement because I feel that it is scarcely likely that the main difficulties of the powder system will be overcome. The main difficulty with any powder system is that it is impossible to make certain that all the particles of powder attain the same temperature within the flame zone. In France a powder pistol is used to a limited extent which has a double air cap such as is found on the French wire pistol. It is claimed by this means that very much better results are obtained than with the ordinary powder nozzle, but even so the makers do not claim that the powder process approaches the wire system in technical efficiency.

Mr. J. C. Bowen * (Member): With regard to the oxide content of sprayed metal coatings and the factors influencing the percentage of oxide, it is stated that the wire pistol is not working at its maximum efficiency with a reducing flame. This is not quite true. When hydrogen is used the flame is always reducing, as there is always an excess of hydrogen over the amount required for combustion. The actual volumes consumed when spraying zinc are 72 ft.^{3} of hydrogen and 25 ft.^{3} of oxygen. The design of the pistol does not permit any great variation between the relative pressures of oxygen and hydrogen, the difference between the two pressures can only be 1 or 2 lb./in.^{2}.

When coal-gas is used with the same pistol, the orifices through which the gases enter are the same and it will be seen, therefore that as the specific gravity of coal-gas is so much greater than that of hydrogen (coal-gas, 0·42–0·49; hydrogen, 0·06958; air, 1·0), there will be a smaller excess of combustible gas and the conditions will be less reducing. There is therefore a tendency for

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* General Manager, Metal Sprayers, Ltd., London.

metal sprayed with coal-gas to have a higher oxide content than that sprayed with hydrogen.

The main factor controlling oxide content is the spraying distance; *i.e.* the period during which the hot metal particles are exposed to the oxidizing action of the compressed-air stream. Tin is particularly sensitive to oxide formation if the spraying distance is more than 4 in. Up to this distance a clean grey deposit is obtained, but when the pistol is held at a greater distance a yellowish brown coating full of oxide is produced.

The unsatisfactory nature of the powder spraying deposits are obviously due to too great a spraying distance and an insufficient supply of combustible gas and oxygen. Until the powder pistol is redesigned so that the whole of the powder is melted in passing through the flame, it would seem that its application will be limited.

Dr. U. R. Evans,* M.A. (Member): Two sets of tests on metal-sprayed steel have been organized from Cambridge, the short-time laboratory tests to which Mr. Rollason refers,† and some outdoor exposure tests lasting 4–6 years.‡

The laboratory tests included sand-blasted steel sprayed by the wire-process with copper, nickel, zinc, or aluminium, applied as thick, thin, and discontinuous coats, some being doped with varnish, and others undoped. The testing conditions included partial immersion in Cambridge tap-water and sodium chloride solution, intermittent spraying with dilute sulphuric acid or sodium chloride, and exposure to air containing sulphur dioxide or hydrogen chloride; special attention was devoted to places where the coats were, of intention, cracked. Cathodic coatings, such as nickel and copper, gave no protection at cracks, and the corrosion set up by the salt-spraying of porous coats produced rust *below* the coats, which tended to rise as blisters, especially on special specimens where the coating had been (intentionally) applied to *greasy* steel. Anodic coatings (zinc or aluminium), gave different results, since here any corrosion at pores or cracks affected the covering metal (not the steel), and there was no tendency for the coating to be pushed up by rust formed below; zinc spraying was much less sensitive to grease on the steel than copper or nickel spraying. Moreover, the steel remained immune from rusting even at breaks in the coat, provided that the coating metal was attacked sufficiently quickly to give cathodic protection to the exposed steel. In deciding whether cathodic protection would occur, the size of the gaps in the coat and also the nature of the liquid wetting the metal was important. In salt-water, either zinc or aluminium coats were attacked sufficiently fast to protect the steel at small gaps, but zinc was destroyed much more rapidly than aluminium. Since protection must cease when the covering metal has disappeared, aluminium appears more suitable for protection against salt-water than zinc. For hard water, such as the Cambridge public supply of 1928, the reverse was the case; aluminium was not attacked sufficiently rapidly to give cathodic protection to steel exposed at gaps and consequently rusting occurred; zinc was attacked sufficiently rapidly to ensure cathodic protection of the steel, but not so rapidly as to disappear prematurely. In this hard water, therefore, zinc is a suitable protective, whilst aluminium, although the most suitable if the coating can be made continuous, will be unsuitable if the coating contains cracks.

These tests suggested that aluminium would probably be the best metal

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* Cambridge.

† U. R. Evans, *J. Inst. Metals*, 1928, **40**, 99.

‡ S. C. Britton and U. R. Evans, *J. Soc. Chem. Ind.*, 1932, **51**, 217T; 1936, **55**, 340T.

to protect steel against outdoor corrosion. Accordingly, in 1931, a series of aluminium-sprayed specimens were exposed outdoors by Britton and myself in :

(1) A marine atmosphere (Selsey),
(2) An urban atmosphere (London),
(3) A country atmosphere (Grantchester Meadows), and
(4) A mixed atmosphere (Cambridge).

The specimens included three different kinds of aluminium, applied both as thin and thick coatings, and with and without doping; in all 104 specimens were exposed. After 4–6 years, no rusting of the steel was observed on any of these specimens, although in London and at Selsey there was some attack on the aluminium, whilst the specimens at London and Cambridge had become very black. Three specimens removed from the London rack after 5 years' exposure seemed on close examination to suggest that the corrosion of the aluminium was taking place locally between the steel and the coat, which was being pushed up in small blisters; evidence of similar changes has been found in some of the specimens from Selsey, but it does not follow that the lives of the coatings are approaching their ends. Since none of the specimens shows any rust at all, it is evident that even the worst form of coat included has given satisfactory results.

Since sprayed aluminium coatings are somewhat soft, the behaviour of the steel where it has become exposed at scratches seemed to demand study. Accordingly, on most of the specimens at Cambridge and Grantchester Meadows, scratches were intentionally made, penetrating through to the steel. A little rusting appeared along these scratch lines at first, but it ceased to develop and finally the rust disappeared. Evidently cathodic protection has occurred; it takes a little time to develop, but has prevented any serious destruction at the scratch lines even after 6 years. This seems to show that the occasional damage of such coatings by scratching may not be so serious a matter as is sometimes supposed.

In any case, it is possible to cover the metal coat with another and harder composition. Moreover, for decorative purposes, the painting of metallized coats may be desired. Accordingly, at all stations, additional specimens were exposed which carried paint (red iron oxide and green chromic oxide) over the aluminium coats. These paints retained their appearance very well during the period (4–6 years)—much better than paint applied direct to steel, since in the British climate the failure of paint due to under-rusting proceeds more quickly than the deterioration of the paint starting from the outside.

Under suitable conditions, metal-spraying should be a most valuable means of combating corrosion. Like all other protective processes, the method has its limitations as well as its uses. The proprietors of the various processes would be well advised to define their respective limitations, thus avoiding the real danger that the reputation of a good method may suffer damage through its application in cases to which it is unsuited.

Dr. J. C. Hudson,* A.R.C.S. (Member): This paper serves a very good purpose in directing attention to the possibilities of the metal-spraying processes, accurate data concerning which are of direct interest to those concerned with the protection of iron and steel. The author is correct in emphasizing the importance of the preparation of iron and steel surfaces, if the maximum protection is to be obtained from protective paint coatings applied to them. There is no doubt that the present tendency, based alike on the results of research and of practical experience, is to pay much more attention to the

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* Investigator, Corrosion Committee of the Iron and Steel Institute and British Iron and Steel Federation, Birmingham.

preparation of iron and steel surfaces prior to painting, generally by the adoption of some descaling process. It is, as the author suggests, a logical step forward to apply metallic coatings to such descaled surfaces and there is a distinct possibility that in the future the protective measures adopted for iron and steel structures exposed to corrosion will consist, in an appreciable number of cases, in the application of a metallic coating directly to the metal, followed by painting.

The author's corrosion experiments, reported in Table II, may be broadly interpreted, as he points out, by the statement that the life of zinc coatings is approximately proportional to their thickness, assuming that they are correctly applied. This conclusion was also reached in field tests conducted by the American Society for Testing Materials. In connection with the increases in weight of the specimens after 28 days, given in Table II, it should perhaps be pointed out that these cannot be taken as directly proportional to the corrosion and it would be of value if the author could give an estimate of the amounts of salts derived from the spray contained in the corrosion products.

As regards the paint tests described in Table IV, was the paint applied directly over the galvanized surface, or was this so prepared by weathering or in some other way, as to ensure a good bond for the paint? This, of course, would materially affect the adhesion of paint to a hot-galvanized surface.

Mr. R. F. Lumb *: The subject of this paper has been handled with the utmost impartiality by Mr. Rollason, but at the same time I must point out that: (1) The powder pistol is not restricted to the spraying of shallow work only, and tubes of 1½ in. inside diameter can be sprayed internally by this process. (2) In regard to the tests on the zinc coatings, it seems that too much importance was given to the porosity test and not enough to the corrosion test, which must surely be the most important. If the latter is studied it will be observed that the samples sprayed by the powder pistol compare more than favourably with those sprayed by other processes. (3) The results attained commercially have proved that zinc spraying with the powder pistol is the cheapest and most efficient method of protecting steel against ordinary corrosive influences. It may be mentioned that 85 per cent. of the powder pistols sold have been in replacement of the older methods of spraying.

Mr. R. A. Parkes † (Member): There is one small point mentioned in the theoretical part of the paper which does not appear to be substantiated in practice. I refer to the statement that the base upon which the metal is deposited conducts away only a small proportion of the heat contained therein. Photographs of sprayed particles on glass, itself a poor conductor, show that the metal first splashes out, but then cools instantaneously with the result that the splash-formation is retained in the solid metal. This surely must indicate that the heat contained in the particle is very rapidly transferred to the base, although in view of the microscopic dimensions of the sprayed particle the actual heat given up admittedly is very small.

The accelerated corrosion tests on zinc appear to have given a false impression in so far that a statement is made leading to the conclusion that zinc coatings of the same thickness give equal protection whether applied by wire, powder, or molten metal pistols. This does not agree with my own experience, deposits from the powder pistol in particular offering less resistance than those from the other two methods, owing no doubt to the higher degree of porosity. This is confirmed by the author's field tests (Table III) indicating

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* Schori Metallising Process, Ltd., London.

† Metallurgist, Metallisation, Ltd., Dudley.

that zinc coatings of approximately the same thickness applied by the powder and wire methods showed a wide variation in weight increase. I refer particularly to samples 17 and W.6.

Regarding the tests on coatings resistant to high temperature oxidation, the method of quenching in water after each heat naturally has a very drastic effect on the surface scale as the author states, but it is also likely to have a similarly drastic effect on the coating itself. Tests which I have carried out indicate that it is possible to set up cracks in the protective layer due to differential expansion and contraction, thus allowing oxidation to take place in the exposed underlying metal. In view of the severe nature of this test the coatings have behaved remarkably well, although the results from the powder and molten metal pistols do not compare favourably with the deposits obtained by wire. This can be explained to a large extent by the high degree of porosity in the powder deposits, and the presence of silicon in the molten deposits, silicon having been found to have a definite adverse effect on the penetration of aluminium into the steel.

The method of estimating porosity appears to be somewhat complex and open to objection on the grounds that boiling in toluene might not expel all traces of air from the pores. I carried out a series of tests on porosity in 1925, the method being to immerse weighed samples in paraffin under vacuum until the air ceased to exude, and then re-weigh after lightly rubbing the surfaces to remove the outer film of paraffin. By this method the following porosities were obtained :

	Per cent.
Copper	11·65
Zinc	7·88
Aluminium	6·85
Tin	0·09

All of these coatings were sprayed at a normal distance, but it is quite conceivable that changes in technique and operating conditions in the intervening years have affected the degree of porosity of the coatings.

It would be interesting if the author could check his results by this method, using the actual samples originally employed.

Mr. A. J. Sidery,* Assoc.Met. (Member) and Mr. C. Braithwaite *: In connection with the corrosion tests carried out on sprayed samples, the author states on p. 43 that " all the zinc coatings made under best commercial practice have approximately the same rate of corrosion." It is suggested, however, that the results given in Table II indicate that, so far as zinc coatings are concerned, better protection is afforded by normal coatings applied by means of pistols employing powder or wire than by coatings applied by the " molten metal " type of pistol. When considered from the point of view of weight per unit area of sprayed surface, coatings applied by the " wire " process would appear to be rather more efficient than those applied by the " powder " pistol.

In our experience, better adhesion to the basis material is exhibited by coatings of aluminium or zinc applied by the " wire " pistol than by coatings applied by the " powder " pistol, and this superior adhesion obtained by the former method has been particularly advantageous in the case of aluminium coatings under conditions involving exposure at elevated temperatures to an oxidizing atmosphere and exposure to the influence of sea-water spray.

Under conditions of exposure to marine conditions in tropical waters over a period of 200 days, aluminium coatings sprayed by a " wire " pistol gave

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* Royal Aircraft Establishment, South Farnborough.

excellent protection to samples of mild steel sheet, high-tensile nickel-chromium alloy steel strip (approx.: carbon 0·3, nickel 4·0, chromium 1 per cent.) and Duralumin sheet, but it was observed that no benefit was derived by the application of supplementary organic protectives such as stoving enamel or pigmented oil varnish to the metal-sprayed surfaces. Indeed, samples to which coatings of stoving enamel had been subsequently applied showed greater deterioration than did those carrying sprayed coatings of aluminium only.

On account of the comparatively high porosity of the coating, metal-sprayed surfaces appear to require about twice as much enamel or varnish as ordinary metallic surfaces for the production of films of normal appearance. The total weight of the protective scheme per unit area thus becomes somewhat high and tends to render the scheme less attractive in cases where weight is of prime importance, as, for example, on aircraft.

It appears desirable to search for organic protectives which can improve the protective effect of sprayed coatings without unduly increasing the weight.

Has the author yet made any tests on samples carrying sprayed coatings of aluminium or zinc of high purity, as compared with coatings of normal commercial purity?

Mr. T. HENRY TURNER,* M.Sc. (Member): The author has mentioned the paper which Ballard and I read in 1924. A still earlier paper was presented to the Institute by R. K. Morcom in 1914. Between 1914 and 1924 there had been very little development, but in the period 1924 to the present year there had been a real practical use of various modifications of the process in a great number of industries. It is interesting, therefore, to recall that one of the most famous of the Institute's scientific members criticized the book written by Budgen and myself, on the grounds that metal spraying was not worth the trouble of investigation. The commercial development of the processes has justified the three papers, as well as the book.

During recent years, I have tried to keep in touch with the three processes and have had test panels sprayed by each of them. These were exposed on test racks at Stratford (London, E.15), at the Forth Bridge, in tunnels and elsewhere, and it has been found that so far as the tests went, 4/1000 in. of aluminium applied by the wire process has given the best results. Aluminium 4/1000 in. thick, applied by the powder process failed in less than a month at the Forth Bridge.

Generally speaking, the wire process, with zinc and aluminium, has withstood an industrial atmosphere for 2 years and then failed, and in each case the rust appeared to be following the "strokes" of the application. This appears to be an important observation, as it is one which may suggest to the operator improvements in the method of application.

The testing of metal-sprayed coatings is in reality a very complicated business and one which the scientific members of the Institute might well regard as not below their dignity. For example, one must first ascertain the effect of the method of preparation of the steel base. If a sand blast is used, the optimum angle at which to hold the nozzle and the best blast pressure, size of particle, and type of sand require consideration; if shot blast is used, the same variables must be examined; if one uses a wire brush, the pressure on the brush, the gauge of the wire, and the composition of the wire is most important, as is the direction in which the brush is moved.

One then has to test a variety of metals, alloys, or mixtures of metals and silicates, bitumen, and other materials which may be sprayed on the metal so prepared, and these coatings can then vary in thickness of deposit and in order

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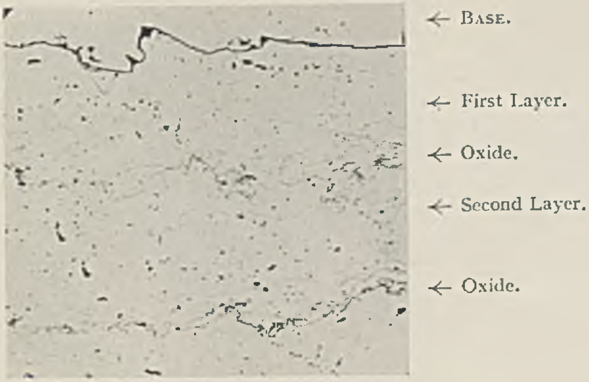

FIG. A.—Section Through Sprayed Copper Built Up of Three Layers.

of application. Furthermore, they may be applied by spray guns of many types of construction, in that each of the three fundamental processes has minor modifications, and lastly the nature of the fuel, that is to say, the chemical composition of the gas or the type of electric power and the condition of the air, whether it is preheated and especially whether it is dried, or whether exhaust or other gases be used instead of air, are variables which anyone must consider who has studied the process as now used in various countries.

Metal spraying has great possibilities, but will never be able to be used indiscriminately for all types of surface protection. The coating required in the acid conditions of a tunnel or an industrial district will obviously have to be different from that for a normal atmosphere, as encountered either inland or by the sea. Wherever possible sprayed metal coatings should be helped with dopes, varnishes, or paints. Such a combination of base metal cleaning, spraying with metal and finally painting is to be widely recommended.

The AUTHOR (*in reply*): I agree with Mr. Phipps that, owing to the attack of the container of the pistol by the molten zinc, an iron–zinc alloy will form, but there will be a tendency for this compound to dissolve in the excess zinc owing to the time allowed. On the other hand, the iron abraded from the nozzle will only have time to form a zinc compound very rich in iron, with a density greater than zinc, with the result that it tends to drop out of the spray. At short spraying distances a small quantity of this compound is trapped in the coating, but at normal nozzle distances it is practically absent. Mr. Phipps compares specimen 7 with W1 in Table II, but the spraying conditions employed for the production of the former are not normally used industrially and the statement that the life of the coatings is limited by their thickness was specified for only those made under the best commercial practice.

The reason why the thickness of the two layers is rarely twice that of one is that in depositing the first layer the operator allows the "strokes" of the pistol to overlap in order to cover the base, the colour of which differs from the sprayed metal. In making the second layer no such colour difference exists and the operation is accelerated, with the result that only a thin layer is deposited.

Mr. Ballard's contributions are very welcome, and I agree that the thickness of the coating should be specified in preference to the number of layers. Nevertheless, there is every justification, in experiments of this kind, for including the number of layers in Table II, because it brings out the fact that the second layer is rarely as thick as the first owing to the faster movement of the pistol when the basis metal cannot be seen by the operator. There can be variations in the properties of the coating depending on the number of layers. Fig. A (Plate VII) illustrates a copper deposit built up of three layers which are separated by heavy oxide layers owing to contact with air between the strokes of the pistol. This coating may behave differently from a similar deposit of identical thickness made as one layer. The example chosen by Mr. Ballard is a special case of exceptional conditions used in these experiments to study the influence of nozzle distance and nozzle wear. In commercial operation of the molten metal pistol, the operator always quickens the speed of spraying to keep the thickness uniform. The method of measuring the thickness of a deposit by micrometer readings may be misleading and in these experiments an average thickness was calculated from weights of metal deposited.

Improvements in the coatings produced by the powder pistol are mainly due to right choice of powder size in relation to the nozzle setting.

Mr. Bowen's contribution is interesting but does not disprove my statement that the pistol is not working at its maximum efficiency with a reducing flame. To get the ideal thermal efficiency the fuel-gas should be in the correct ratio to the total oxygen present at the nozzle. The flame is surrounded by compressed air which also supplies oxygen to burn the fuel-gas. Although hydrogen is used apparently in excess, it is a light gas and mixes freely with the compressed air with the result that, in practice, the flame may not be reducing. According to results by Ballard and Harris,[56] the type of fuel-gas has little effect on the oxide content of sprayed copper. Hydrogen is sometimes an advantage in spraying high melting point metals since the flame produced is hotter than that of coal-gas and the speed of spraying can be increased, thus decreasing the time of contact of the metal with oxidizing gases. The speed of propagation of a hydrogen flame is very high, and this results in a tendency to back-fire. Consequently the pistol orifices are reduced in size, and hydrogen in excess of that required by the compressed oxygen, is necessary to get smooth working of the pistol.

Dr. Evans's contribution is particularly interesting.

In reply to Dr. Hudson, the increases in weight of specimens given in Table II were measured after most of the sodium chloride had been removed by a short-time immersion in distilled water. In the paint tests described in Table IV, the paint was applied directly over the galvanized surface, and this procedure is the cause of the poor adhesion of the paint.

In reply to Mr. Lumb I can only state that I have never seen tubes sprayed internally by the powder process, but since the powder would possibly be blown along the nozzle extension tube, I anticipate that trouble may be expected owing to the "packing" of the powder. In the particular corrosion tests recorded in this paper the porosity of the zinc coatings does not seem to be a major influence in their life owing to the pores being filled with corrosion products. The life of the coatings seems to depend largely on the weight of zinc deposited, although the purity of the metal also effects the corrosion rate.

I cannot agree with Mr. Parkes that the conduction of heat to the base is the way in which the particles are cooled. The rapidly moving air across the area exposed by a "splashed" particle would instantly chill the molten metal.

Mr. Parkes's method of estimating porosity by immersing his samples in paraffin under a vacuum is open to the objection that the paraffin does not penetrate the pores in the coatings as readily as toluene, and the vacuum serves no useful purpose when used as suggested. A more satisfactory way would be to enclose the specimens in a container without paraffin, evacuate, and then allow paraffin to flood the specimens. The pressure of air in the pores of the specimen would be reduced to a fraction of an atmosphere and, on flooding, the paraffin would compress the air to a negligible volume. The total volume of the specimen has still to be found experimently unless the shape and dimensions are such as will allow accurate computation.

The contributions of Messrs. A. J. Sidery and C. Braithwaite and Mr. T. H. Turner are valuable and bring out many interesting points.

AN ALUMINIUM STATUE OF 1893: GILBERT'S "EROS." * 759

By Professor R. S. HUTTON,† M.A., D.Sc., Fellow, and RICHARD SELIGMAN,‡ Ph.nat.D., Past-President and Fellow.

Synopsis.

The freedom from serious corrosion of the "Eros" statue in Piccadilly Circus, London, after 38 years' exposure and the fact that it is made of un-alloyed aluminium are recorded. Whether the metal used in 1893 was produced by the old chemical or new electrolytic process is undecided, but the results of analyses of specified examples of old aluminium are reported.

Those who took part in the Annual Dinner of the Institute in March, 1935, will remember the jocular suggestion of one speaker that a statue of a distinguished and popular member should be cast in aluminium and erected in Piccadilly Circus. The speaker was unaware that a statue in aluminium of "Eros" had formed part of the Shaftesbury Memorial in Piccadilly Circus for over 40 years!

In June, 1893, the memorial to the great philanthropist was unveiled—"the only aluminium monument erected in England . . . the work of a young, but already rising sculptor, Mr. Alfred Gilbert, R.A.," as Mr. H. R. Williams described it at the unveiling. At the same ceremony the Duke of Westminster spoke of "This beautiful work of art, which will not soon perish." It may well be asked how many metallurgists, with the knowledge of atmospheric corrosion phenomena available to-day, would have endorsed the opinion of the Duke of Westminster. Indeed, even before the year was out there were not wanting those who foresaw disaster, and in September, 1893, the late Edmund Gosse wrote that "the monument already looks dingy and decayed." We know now, however, that the Duke was right, and the imaginary metallurgists of 1893 would have been at fault.

During the building of the present Underground Station at Piccadilly Circus the statue was removed to, and subjected to cleansing at the foundry of Mr. A. B. Burton in Thames Ditton. Almost immediately

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* Manuscript received October 12, 1936. Presented at the Annual General Meeting, London, March 10, 1937.

† Professor of Metallurgy, Cambridge University.

‡ Managing Director, Aluminium Plant and Vessel Company, Ltd., London.

after its re-erection the statue was damaged in a revel during the night of December 31, 1931, and had to be dismantled once more for repair.

The present authors thought that such an opportunity to inspect the metal should not be missed, and after considerable difficulty received permission to visit the foundry.

Although the cleansing operations had been completed it was quite evident that nothing in the nature of deep-seated corrosion had taken place during the 40 years which had elapsed since the statue was cast. The surface, Mr. Burton stated, had been covered with a layer of corrosion products about $\frac{1}{16}$ in. thick. This had been removed with scrapers, leaving a perfectly smooth surface, only discoloured by the subsequent exposure to the smoke and other atmospheric contamination of Piccadilly Circus.*

It appeared to be of considerable interest to ascertain the composition of the metal. The intricacy of the casting made it appear that an alloy must have been used, but the evident resistance to corrosion seemed to contradict this view. As no massive piece of the statue was then available for chemical analysis, some minute drillings, resulting from the repair work, were examined spectrographically by Mr. D. M. Smith, B.Sc., of the British Non-Ferrous Metals Research Association, after they had been carefully washed in very dilute hydrochloric acid. Mr. Smith subsequently re-examined the plates secured in 1932 in the light of his later knowledge of the spectrographic analysis of aluminium [1] and reported the figures given in col. 1 of Table I.

Mr. Smith emphasized that the numerical estimates are, in all cases, only approximate and should not be regarded as accurate to more than one significant figure. Subsequently, Mr. Pitts kindly supplied a small piece cut, many years before, from the skirt of the figure, which Mr. Smith analyzed with the result given in col. II, Table I.

Whilst these analyses do not show perfect agreement, they do show that no alloy had been used, and it is certainly remarkable that such a casting, reproducing the fine details of Gilbert's work, had been made in " pure " aluminium at so early a date. The bow, Mr. Pitts informed the authors, was re-cast in an alloy at a later date.

Most of those familiar with the metal will also be surprized at the small amount of the impurities revealed, and it was very desirable, therefore, to ascertain the origin of the metal and, particularly, whether it was made by the electrolytic or by a purely chemical process. In this

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* Mr. F. E. Pitts who, in 1918, acquired the firm of Broad, Salmon & Company, Ltd., by whom the statue was originally cast, informed the authors that a similar amount of corrosion products had been removed by electrically driven wire brushes, when the statue had been removed from Piccadilly Circus for safety during the war of 1914–1918.

Table I.—*Analyses.*

	I.	II.	IIa.	III.	IV.	V.	VI.	VIa. Chem. Anal.	VII.	VIIa. Chem. Anal.	VIII.	IX.	X.
Iron .	0·6–0·7	0·27	0·30	*ca.* 1·00	*ca.* 1·00	0·7	>1·00	1·77	0·3	0·35	0·27	1·08	0·90
Silicon .	0·5	0·60	0·76	*ca.* 1·00	*ca.* 1·00	0·8	0·4	0·39	0·5	0·66	0·15	1·94	0·81
Copper .	0·02	0·01	...	>0·03	0·02	>0·03	0·05	0·06	>0·25	...	0·35	...	...
Manganese	0·02	0·004	...	0·04	0·03	0·007	0·015	0·01	0·04	...	...	...	...
Titanium .	trace	trace	...	0·015	0·03	0·005	0·025	0·03	0·008	...	trace	...	...
Calcium .	trace	trace	...	*ca.* 0·001	*ca.* 0·001	*ca.* 0·001	0·001	0·05	0·001	...	...	...	...
Magnesium	*ca.* 0·01	0·001	...	trace	trace	trace	0·001	...	0·001	...	...	...	...
Silver .	...	...	...	det.	det.	det.	n.det.	...	n.det.	...	...	...	...
Lead .	*ca.* 0·005	trace	...	det.	det.	n.det.	0·07	...	trace	...	...	...	...
Gold .	...	...	...	n.det.	n.det.	det.	n.det.	...	n.det.	...	...	...	...
Zinc .	*ca.* 0·005	n.det.	...	det.	n.det.	det.	n.det.	0·02	trace	...	...	...	...
Gallium .	trace	trace	...	n.det.	n.det.	n.det.	trace	...	trace	...	...	...	...
Tin . .	<0·03	n.det.	...	n.det.	n.det.	n.det.	n.det.	0·08	n.det.	...	...	...	...
Sodium .	...	...	0·001	...	...	...	...	0·002 to 0·004	...	...	0·10	...	...

det. = presence detected. n.det. = presence not detected.

the authors have been entirely unsuccessful, but in the course of their searches they have been fortunate enough to locate several specimens of chemically prepared aluminium, and it seems desirable to place on record the composition of these, as determined by modern methods.

The specimens, the results of the spectrographic examination of which, by Mr. D. M. Smith, are given in Table I, were:

> III. A very small amount of metal obtained on loan from Mr. O. E. Sims, through the good offices of Mr. W. Murray Morrison. This metal had been in the possession of Mr. Sims's grandfather (1800–1857) and had, therefore, been made before 1857.
>
> IV. A very small specimen, made over 50 years before, by Alexander Sutherland, probably from Antrim bauxite. This was obtained on loan from Mr. James Sutherland, through Mr. Murray Morrison.
>
> V. A medal of aluminium made by the Aluminium Company, Ltd., by the Deville–Castner process, prior to 1889, and given by Professor F. Soddy, F.R.S.
>
> VI. A small ingot of metal made in 1863 by Bell Brothers of Washington, Co. Durham, and given by Professor Alexander Scott, F.R.S. The manufacture of aluminium was commenced at Washington about 1860 by the firm of Bell Brothers, of which Sir Lowthian Bell was the moving spirit. J. W. Mellor[2] states that the Deville process was used. It is, perhaps, not without significance that Sir Lowthian Bell's son, Sir Hugh Bell, an original member of this Institute was, for a time, a pupil of H. St. Claire Deville.[3]
>
> VII. A small ingot of metal, obtained by the good offices of Mr. C. E. Pearson, M.Met., which was made at Wallsend by the Netto process in which cryolite was reduced by sodium.[4]

Of No. VI a chemical analysis was made in Dr. A. G. C. Gwyer's laboratory, and of No. VII a partial analysis by Mr. G. B. Brook. Their results are given in Table I as Nos. VI*a* and VII*a*, respectively. Mr. Brook also made a partial analysis of the fragment of the statue which is recorded as No. II*a*.

Unfortunately the authors have no sample available of the earliest electrolytic metal for examination by modern methods, but in col. VIII are given H. Moissan's figures for metal produced electrolytically at Pittsburg in 1895, in col. IX for Neuhausen metal of the same year, and in col. X for another sample of electrolytically produced aluminium of 1896.[5–11]

It will be noted that the composition of the samples taken from the statue is very similar to that of metal of known chemical origin, Nos. V, VI, and VII. It differs rather more from that of metal produced by electrolysis at about the same time, to judge by Moissan's analyses. On the other hand, metal of composition very similar to that of the statue, as shown by col. II, is frequently produced electrolytically to-day.

It was hoped that a determination of the sodium content would throw light on the problem, since it has been generally assumed that chemically prepared aluminium contained much more sodium than that made by electrolysis. Analyses kindly made by Mr. G. B. Brook revealed, however, 0·002–0·004 per cent. of sodium in the sample of metal made by the Bell process (No. VI) whilst the small piece of the statue (No. II*a*), gave 0·001 per cent., figures which are similar to those found in pure metal to-day (0·001–0·002 per cent.). Mr. Brook used a modification of Scheuer's method of analysis,[12] which he intends to describe shortly, and on which he places absolute reliance.* These figures suggest once more that the metal used for the statue was produced chemically, since Moissan found 0·1–0·42 per cent. sodium in metal from the three main electrolytic sources of his day (La Praz, Neuhausen, and Pittsburg). His determinations were made, however, by the nitrate method (according to a private communication from Mr. P. Williams, who was working in Moissan's laboratory at the time), and this process, though the best available then, is not held to be reliable to-day.

ACKNOWLEDGMENTS.

The writers wish to express their thanks to the many gentlemen who helped by making available and/or analyzing specimens of old chemically prepared aluminium, and especially to Mr. D. M. Smith, B.Sc., for his spectrographic work, which has once more illustrated the advantage to be derived from this method of examining minute quantities of metals.

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[4] J. P. Bedson, *J. Soc. Chem. Ind.*, 1889, **8**, 985.
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[13] D. M. Fairlie and G. B. Brook, *J. Inst. Metals*, 1924, **32**, 283.

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* The standard method in this country prior to Scheuer's communication was that described by Fairlie and Brook.[13]

DISCUSSION.

Mr. W. Freeman Horn * (Member): I am interested in this subject, because when Eros was taken down for the reconstruction of Piccadilly Circus I investigated the history of it fairly thoroughly, but I am sorry to say that I found almost nothing on the technical side. I came to the same conclusion as the authors, that it was probably pure metal and not alloy, and that, of course, has now been proved; it was difficult to believe, because of the intricate casting. We also concluded that it was probably a chemically-produced metal. Against that is the recorded fact that Gilbert chose aluminium instead of copper because it was cheaper, and I find it difficult to believe that chemically-produced aluminium was at that time cheaper than copper. It is said that Gilbert undertook to produce this statue at a certain price, and afterwards discovered that he could not do so, either because the price of copper had increased or for some other reason. He became rather annoyed and very nearly did not finish it at all; in the end he said that he would use some cheaper metal. I do not know whether he was thinking of some other metal, and then finally decided on aluminium, but it is on record that he did use aluminium in place of copper because it was cheaper.

Since that time I have had some discussions with various people who were concerned with the industry in those days, and particularly with Messrs. Johnson, Matthey and Company, with whom I believe Dr. Seligman himself has had some dealings. They are quite positive that they produced the metal. They cannot produce any documentary evidence, but it is an accepted dictum among their older employees that they produced it, and they showed me a small medal made out of chemically-produced metal which was struck for the Paris Exhibition of 1878 and which is probably, therefore, the oldest aluminium medal in existence in this country. It is in an extraordinarily good state of preservation. It has probably been locked up, wrapped in tissue paper. For comparison, I have brought with me certain other aluminium medals. The first is made from the very first lot of electrolytically-produced aluminium in this country, made at Foyers in 1896, the second is from the first aluminium produced at Kinlochleven in 1907, and the third is from the last stage in the history of The British Aluminium Company at Lochaber in 1929. If the Institute of Metals ever makes an historical collection of this kind, I can produce several interesting things; I have a piece of the very first Zeppelin ever built, given to me by Graf Zeppelin himself.

Professor Hutton (*in reply*) referred to the disappointment which he and Dr. Seligman had felt in failing to trace in the newspapers and technical journals of the time any useful information about the composition and founding of this statue. Even Gilbert himself, in his later references to it, seemed to have forgotten that the statue was made of aluminium, although the basin and pedestal are of bronze.

Some reference should be made to an even earlier use of aluminium as part of a public monument. Mr. E. H. Dix, Jr., Chief Metallurgist of the Aluminum Research Laboratories in America had recently published † a report on the 100-ounce cap-piece of the Washington Monument which had been in service since December 6, 1884. Although the top had been fused by a lightning stroke, the corrosion-resistance had been remarkably good. Spectroscopic analysis in this case gave iron 1, silicon 0·75, manganese 0·3, copper 0·05, tin 0·02, sodium 0·01, and aluminium (by difference) 97·87 per cent.

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* Intelligence Department, The British Aluminium Company, Ltd., London.

† *Metal Progress*, 1934, 26, (6), 32–34.

Gilbert's "Eros," Piccadilly Circus, London.

The fountain itself is in bronze with the lower, central, and upper basins surmounted by a life-size figure in aluminium. The whole is 36 ft. high from the ground line and 17 ft. 6 in. in width at the base.

[*To face p.* 72.

The evidence given in a paper by A. E. Hunt, President of the Pittsburg Reduction Company (now Aluminum Company of America), whilst not directly bearing on this case, is worthy of notice. In April, 1892,[*] Mr. Hunt refers to the close similarity and high purity of chemical and electrolytic aluminium and states that this metal was at that time only being manufactured by electrolysis and that a branch of the American company, under the name Metal Reduction Syndicate, Ltd., was producing the metal at Patricroft, Lancashire.

CORRESPONDENCE.

Mr. G. B. Brook,[†] F.R.S.E. (Member): The question of the sodium content of the metal from which the statue of Eros was made, was fairly well dealt with in the paper; making use of the information that I communicated to them, the authors point out that remelting always reduces the amount of sodium, and if carried out at a high temperature, the loss of such sodium would be very rapid.

I have before me the results of two typical tests carried out on an alloy in which it was desirable to reduce a certain amount of sodium. The figures given in Table A show that sodium decreases rapidly if the metal is held at temperatures even as low as 710° and 685° C., respectively. From the Table it will be seen that both samples rapidly lost sodium until at the end of approximately half an hour the original sodium content had decreased more than 50 per cent. If such loss of sodium occurred at a temperature just above the melting point, how much more rapidly would this loss occur when this procedure was carried out in a rough and ready manner, in which case the temperature would reach say 800° C., and it may be that the aluminium constituent would be remelted during the life of the metal or alloy. This, I think satisfies the point at issue.

Table A.—*Typical Examples of the Loss of Sodium from Molten Aluminium (Silicon Alloy).*

No. 1.

Period Held Molten, Minutes.	Sodium Per Cent.	
0	0·007	Average Temperature, 710° C.
5	0·006	
10	0·006	
16	0·006	
21	0·005	
25	0·003	

No. 2.

Period Held Molten, Minutes.	Sodium Per Cent.	
0	0·012	Average Temperature, 685° C.
6	0·008	
11	0·007	
18	0·008	
24	0·006	
28	0·005	

At any rate, the fact that the statue of "Eros" is low in sodium confirms the facts of the case to which attention is being directed, *i.e.* that metal with

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[*] *J. Franklin Inst.*, 1892, 133, 241–271.

[†] Chief Chemist, The British Aluminium Company, Ltd., Kinlochleven.

low sodium content will resist corrosion better than one containing a considerable amount of this impurity.

Dr. SELIGMAN (*in reply*): Mr. G. B. Brook has raised an interesting point in directing attention to the loss of sodium from aluminium when maintained at temperatures above the melting point. It does not appear, however, that his final conclusion is completely justified, since no comparison between metal low in sodium and metal high in sodium has been possible on this occasion. All that can be concluded from the information presented is that the metal used for the statue of Eros was very low in sodium, and has shown remarkable resistance to corrosion.

THE EFFECT OF THE ADDITION OF SMALL PERCENTAGES OF IRON AND SILICON TO A HIGH-PURITY 4 PER CENT. COPPER–ALUMINIUM ALLOY.* 763

By MARIE L. V. GAYLER,† D.Sc. (Mrs. Haughton), Member.

Synopsis.

It has not been possible to attain a state approaching equilibrium in 4 per cent. copper–aluminium alloys containing up to 0·6 per cent. iron and 1·0 per cent. silicon, under the conditions of casting and subsequent working and heat-treatment described.

The phases $CuAl_2$, αFeSi, βFeSi, and silicon have been identified in the alloys, but $FeAl_3$ was not observed. Silicon is held in solid solution to a limited amount at 500° C., and is precipitated during slow cooling to 190° C. together with $CuAl_2$.

The addition of 0·1 per cent. iron inhibits the age-hardening of a 4 per cent. copper alloy at room temperature but not at high temperatures, while the addition of 0·6 per cent. iron reduces, to a marked extent, ageing at high temperatures. The addition of 1·0 per cent. silicon does not inhibit the effect of 0·6 per cent. iron. It would appear that the age-hardening which takes place at high temperatures may be attributed to the precipitation of silicon as well as of $CuAl_2$.

This paper forms part of a research carried out for the Metallurgy Research Board of the Department of Scientific and Industrial Research.

I. Constitution of the Alloys.

The constitution of the ternary alloys of iron–silicon–aluminium has been studied by various investigators,[1] but the equilibrium diagram of the aluminium corner of the system is still uncertain. Gwyer and Phillips have studied the constitution of alloys containing up to 2 per cent. iron and silicon, respectively, and have given the "phase boundaries after annealing for 100 hrs. at a temperature of 500° C." Gwyer, Phillips, and Mann[2] also studied the effect of the addition of copper on the constitution of these alloys, and have drawn diagrams representing the changes occurring during the process of freezing for particular rates of cooling. They examined the constitution of chill-cast 4 per cent.

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* Manuscript received November 24, 1936. Presented at the Annual General Meeting, London, March 10, 1937.

† Scientific Officer, Department of Metallurgy, National Physical Laboratory, Teddington.

copper alloys containing up to 1·5 per cent. iron and 5·0 per cent. silicon, and constructed the diagram shown in Fig. 1. In the quaternary system, Gwyer, Phillips, and Mann identified a compound which they found to be the product of a peritectic reaction between $FeAl_3$ and liquid. They identified this with the " N " and " X " constituent of the ternary systems aluminium–copper–iron and aluminium–silicon–iron, respectively, and deduced that these two ternary constituents were isomorphous in the quaternary system aluminium–copper–iron–silicon. Dix and Heath [1] also recognized the existence of two phases in the ternary system aluminium–silicon–iron which they termed α(FeSi) and β(FeSi); the former being identical with the " Chinese script," or β phase, of Gwyer and Phillips, and the latter with their " X " compound.

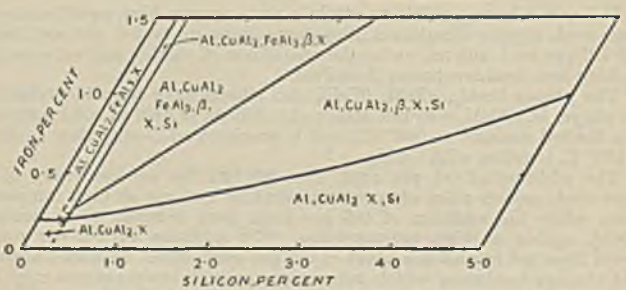


Fig. 1.

By means of X-ray analysis, Fink and Van Horn [3] concluded that α(FeSi) was a solid solution of silicon in $FeAl_3$, but they state that "there is information which does not seem to be entirely consistent with this conclusion." The X-ray diffraction pattern of β(FeSi) indicated either a definite compound or a constituent in which the parameters are a function of the aluminium content. The authors remark: " It would seem, therefore, that β(FeSi) is a ternary compound which may have excess of aluminium in solid solution, which causes an expansion of the lattice."

Fuss,[4] by means of the microscopic examination of series of alloys of iron and silicon with aluminium, deduced the existence of a ternary compound, formed by a reaction between liquid and $FeAl_3$, to which he assigned the formula $Al_6Fe_2Si_3$. This compound was characterized by its " Chinese script " form. Fuss found that $FeAl_3$ and Si formed a quasi-binary system, but Dix and Heath [1] concluded that it was not real, since they found two ternary bodies which existed in the vicinity of the section $FeAl_3$–Si.

In the present investigation no attempt has been made to deal with the above-mentioned problem, since it is beyond the range of the alloys investigated; the constitution and age-hardening of the quaternary aluminium alloys containing 4 per cent. copper and up to 0·6 per cent. iron and 1 per cent. silicon have been studied.

The identification of the constituents present in the alloys is of chief importance; Dix and Heath[1] have remarked in the case of aluminium–silicon–iron alloys, ". . . the work of comparison and differentiation of the micro-constituents proved to be the most difficult of the entire investigation." A search was made for etching reagents suitable for distinguishing the constituents when present in small quantities. It is comparatively easy to distinguish large amounts of the different phases, either separately or together, by their characteristic form or colour, but when very small particles in the annealed state have to be distinguished, colour and form are seldom reliable indicators.

Experimental Procedure.

The compositions of the alloys investigated embrace a small corner of the 4 per cent. copper section of the quaternary system copper–silicon–iron–aluminium, containing up to 0·6 per cent. iron and 1·0 per cent. silicon. The alloys were made from the purest material available at the time (see Appendix I, Tables IX and X).

When this research was started several years ago, the supply of Hoopes' aluminium was only sufficient for ½ in. sand- or chill-castings. In a previous investigation[5] it was found that Brinell hardness impressions made on either end of forged and heat-treated bars were sometimes variable. Kempf and Dean[6] suggested that this might be due to grain-size, while the authors suggested inverse segregation as a possible cause. Half-inch sand-castings were therefore made in the present investigation in order to reduce such segregation. Chemical analysis of four alloys showed, however, that though reduced, this was not prevented (Appendix I, Table XI, A). It was evident that the rate of cooling in the ½ in. sand mould approximated to that in a chill mould of larger diameter. Additional hardness measurements made later on a forged and heat-treated 1 in. diameter sand-casting showed that little or no irregularity in hardness was present, and chemical analysis of two alloys showed that no inverse segregation was present (Appendix I, Table XI, B). Dix and Heath,[1] as well as Gwyer and Phillips,[1] have noted the remarkable sensitivity of these alloys to the rate of cooling. Table I shows the phases present in ½ in. and 1 in. sand-castings. It is possible that the crystallization of different phases may account for irregularities in Brinell hardness which have been found in forged and heat-treated castings.

From Table I it is seen that the β(FeSi) phase tends to be formed in the the 1 in. sand-casting, while, comparing the structures of both, there is appreciably more $CuAl_2$ and silicon in the 1 in. than in the ½ in. casting.

The materials were melted in an alumina, or Salamander crucible, according to the composition of the alloy, and cast at about 720°–740° C. in warm sand moulds. The castings were then soaked for about 5 hrs. at 450° C., and forged at that temperature down to a thickness of $\frac{3}{16}$ in. and $\frac{5}{16}$ in. for ½ in. or 1 in. castings, respectively. The surfaces of the bars were than prepared for hardness measurement before heat-treatment.

TABLE I.

Alloy, Per Cent.			½ in. Sand-Casting.	1 in. Sand-Casting.
Copper.	Iron.	Silicon.		
4	0·6	0·1	Al + $CuAl_2$ + α(FeSi) + β(FeSi)	Al + $CuAl_2$ + α(FeSi) + β(FeSi)
4	0·6	0·24	Al + $CuAl_2$ + α(FeSi)	Al + $CuAl_2$ + α(FeSi) + β(FeSi) ?
4	0·6	0·6	Al + $CuAl_2$ + α(FeSi) + Si	Al + $CuAl_2$ + α(FeSi) + Si
4	0·3	0·8	Al + $CuAl_2$ + α(FeSi) + Si	Al + $CuAl_2$ + α(FeSi) + Si + β(FeSi)
4	0·1	0·8	Al + $CuAl_2$ + Si + α(FeSi) ?	Al + $CuAl_2$ + α(FeSi) + Si + β(FeSi)

For determining the constitution of the alloys, small specimens were cut from these bars and heat-treated.

In Appendix II, *A*, is given the heat-treatment of the bars, and in *B*, that given to the specimens for determining the constitution of the alloys.

II. THE CONSTITUTION OF THE QUATERNARY ALLOYS.

(a) *Micrography.*

Throughout this paper the nomenclature of Dix and Heath has been adopted for the iron-rich constituents, the β and "X" phases of the iron–silicon–aluminium ternary system being designated α(FeSi) and β(FeSi), respectively. These phases occur also in the quaternary system with copper, and therefore are given the same notation.

As already mentioned, great difficulty has been experienced in identifying small particles of the constituents which appear singly or together in the alloys. Several etching reagents were tried, with varying success, and the three described below were found the most satisfactory. It was not possible, however, to superimpose these etching reagents on each other; it was necessary to re-polish, and generally to re-grind, the specimen after using any of the reagents before using another, consequently the difficulty of identifying small particles was greatly enhanced.

Dix and Heath[1] found that swabbing a specimen for a second or two with ½ per cent. hydrofluoric acid before etching ensured a true surface. This method was adopted throughout, and found to be most satisfactory.

Etching Reagents Employed.

(a) *For $CuAl_2$ only.*—30 seconds' immersion in cold aqueous 10 per cent. ferric nitrate. (Gwyer, Phillips, and Mann.[2])

(b) *For α(FeSi) only.*—5 to 10 seconds in 20 per cent. aqueous sulphuric acid at 70° C. (Dix and Keith.[7])

(c) *General etching reagent.*—5 to 15 seconds in Vilella's reagent: 3 parts glycerol, 2 parts hydrofluoric acid, 1 part nitric acid.

A preliminary series of alloys was made containing higher percentage of silicon and iron than was used for constitutional work. These alloys were very slowly cooled from the molten state in the furnace and their structures examined microscopically. The phases present were therefore easily identified by their colour and characteristic form; on etching with the three reagents mentioned above, the results in Table II were obtained.

TABLE II.

Etching Reagent.		$CuAl_2$.	$FeAl_3$.	α(FeSi).	β(FeSi).	Si.
i.	20 per cent. H_2SO_4 at 70° C.	outlined	black, but uncoloured in the presence of α(FeSi)	very dark brown	untouched	outlined
ii.	10 per cent. $Fe(NO_3)_3$	blackened	untouched	untouched	untouched	untouched
iii.	Vilella's reagent	untouched	roughened and perhaps darkened	rich brown	uncoloured, but definite outline	uncoloured, but outlined not as deeply as β(FeSi)

The composition of, and the phases in, the alloys examined are given in Table III.

Alloys A, B, C, F contained αFeSi in the characteristic script form in a greater or less degree, whilst $FeAl_3$ was only found in E. In no other specimen were there any indications of $FeAl_3$, which was rather

DESCRIPTIONS OF PHOTOMICROGRAPHS.

PLATE IX. FIG. 2.—Cu 5, Si 1, Fe 1%. Slowly cooled in furnace. $CuAl_2$ light; Si, half-tone; α(FeSi) dark.
FIG. 3.—Cu 5, Si 3, Fe 1%. Slowly cooled in furnace. $CuAl_2$ light; Si half-tone; needles of β(FeSi).
FIG. 4.—½ in. Sand-casting. Fe 0·6, Si 0·1, Cu 4%. $CuAl_2$ light; α(FeSi) dark; needles of β(FeSi).
FIG. 5.—1 in. Sand-casting. Same alloy as Fig. 4. $CuAl_2$ light; α(FeSi) dark; needles of β(FeSi).

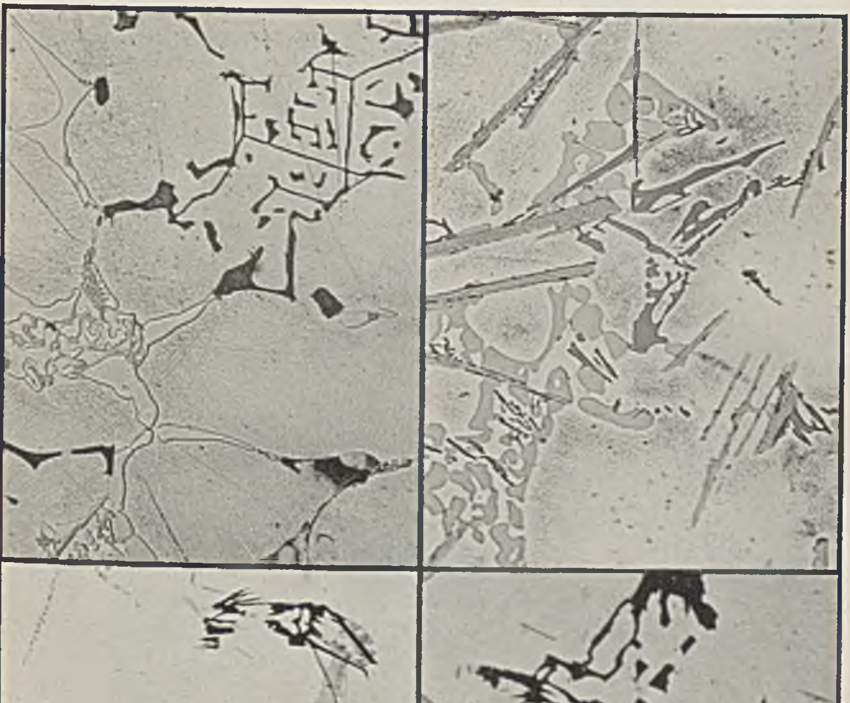
PLATE X. FIG. 6.—Same alloy as Fig. 5. $CuAl_2$ light; α(FeSi) dark.
FIG. 7.—1 in. Sand-casting. Si 0·8, Fe 0·1, Cu 4%. $CuAl_2$ light; Si half-tone; α(FeSi) dark; needles of β(FeSi).
FIG. 8.—Fe 0·3, Si 1·0, Cu 4%. Annealed at 500° C. α(FeSi) dark; β(FeSi) light; Si half-tone.
FIG. 9.—Fe 0·3, Cu 4%. α(FeSi) dark; β(FeSi) light; Si half-tone.

PLATE XI. FIG. 10.—Fe 0·1, Si 1·0, Cu 4%. Annealed at 500° C. $CuAl_2$ light; β(FeSi) half-tone; α(FeSi) dark streaks; Si black and round.
FIG. 11.—Fe 0·3, Si 0·9, Cu 4%. Annealed at 500° C. α(FeSi) dark; Si dark grey; β(FeSi) light.
FIG. 12.—Same field as Fig. 10. $CuAl_2$ black; Si dark grey; α(FeSi) and β(FeSi) light.
FIG. 13.—Fe 0·6, Si 0·45, Cu 4%. Annealed at 475° C. α(FeSi) dark; β(FeSi) and probably some $CuAl_2$ light.

PLATE XII. FIG. 14.—Fe 0·6, Si 0·45, Cu 4%. Annealed at 475° C. $CuAl_2$ black; α(FeSi) + β(FeSi) light.
FIG. 15.—Fe 0·6, Si 0·45, Cu 4%. Annealed at 475° C. α(FeSi) black; $CuAl_2$ light.
FIG. 16.—Fe 0·6, Si 0·45, Cu 4%. Annealed at 475° C. α(FeSi) dark; $CuAl_2$ light; β(FeSi) light streaks.
FIG. 17.—Fe 0·1, Si 0·5, Cu 4%. Annealed at 475° C.

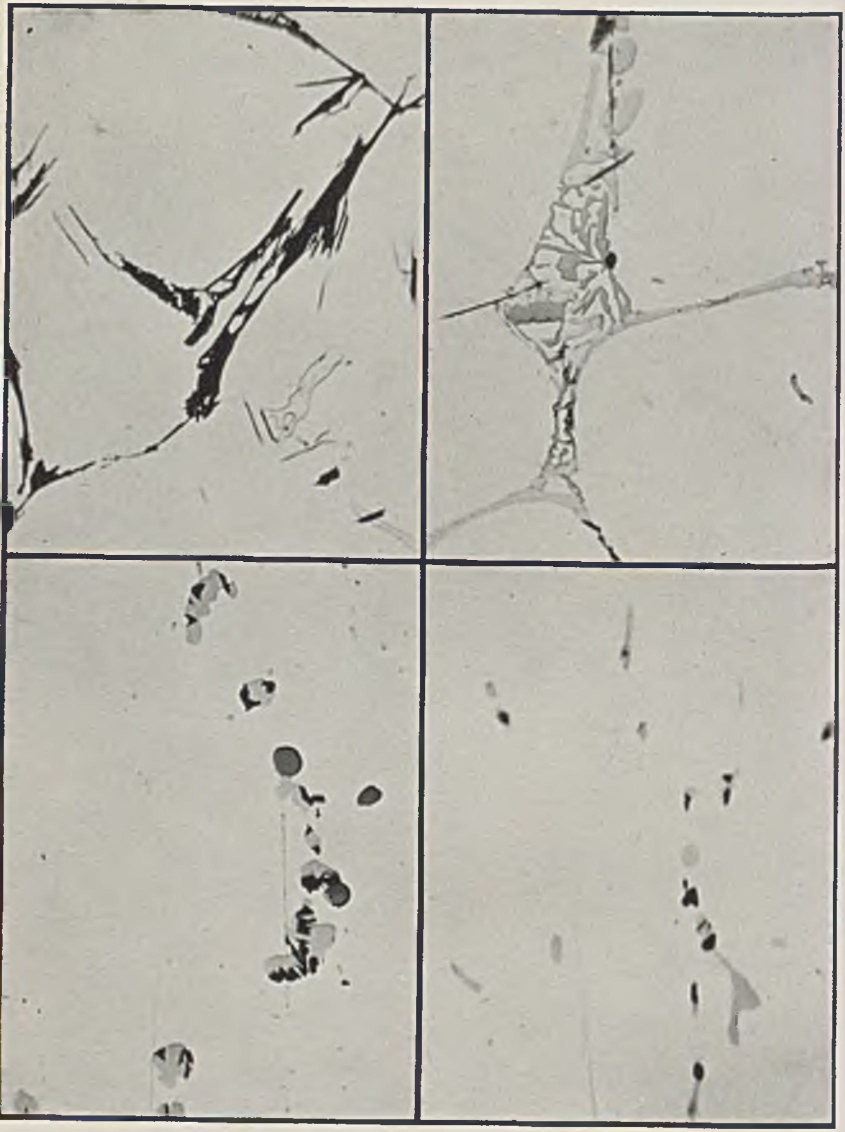
PLATE XIII. FIG. 18.—Same as Fig. 17. $CuAl_2$ dark; α(FeSi) + β(FeSi) light.
FIG. 19.—Fe 0·12, Si 0·007, Cu 4%. Slowly cooled to 190° C. $CuAl_2$ dark; β(FeSi) half-tone.
FIG. 20.—Fe 0·12, Si 0·14, Cu 4%. Slowly cooled to 190° C. $CuAl_2$ dark; Si half-tone; β(FeSi) light.
FIG. 21.—Fe 0·1, Si 0·12, Cu 4%. Slowly cooled to 190° C. $CuAl_2$ precipitated.

PLATE XIV. FIG. 22.—Fe 0·6, Si 0·20, Cu 4%. Slowly cooled to 190° C. $CuAl_2$ black; Si half-tone; α(FeSi) + β(FeSi) light.
FIG. 23.—Same field as above. $CuAl_2$ light; Si half-tone; α(FeSi) black; β(FeSi) light.



Figs. 2 and 3.—Etched with Vilella's Reagent. × 300.
Figs. 4 and 5.—Etched with 20% H_2SO_4 at 70° C. × 600.

[*To face p.* 80.



Figs. 6, 7, and 8.—Etched with 20% H_2SO_4 at 70° C. × 600.
Fig. 9.—Etched with 20% H_2SO_4 at 70° C. × 1250.

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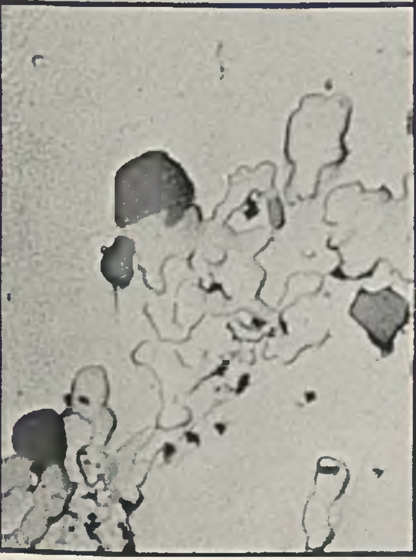

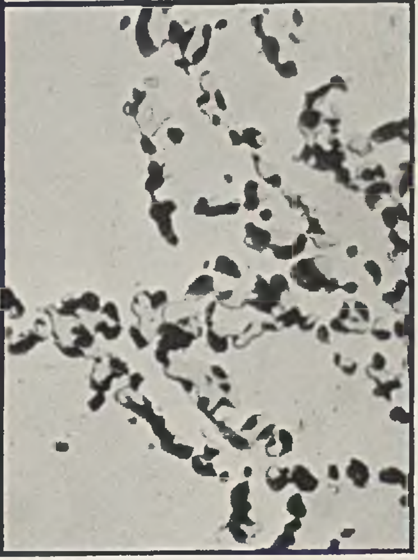

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FIG. 10.—Etched with 20% H_2SO_4 at 70° C. × 1250.
FIG. 11.—Etched with 20% H_2SO_4 at 70° C. × 1000.
FIG. 12.—Etched with 10% $Fe(NO_3)_3$. × 1000.
FIG. 13.—Etched with 20% H_2SO_4 at 70° C. × 750.

PLATE XII.

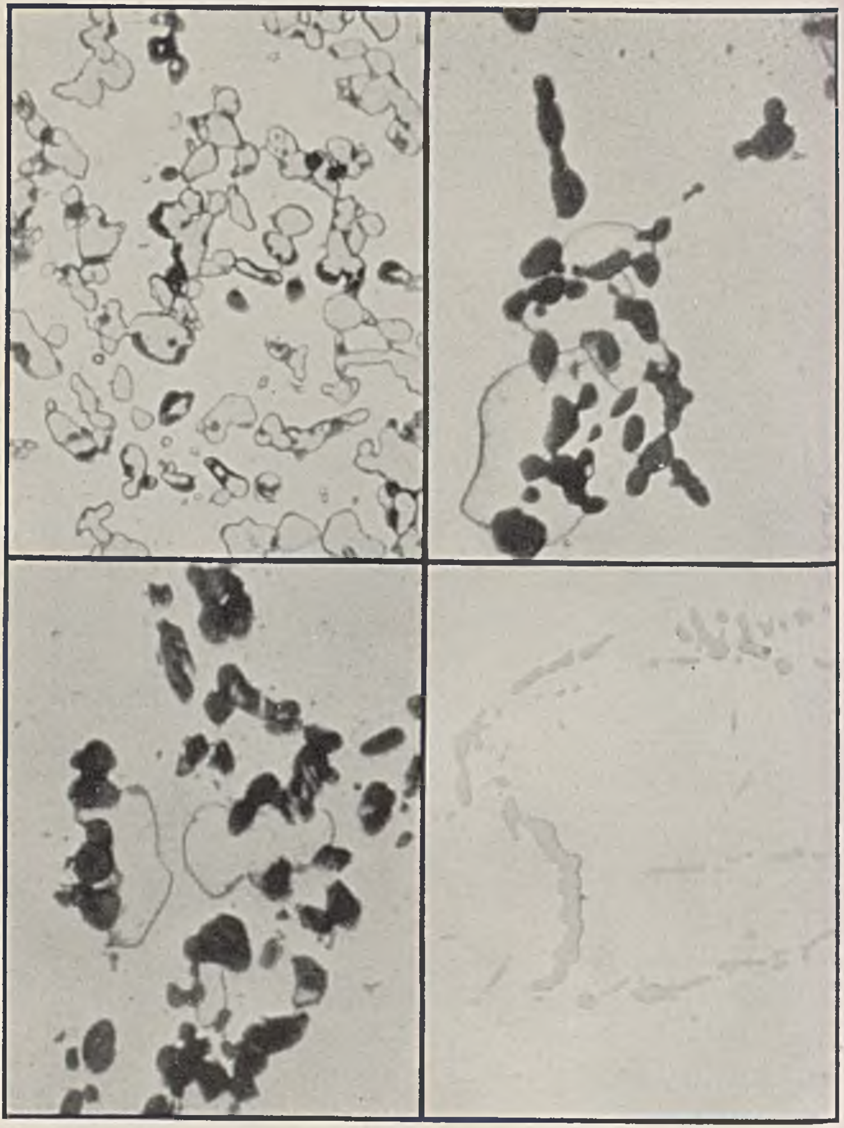
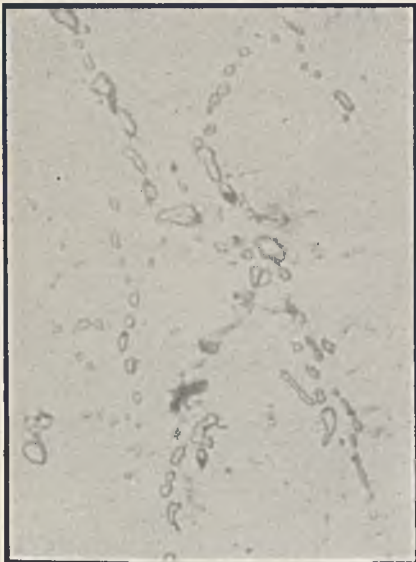


FIG. 14.—Etched with 10% $Fe(NO_3)_3$. × 1000.
FIG. 15.—Etched with 20% H_2SO_4 at 70° C. × 1000.
FIG. 16.—Etched with 20% H_2SO_4 at 70° C. × 1000.
FIG. 17.—Unetched. × 750.

PLATE XIII.



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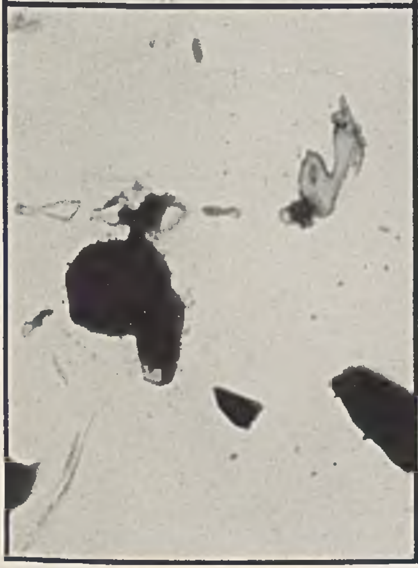

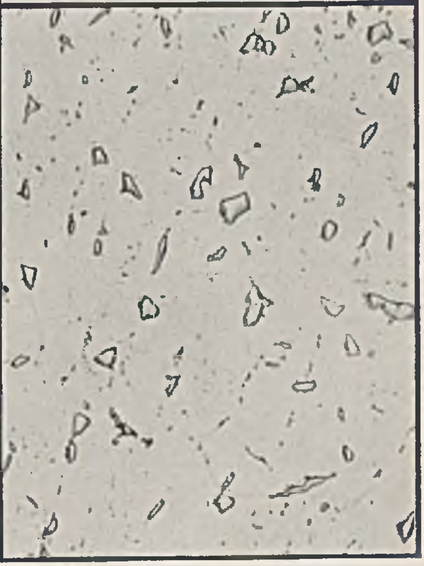

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FIG. 18.—Etched with 10% $Fe(NO_3)_3$. × 750.
FIG. 19.—Etched with 10% $Fe(NO_3)_3$. × 1250.
FIG. 20.—Etched with 10% $Fe(NO_3)_3$. × 1000.
FIG. 21.—Unetched. × 150.

PLATE XIV.

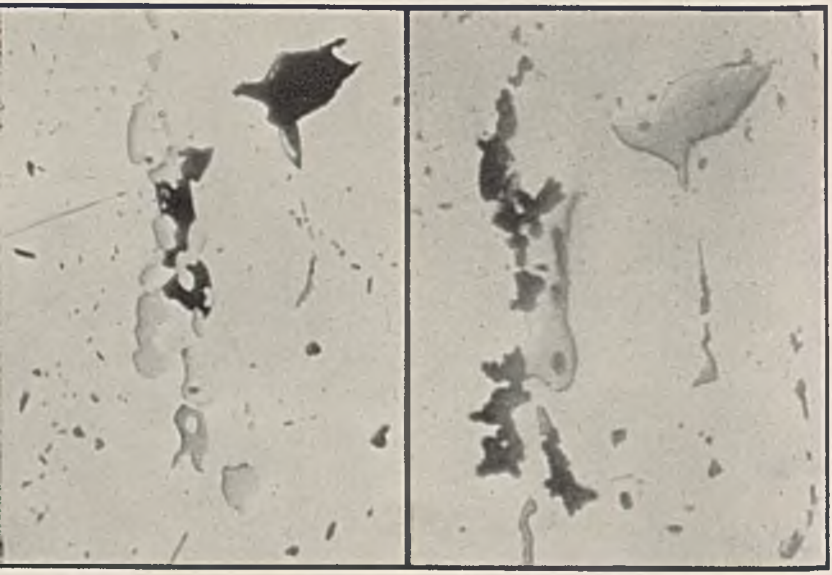

FIG. 22.—Etched with 10% $Fe(NO_3)_3$. × 1000.
FIG. 23.—Same field as Fig. 22, Etched with 20% H_2SO_4 at 70° C. × 1000.

surprising considering their composition and rate of cooling (cf. Gwyer, Phillips, and Mann [2]).

TABLE III.

Alloy.	Copper, Per Cent.	Silicon, Per Cent.	Iron, Per Cent.	Constituents Identified on Etching.
A	5	0·3	1	$\alpha(FeSi) + \beta(FeSi) + CuAl_2$
B	5	1·0	1	$\alpha(FeSi) + Si + CuAl_2$
C	5	3·0	1	$\alpha(FeSi) + \beta(FeSi) + Si + CuAl_2$
D	5	10·0	1	$\beta(FeSi) + Si + CuAl_2$
E	5	$<0·1$	2	$FeAl_3 + \alpha(FeSi) + \beta(FeSi)? + CuAl_2$
F	5	5·0	2	$\alpha(FeSi) + \beta(FeSi) + Si + CuAl_2$

Dix and Heath[1] used 20 per cent. sulphuric acid at 70° C. to identify $FeAl_3$; they found, however, that "$\alpha(FeSi)$ and $\beta(FeSi)$ were attacked about equally, both being roughened, but not darkened much." The alloys examined by these authors contained much higher percentages of iron and silicon than used in the present research, and also no copper. These facts may account for the difference between the results obtained by the present author with the same etch, for $\alpha(FeSi)$ appears in its characteristic script form in alloys A, B, C, and F, and when etched with 20 per cent. sulpuric acid at 70° C., this phase always coloured a beautiful rich brown. Alloy E contained a slate grey constituent surrounded by a lighter phase forming an irregular jagged outline, also patches of long bent needles sheathed (or not sheathed) with the lighter phase. On etching, the phase surrounding the darker grey constituent etched dark brown whilst the surrounded phase remained uncoloured: of the thin needles some remained uncoloured, others were blackened. It was deduced that these two constituents must be $FeAl_3 + \alpha(FeSi)$ for the following reasons: The $\alpha(FeSi)$ and $\beta(FeSi)$ phases are both light coloured, and are very difficult to identify when existing in small quantity; $FeAl_3$, on the other hand is a very definite slate grey. The centre core above must, therefore, be $FeAl_3$ and the surrounding jagged phase $\alpha(FeSi)$ or $\beta(FeSi)$, both of which may be formed as reaction products. Since this phase etched black, it must be $\alpha(FeSi)$, and not $\beta(FeSi)$. The long dark needles must primarily have separated as $FeAl_3$, but, as a result of reaction with the liquid, must have changed to $\alpha(FeSi)$.

It appears, therefore, that contrary to the findings of Dix and Heath, in the presence of $\alpha(FeSi)$, $FeAl_3$ remains uncoloured by the sulphuric acid etching reagent. On etching alloy C, needles of $\beta(FeSi)$ remained uncoloured, while the characteristic $\alpha(FeSi)$ script etched a rich brown. Similarly, Vilella's reagent also colours $\alpha(FeSi)$ a dark red-brown, $\beta(FeSi)$, however, becomes outlined with a black line and consequently, if the needles are thin, they frequently appear almost black; $FeAl_3$ is roughened and perhaps slightly darkened.

Figs. 2 and 3 (Plate IX) are photomicrographs of alloys B and C under a magnification of 300 diam.: the alloys have been etched with Vilella's reagent after swabbing for 5 seconds with ½ per cent. hydrofluoric acid. The light phase in Fig. 2 is $CuAl_2$, the half-tone phase is silicon, whilst the dark phase in script form is $\alpha(FeSi)$. In Fig. 3 no $\alpha(FeSi)$ is visible, since only a very small amount was found in the specimen; the light phase is $CuAl_2$, the half tone is silicon, whilst the needles are $\beta(FeSi)$.

(b) *The Constitution of the Alloys.*

The constitution of alloys containing 4 per cent. copper and up to 0·6 per cent. iron and 1·0 per cent. silicon, respectively, has been studied at temperatures of about 490° and 190° C.

Dix and Heath,[1] as a result of an intensive metallographic examination of ternary alloys containing up to 40 per cent. iron and 50 per cent. silicon, considered that three ternary systems existed within the ternary silicon–iron–aluminium system.

i. $Al + FeAl_3 + \alpha(FeSi)$
ii. $Al + \alpha(FeSi) + \beta(FeSi)$
iii. $Al + \beta(FeSi) + Si$.

Gwyer, Phillips, and Mann[2] disagreed with this deduction, and said that it was impossible to reconcile Dix and Heath's results with their own. These authors considered that $\beta(FeSi)$ was the only stable ternary constituent under equilibrium conditions in alloys containing 0–10 per cent. iron and 0–20 per cent. silicon.

Table IV gives the constituents found during the course of the present research in five sand-cast alloys containing 4 per cent. copper and varying iron and silicon.

TABLE IV.

Alloy.	Iron, Per Cent.	Silicon, Per Cent.	Constituents in Sand-Castings.	
			½ in. Diameter.	1 in. Diameter.
D4	0·6	0·1	$Al + CuAl_2 + \alpha(FeSi) + \beta(FeSi)$	$Al + CuAl_2 + \alpha(FeSi) + \beta(FeSi)$
C2	0·6	0·25	$Al + CuAl_2 + \alpha(FeSi)$	$Al + CuAl_2 + \alpha(FeSi) + \beta(FeSi)$?
C4	0·6	0·75	$Al + CuAl_2 + \alpha(FeSi) + Si$	$Al + CuAl_2 + \alpha(FeSi) + Si$
A4	0·1	0·75	$Al + CuAl_2 + \alpha(FeSi)$? $+ Si$	$Al + CuAl_2 + \alpha(FeSi) + \beta(FeSi) + Si$
B3	0·3	0·5	$Al + CuAl_2 + \alpha(FeSi) + Si$	$Al + CuAl_2 + \alpha(FeSi) + \beta(FeSi) + Si$

From this table it is seen that in contrast with Gwyer and Phillips' results with chill cast alloys, α(FeSi) rather than β(FeSi) was formed in the sand-cast alloys. None of these alloys contained $FeAl_3$, but all contained α(FeSi) generally in "Chinese script" form. Fig. 4 (Plate IX) shows the etched structure of the ½ in. sand-casting, of the alloy containing 0·6 per cent. iron, and 0·1 per cent. silicon; whilst Figs. 5 and 6 (Plates IX and X) show structures observed in the 1 in. sand-casting of the same alloy. The black phase is α(FeSi), $CuAl_2$ is light, whilst needles of β(FeSi) are seen associated with the $CuAl_2$. Fig. 6 is of interest since α(FeSi) appears in a form other than the typical binary-complex form; the black, irregularly-shaped needles must originally have been $FeAl_3$ at the beginning of crystallization, but have reacted with liquid to form α(FeSi). Hence the irregular outline and unusual form of this constituent. In Fig. 7 (Plate X), small quantities of α(FeSi) etched black, can be seen together with a few needles of β(FeSi), $CuAl_2$ (light), and silicon (half-tone) in the sand-cast structure of the alloy containing 0·8 per cent. silicon and 0·1 per cent. iron. It was deduced, therefore, since α(FeSi), and not $FeAl_3$, existed in the sand-castings, that the phase etching a dark red-brown with Dix and Heath's, as well as Vilella's, reagent in both forged and annealed alloys must be α(FeSi).

If present, β(FeSi) was generally in needle form associated with $CuAl_2$ (ternary complex separation); in a few instances it was seen associated with α(FeSi) as the result of reaction in the solid state. In these cases, the β(FeSi) appeared as "streaks" in the α(FeSi) phase. Figs. 8 and 9 (Plate X) show the microstructures of alloys containing 0·3 per cent. iron, 1·0 per cent. silicon; and 0·3 per cent. iron only, respectively, which have been annealed for 8 weeks at 500° C., and etched with 20 per cent. sulphuric acid at 70° C. The α(FeSi) phase is etched dark, β(FeSi) (light) is unattacked, whilst silicon appears as dark grey in the photomicrograph. In order to determine whether no $CuAl_2$ was present, the specimen was re-polished and etched with 10 per cent. ferric nitrate; no $CuAl_2$ was found.

The structure of the annealed alloy containing 0·1 per cent. iron, 1·0 per cent. silicon, etched with 20 per cent. sulphuric acid at 70° C., is given in Fig. 10 (Plate XI). The large black rounded particles are silicon, the lightest constituent, $CuAl_2$, the half-tone β(FeSi), whilst the dark-etching "streaky" phase is α(FeSi). The same phases are present in different amounts, in an alloy etched as above containing 0·3 per cent. iron, 0·9 per cent. silicon (see Fig. 11), but when etched with 10 per cent. ferric nitrate, however, a very small amount of dark etching $CuAl_2$ is observed as shown in Fig. 12 (Plate XI), which is the same field as seen in Fig. 11.

The structure of the alloy containing 0·6 per cent. iron and 0·45 per cent. silicon is of interest and is shown in Figs. 13–16 (Plates XI and XII). This alloy was forged, annealed for an additional 6 weeks at 475° C. (cf. Appendix II, Table XIII), and etched with 20 per cent. sulphuric acid at 70° C. The constituents tended to be segregated in patches, such as are shown in Fig. 13. The dark phase is α(FeSi), the light β(FeSi) and probably some $CuAl_2$. In Fig. 14, the alloy has been etched with ferric nitrate and quite large, as well as small pieces, of $CuAl_2$ have etched black. In certain parts the $CuAl_2$ has segregated in comparatively large pieces, such as shown in Fig. 15, where α(FeSi) has been etched black with 20 per cent. H_2SO_4 at 70° C. Fig. 16 shows a similar place, where

TABLE V.

No.	Alloy.	Constituents Present.
Series A : 0 per cent. Silicon		
1	0·03 per cent. iron	Al + small amount $CuAl_2$ + possibly a minute amount of an iron phase.
2	0·06 „ „	Al + small amount $CuAl_2$ + slightly more of the iron phase.
3	0·1 „ „	Al + $CuAl_2$ + α(FeSi) + β(FeSi) ? ?
4	0·32 „ „	Al + $CuAl_2$ + α(FeSi)
5	0·06 „ „ 0·08 „ silicon	Al + $CuAl_2$ + α(FeSi) + β(FeSi) ?
Series B : 0·1 per cent. Silicon		
1	0 per cent. iron	Al + $CuAl_2$
2	0·1 „ „	Al + $CuAl_2$ + α(FeSi) + very little β(FeSi)
3	0·34 „ „	Al + $CuAl_2$ + α(FeSi) + β(FeSi)
4	0·62 „ „	Al + $CuAl_2$ + α(FeSi) + β(FeSi)
Series C : 0·24 per cent. Silicon		
1	0 per cent. iron	Al + $CuAl_2$
2	0·12 „ „	Al + $CuAl_2$ + α(FeSi) + β(FeSi) ? ?
3	0·32 „ „	Al + $CuAl_2$ + β(FeSi)
4	0·58 „ „	Al + $CuAl_2$ + α(FeSi)
Series D : 0·5 per cent. Silicon		
1	0·12 per cent. iron	Al + α(FeSi) + β(FeSi)
2	0·32 „ „	Al + $CuAl_2$ + α(FeSi)
3	0·6 „ „	Al + $CuAl_2$ + α(FeSi) + Si
Series E : 0·75 per cent. Silicon		
1	0·1 per cent. iron	Al + $CuAl_2$ + α(FeSi) + Si
2	0·3 „ „	Al + α(FeSi) + β(FeSi)
3	0·6 „ „	Al + α(FeSi) + Si
Series F : 1·0 per cent. Silicon		
1	0·1 per cent. iron	Al + $CuAl_2$ + α(FeSi) + β(FeSi) + Si
2	0·3 „ „	Al + $CuAl_2$ + α(FeSi) + β(FeSi) ?
3	0·58 „ „	Al + $CuAl_2$ + α(FeSi)

there is evidence that β(FeSi) has been formed from α(FeSi) by the streaky appearance of the latter.

Fig. 17 (Plate XII) shows the unetched structure of the alloy containing 0·1 per cent. iron and 0·5 per cent. silicon; if this alloy be etched with 10 per cent. ferric nitrate, the presence of a small amount of $\mathrm{CuAl_2}$ is detected, as shown in Fig. 18. Etching with 20 per cent. sulphuric acid at 70° C. colours the constituent present in greater amount, dark brown, which indicates that it is α(FeSi).

Table V gives a list of the phases found in the alloys heat-treated at 475°–500° C.

TABLE VI.

No.	Alloy.	Constituents Present.
Series G :		
1	0·07 per cent. iron + 0·08 per cent. silicon	Al + $\mathrm{CuAl_2}$ + β(FeSi)?
2	0·015 per cent. iron + 0·013 per cent. silicon	Al + $\mathrm{CuAl_2}$
3	0 per cent. iron + 0·16 per cent. silicon	Al + $\mathrm{CuAl_2}$ + Si
Series H : 0·1 *per cent. Iron :*		
1	0 per cent. silicon	Al + $\mathrm{CuAl_2}$ + β(FeSi)
2	0·12 ,, ,,	Al + $\mathrm{CuAl_2}$ + β(FeSi)
3	0·14 ,, ,,	Al + $\mathrm{CuAl_2}$ + β(FeSi) + Si
Series K : 0·32 *per cent. Iron*		
1	0·10 per cent. silicon	Al + $\mathrm{CuAl_2}$ + α(FeSi)
2	0·18 ,, ,,	Al + $\mathrm{CuAl_2}$ + α(FeSi) + Si
3	0·5 ,, ,,	Al + $\mathrm{CuAl_2}$ + α(FeSi) + Si
Series L : 0·6 *per cent. Iron*		
1	0·11 per cent. silicon	Al + $\mathrm{CuAl_2}$ + α(FeSi)
2	0·20 ,, ,,	Al + $\mathrm{CuAl_2}$ + α(FeSi) + Si

It is seen from Table V that equilibrium has by no means been attained in the alloys; it is improbable that they would reach a stable state even after prolonged heat-treatment.

Comparing these results with those obtained by Gwyer and Phillips, and Dix and Heath, the conclusion must be reached that the constitution of heat-treated alloys, whose compositions lie within the range investigated, depends on the phases which separate during casting. Since the metastable constituents formed can only revert at infinitely slow speed to the stable state, it follows that the constitution of the alloys will differ with small variations in the condition of casting. This probably accounts for the difference in the results obtained by these investigators mentioned above, and also for the fact that the results of the present investigation differ from both.

The effect of slowly cooling the alloys to 190° C. has been studied by heat-treating half of each specimen heat-treated at 500° C. (Appendix II, Table XIV). $CuAl_2$ is precipitated from solid solution, and the limit of solid solubility of silicon is reduced to a value of about 0·1 per cent., this value being only very slightly affected by the addition of iron. Table VI gives the constituents present in the alloys heat-treated as above.

Typical microstructures are given in Figs. 19–23 (Plates XIII and XIV).

Fig. 19 shows the microstructure of the alloy containing 0·12 per cent. iron and no added silicon; the black phase is $CuAl_2$ (etched with 10 per cent. ferric nitrate), the half tone is the β(FeSi) phase. The addition of 0·14 per cent. silicon to such an alloy results in the presence of free silicon, as shown in Fig. 20, etched as above. Fig. 21 shows (× 150), the precipitation of $CuAl_2$ in the alloy containing 0·1 per cent. iron and 0·12 per cent. silicon. The alloy containing 0·6 per cent. iron, 0·20 per cent. silicon etched with 10 per cent. ferric nitrate is shown in Fig. 22; the same field re-polished and etched with 20 per cent. sulphuric acid at 70° C. is seen in Fig. 23. $CuAl_2$ has etched black in Fig. 22, but remains uncoloured in Fig. 23; silicon is the half-tone constituent in both photomicrographs, while the α(FeSi) phase is the light unattacked constituent in Fig. 22, which is coloured black with the sulphuric acid etch as shown in Fig. 23.

TABLE VII.

Temperature.	Iron, Per Cent.	Silicon, Per Cent.
500° C.	0·6 0·3 0·1	0·5 0·6 0·67
190° C.	0·6 0·3 0·1	0·1 0·12 0·13

The limits of solid solubility of silicon in the alloys at 500° and 190° C. are approximately as given in Table VII.

Conclusions.

(1) Under the conditions of casting and subsequent working and heat-treatment, as described, of 4 per cent. copper–aluminium alloys

containing up to 0·6 and 1·0 per cent. iron and silicon, respectively, it has not been found possible to attain a state approaching equilibrium, and consequently no diagram can be submitted. Neither has a constitutional diagram been given, since it is clear from the results of this investigation and those of previous workers that a " constitutional " diagram depends on factors which must be very carefully controlled if similar results are to be obtained by others.

(2) The α(FeSi) and β(FeSi) phases have been identified in the alloys examined, together with $CuAl_2$ and Si.

(3) $FeAl_3$ was not seen in any of the microsections examined.

(4) Silicon is held in solid solution to a limited amount at 500° C., and is precipitated during slow cooling to 190° C.

(5) $CuAl_2$ was present in some of the alloys heat-treated at the higher temperature, but was precipitated in large amount on slowly cooling to 190° C.

III. THE AGE-HARDENING OF THE QUATERNARY ALLOYS.

The age-hardening of four quaternary alloys has been studied by means of Brinell hardness measurements. The alloys were chosen in order to demonstrate the effect of small additions of iron and silicon independently or together on the age-hardening of the high-purity 4 per cent. copper–aluminium alloy. The age-hardening of this alloy (made with Hoopes' aluminium) has been already studied,[5] and these results form the basis of comparison. Table VIII gives the compositions of the alloys.

TABLE VIII.

	Per Cent. Copper.	Per Cent. Silicon.	Per Cent. Iron.
Alloy 1 . . .	4	...	0·1
„ 2 . . .	4	1·0	0·1
„ 3 . . .	4	0·1	...
„ 4 . . .	4	0·1	0·6

The alloys were cast into 1 in. sand moulds, and forged to a thickness of about $\frac{1}{16}$ in. after 5 hrs.' annealing at 450° C. After preparing the surface for hardness measurements, the forged bars were heat-treated for 4 days at 500° C. before quenching. The bars were aged at room temperature and then heat-treated for periods up to 8 days at 50°, 100°, 150°, 200° C.; the results are embodied in Figs. 24–27 inclusive, and the heat-treatments are given in Appendix II, *A*. It will be seen, that the first effect of heat-treating the alloys is to cause softening to a greater or less degree.

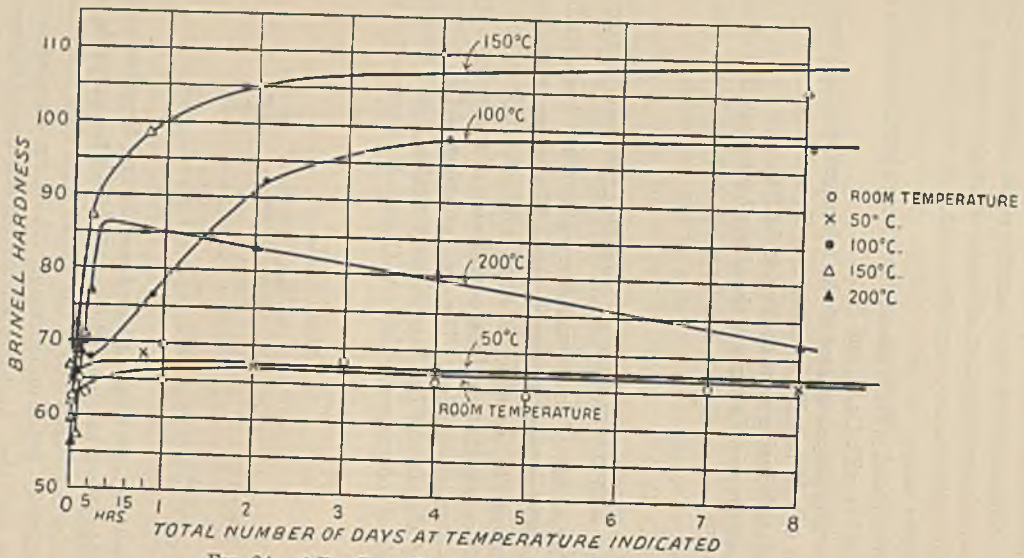

Fig. 24.—4 Per Cent. Copper, 0·1 Per Cent. Iron.

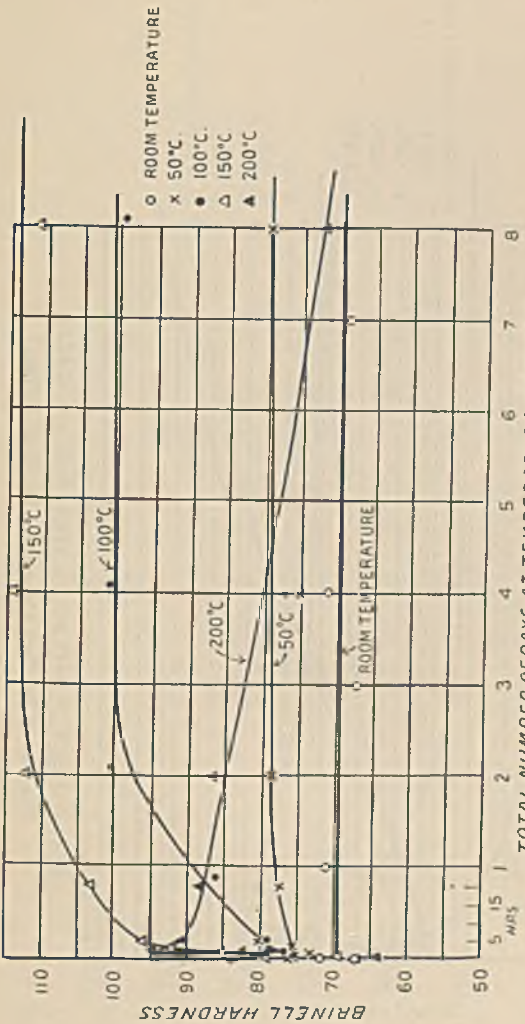

Fig. 25.—4 Per Cent. Copper, 0·1 Per Cent. Iron, 1·0 Per Cent. Silicon.

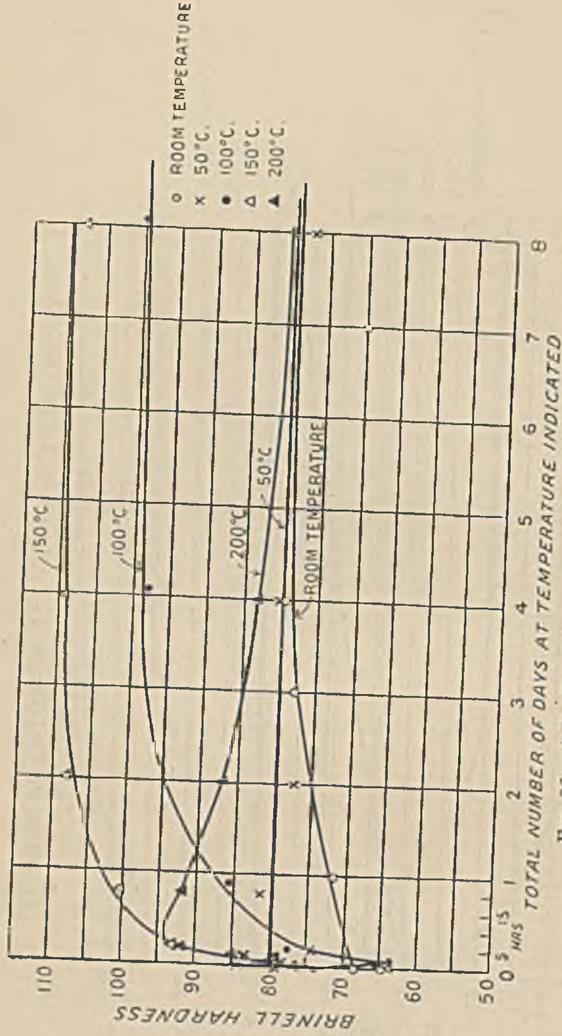

FIG. 28.—4 Per Cent. Copper, 0·1 Per Cent. Silicon.

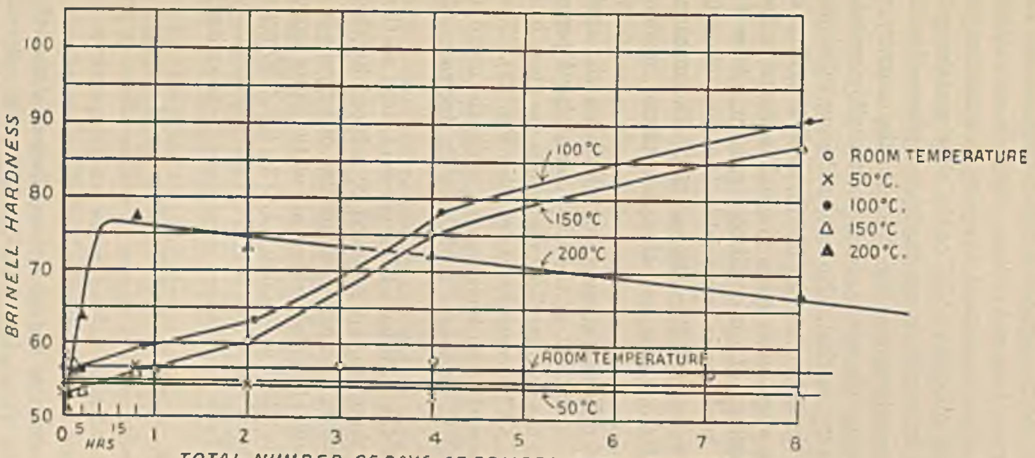

Fig. 27.—4 Per Cent. Copper, 0·1 Per Cent. Silicon, 0·0 Per Cent. Iron.

The addition of iron is well known to inhibit the age-hardening of 4 per cent. copper-aluminium alloys.[8] Figs. 24 and 26 are of interest since they show that the ageing at higher temperatures of alloys containing 0·1 per cent. iron and 0·1 per cent. silicon, respectively, differ little from each other, in contrast to ageing at room temperature.

If 1·0 per cent. silicon be added to the alloy containing 0·1 per cent. iron, an increase in maximum age-hardness is observed on heat-treating at the same temperatures (see Fig. 25). On the contrary, the effect of 0·6 per cent. iron on the age-hardening of the alloy containing 0·1 per cent. silicon is very marked. No age-hardening takes place at room temperature or heat-treating at 50° C., whilst ageing at 100° and 150° C. causes a very much more gradual increase in hardness than when only 0·1 per cent. of iron or silicon is present. After 8 days at 100° and 150° C. the hardness is appreciably less than when 0·1 per cent. silicon only is present (cf. Figs. 26 and 27). The maximum hardness obtained at 200° C. is also less, though attained in about the same time.

The effect of different amounts of silicon on the ageing at room temperature and at 200° C. of the alloy containing 4 per cent. copper, 0·6 per cent. iron has been studied; the results are given in Appendix II, Tables XV and XVI, respectively (cf. also Fig. 27). No appreciable ageing takes place at room temperature, while the maximum hardness attained at 200° C. increases slightly with increase of the silicon content.

The effect of the addition of 0·6 per cent. iron to the 4 per cent. copper alloy is therefore not removed or reduced by the addition of silicon; furthermore, the micro-examination of forged and heat-treated material in the unetched state shows about the same amount of a grey constituent in the alloys containing 0·1, 0·24, 0·5, 0·95 per cent. silicon; excess silicon (above that which is held in solid solution in the aluminium or which is in solution in the iron constituent), shows itself as an additional phase.

Alloys slowly cooled to 190° C., show no observable precipitation of the iron constituent, but copper as well as silicon is precipitated so that the age-hardening taking place at temperatures above room temperature must be attributed to both these two phases.

Kroenig[9] found that the deleterious effect of iron on the mechanical properties of Duralumin is greater the higher the quenching temperature, and concluded that iron reduces the solid solubility of copper in aluminium (owing to the formation of the complex eutectic, Al–Fe–Cu), but that it does not hinder the precipitation of $CuAl_2$ from the supersaturated solid solution during ageing. Koch and Nothing[10] reached the same conclusion with regard to the effect of iron on the ageing of a high-purity 4 per cent. copper–aluminium alloy. These latter authors found that the identification of the constituents present in their heat-treated material was not at all simple, but the examination of alloys cooled in the crucible showed that the amount of $CuAl_2$ present decreases with increasing iron content. At the same time an iron phase appeared, which they identified as Gwyer, Phillips, and Mann's "N" constituent, *i.e.* aluminium–iron–copper phase; and on the basis that this has the definite composition Cu_2FeAl_7, Koch and Nothing calculated that in an alloy containing 4 per cent. copper all the copper is removed from the solid solution in the presence of 1·75 per cent. iron. Hence, both these investigators consider that the effect of added iron on these alloys is due to the removal of copper from the solid solution by the formation of a ternary compound.

During the course of this investigation, anomalous results were continually appearing. At first no cause could be found, but it has since been proved that the purity of aluminium was responsible; its effect on copper–aluminium alloys is now being studied in detail. The results will be communicated shortly.

SUMMARY.

The results of the present investigation into the age-hardening of 4 per cent. copper–aluminium alloys containing up to 0·6 per cent. iron and 1·0 per cent. silicon independently or together may be summed up as follows:

(1) The addition of 0·1 per cent. iron inhibits ageing at room temperature, but not at higher temperatures; while the addition of 0·6 per cent. iron reduces, to a marked degree, ageing at higher temperatures.

(2) The addition of up to 1·0 per cent. silicon does not inhibit the effect of 0·6 per cent. iron; from a study of the constitution of alloys it would appear that the age-hardening which takes place at high temperatures, may be attributed to precipitation of silicon as well as some $CuAl_2$ from the solid solution.

ACKNOWLEDGMENTS.

The author would acknowledge with thanks the valuable assistance she has had from Mr. R. P. Garner (now of Messrs. I.C.I. (Alkali), Ltd., Northwich) in the earlier stages of the research, and also from Mr. Parkhouse, whose skill in metallographic technique is much appreciated. Thanks are also due to Mr. W. Carrington for help in the photographing of the alloys.

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APPENDIX I.

MATERIAL USED.

(1) High-purity silicon and iron, prepared at the National Physical Laboratory.

(2) Electrolytic copper.

(3) Three grades of aluminium.

Aluminium hardeners containing about 8 per cent. iron and 10 per cent. silicon were made up. The less pure aluminium was only used when the compositions of the alloys were high in iron and silicon.

TABLE IX.—*Chemical Analyses.*

	Per Cent.
Silicon:	
Aluminium	0·04
Iron	0·08
Calcium	0·02
Insolubles	0·068
French aluminium:	
Iron	trace
Hoopes' aluminium:	
Iron	0·015
Silicon	0·002
Copper	0·019
Sample from the British Aluminium Co., Ltd.:	
Iron	0·09
Silicon	0·081
Titanium	trace

TABLE X.—*Composition of Alloys.*

Calculated, Per Cent.			By Analysis, Per Cent.		
Silicon.	Iron.	Copper.	Silicon.	Iron.	Copper.
...	0·1	4	0·007	0·12	3·98
0·10	0·1	4	0·11	0·12	4·01
0·24	0·1	4	0·27	0·13	4·06
0·5	0·1	4	0·53	0·12	3·77
0·75	0·1	4	0·84	0·11	3·62
1·0	0·1	4	1·05	0·12	3·87
...	0·3	4	0·008	0·32	4·09
0·10	0·3	4	0·13	0·33	4·05
0·24	0·3	4	0·24	0·32	3·89
0·5	0·3	4	0·85	0·30	3·98
0·75	0·3	4	0·78	0·27	3·98
1·0	0·3	4	0·91	0·29	4·00
0·10	0·6	4	0·10	0·62	3·60
0·24	0·6	4	0·24	0·58	4·05
0·5	0·6	4	0·43	0·60	4·20
0·75	0·6	4	0·61	0·61	4·00
1·0	0·6	4	0·95	0·56	4·00
...	0·3	4	...	0·032	...
...	0·6	4	...	0·058	...
B.A. Co.'s Al	No additions	4	0·08	0·06	4·08
0·10	...	4	0·11	0·01	3·53

TABLE XI.

	Silicon, Per Cent.	Iron, Per Cent.	Outside Layer, Copper, Per Cent.	Intermediate Layer, Copper, Per Cent.	Centre, Copper, Per Cent.
½ *in. Sand-Castings*					
A	0·11	0·01	4·00	3·92	3·92
	0·10	0·62	3·79	3·69	3·32
	0·007	0·12	4·02	3·97	3·95
	1·05	0·12	3·99	3·79	3·91
1 *in. Sand-Castings*					
B	0·09	...	3·80	3·88	3·81
	0·98	...	4·08	4·00	4·02

APPENDIX II.

A. *Age-Hardening Experiments.*

Forged sand-castings were heat-treated for 4 days at 500° C., quenched in water at room temperature, and aged for at least 6 days before heat-treating at higher temperatures.

Brinell hardness impressions in duplicate were made at either end of the bar at various time intervals during these periods of heat-treatment using a 2 mm. ball under a load of 40 kg. for 30 seconds.

The temperatures of heat-treatment were 50°, 100°, 150°, and 200° C., respectively.

B. *Constitution of the Alloys.*

Specimens were cut from alloys forged as above and heat-treated as shown in Table XII.

Table XII.

Heat-Treatment.	Calculated Composition, Per Cent.		
	Silicon.	Iron.	Copper.
7 weeks at 500° C.	...	0·1	4
	0·1	0·1	4
	0·24	0·1	4
	0·5	0·1	4
	0·75	0·1	4
	1·0	0·1	4
	0·1	...	4
	0·1	0·1	4
	0·1	0·32	4
	0·1	0·6	4
	...	0·3	4
	0·24	0·3	4
	0·24	...	4
8 weeks at 500° C.	0·24	0·6	4
	0·5	0·6	4
	0·75	0·6	4
	1·0	0·6	4
	0·75	0·3	4
	1·0	0·3	4

Some of the alloys, listed in Table XII, were reduced by $\frac{2}{3}$ in thickness by hammering in the cold, and then further heat-treated as stated in Table XIII.

TABLE XIII.

Heat-Treatment.	Calculated Composition, Per Cent.		
	Silicon.	Iron.	Copper.
6 weeks + 1 day at 487° C.	...	...	4
	0·08	0·06	4
	0·5	0·32	4
6 weeks + 1 day at 475° C.	0·24	0·6	4
	0·5	0·6	4
	0·75	0·6	4
	1·0	0·6	4

For determining the limits of solubility at 190° C. the alloys shown in Table XIV, heat-treated as noted in Tables XII and XIII, were given the treatment stated in Table XIV.

TABLE XIV.

Heat-Treatment.	Calculated Composition, Per Cent.			
	Silicon.	Iron.	Copper.	
1 day at 492° C. then slowly cooled in 20 days to 190° C. and quenched.	...	0·1	4	Table XII
	0·1	0·1	4	
	0·24	0·1	4	
	0·08	0·06	4	Table XIII
	0·1	...	4	,, XII
1 day at 494° C. then slowly cooled in 20 days to 195° C. and quenched.	0·1	0·6	4	Table XII
	0·24	0·6	4	,, XIII
	0·5	0·6	4	,, ,,
	0·1	0·3	4	Table XII
	0·24	0·3	4	,, ,,
	0·5	0·3	4	,, XIII

BRINELL HARDNESS NUMBERS OF SERIES CONTAINING 0·6 PER CENT. IRON.

TABLE XV.—*Forged Bars Heat-Treated as in Appendix II*, A.

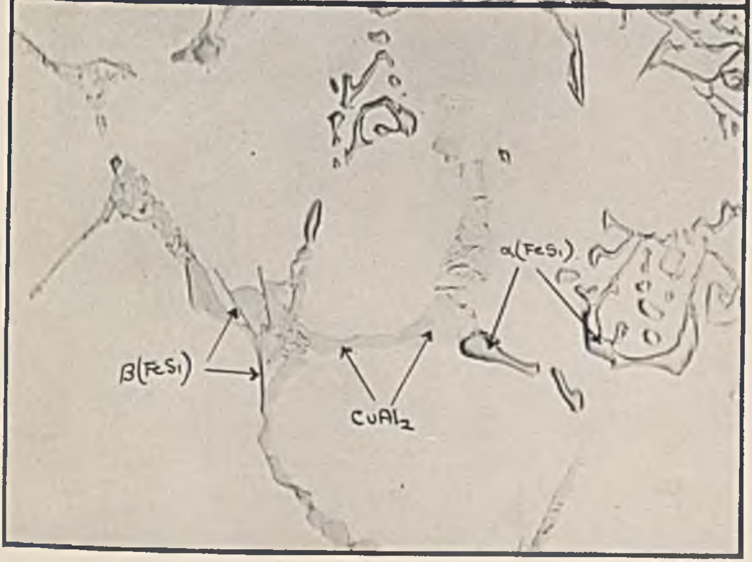
Aged at Room Temperature.	Silicon, Calculated Per Cent.			
	0·24.	0·5.	0·75.	1·0.
	Brinell Hardness Number.			
Immediately after quenching from 500° C.	56	55	56	56
6 hrs.	54	57	58	57
1 day	55	60	56	58
2 days	54	60	58	56
4 ,,	56	58	59	57
8 ,,	58	60	58	57
15 ,,	55	61	60	58
100 ,,	58	59	60	60

TABLE XVI.—*Alloys Heat-Treated Immediately at* 200° *C. after Quenching from* 500° C.

Time at 200° C.	Silicon, Calculated Per Cent.			
	0·24.	0·5.	0·75.	1·0.
	Brinell Hardness Number.			
Immediately after quenching	53	57	60	62
½ hr. at 200° C.	53	58	60	60
1⅓ hrs.	52	58	61	62
4½ ,,	64	64	71	69
20 ,,	80	74	78	76
25½ ,,	74	78	76	76
43 ,,	78	80	80	80
66 ,,	76	80	78	78
117 ,,	76	78	74	72
8 days	72	80	69	69
17 ,,	72	76	65	69
32 ,,	71	71	64	65
64 ,,	61	67	61	59

PLATE XV.

A



B

FIG. A.—Alloy "A" (Cu 5, Si 0·3, Fe 1 Per Cent.) Slowly Cooled in Furnace. Etched with NaOH. × 300.

FIG. B.—Alloy "B" (Cu 5, Si 1, Fe 1 Per Cent.) Slowly Cooled in Furnace. Unetched. × 300.

[*To face p.* 98.

CORRESPONDENCE.

Mr. H. W. L. Phillips * (Member): I fully endorse all that the author has written regarding the difficulty of identifying constituents in the ternary and quaternary alloys of aluminium with silicon, iron, and copper. In our work † we preferred to base our identification of the constituents on their form and colour rather than on their etching properties, but, as the author has rightly pointed out, these means become difficult of application where only small quantities of a constituent are present and almost insuperably so in the case of worked or annealed metal.

I was particularly interested to note the author's findings in the case of the alloys listed in Table III, which, as she points out, differ in some respects from our own. Our views as to the constitution of alloys A, B, C, and D are summarized in Fig. 26 (*a*) of our 1928 paper, and may be tabulated as follows:

Alloy.				Constituents Identified.	
				Gayler.	Gwyer, Phillips, and Mann.
	Cu	Si	Fe		
A	5	0·3	1	α(FeSi), β(FeSi), $CuAl_2$	$FeAl_3$α, (FeSi), β(FeSi), $CuAl_2$
B	5	1·0	1	α(FeSi), Si, $CuAl_2$	Traces $FeAl_3$, α(FeSi), β(FeSi), Si, $CuAl_2$
C	5	3·0	1	α(FeSi), β(FeSi), Si, $CuAl_2$	α(FeSi), β(FeSi), Si, $CuAl_2$
D	5	10·0	1	β(FeSi), Si, $CuAl_2$	β(FeSi), Si, $CuAl_2$

The most remarkable points of difference are the occurrence of $FeAl_3$ in A and of β(FeSi) in B. It is true that the temperature of separation of $FeAl_3$ in alloy A is only about 5° higher than that of α(FeSi) and that its occurrence or otherwise would therefore be governed by conditions of cooling; nevertheless we should expect some to be present in a furnace cooled sample. It is difficult to account for the absence of β(FeSi) in alloy B, as the author had found it to occur in alloys of lower and of higher silicon content.

In order to verify our original conclusions, we have prepared fresh specimens of alloys A and B. Figs. A and B (Plate XV) show their structures as slowly cooled. $FeAl_3$ occurs in alloy A, enveloped in α(FeSi), and the photomicrograph also includes a typical "Chinese script" formation of α(FeSi) and an area in which β(FeSi) occurs associated with $CuAl_2$. We have also confirmed the occurrence of β(FeSi) in alloy B: typical needles of this constituent are visible in the area photographed. We did not, however, confirm the presence of $FeAl_3$ in this alloy.

The Author (*in reply*): Mr. Phillips' remarks and photomicrographs are very interesting, and in consequence I have re-examined the microstructures of the two alloys of similar composition in a direction at right angles to that which had been originally polished. I could not find evidence, however, of any $FeAl_3$ in Alloy A, even after a most careful examination, and I would suggest that the absence of $FeAl_3$, contrary to Mr. Phillips' results, may be due to difference in the rates of cooling in the furnace of the alloys respectively.

In the case of Alloy B, examination of the fresh surface showed a few needles of β(FeSi) in association with more or less isolated patches of $CuAl_2$ but no $FeAl_3$: this fact confirms Mr. Phillips' result. The small amount of β(FeSi) was not observed, however, in the surface first examined.

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* Metallurgist, The British Aluminium Company, Ltd., Warrington.

† A. G. C. Gwyer and H. W. L. Phillips, *J. Inst. Metals*, 1927, **38**, 29, and A. G. C. Gwyer, H. W. L. Phillips, and L. Mann, *ibid.*, 1928, **40**, 297.

NOTE ON THE INFLUENCE OF SMALL AMOUNTS OF TITANIUM ON THE MECHANICAL PROPERTIES OF SOME ALUMINIUM CASTING ALLOYS.*

765

By T. H. SCHOFIELD,† M.Sc., MEMBER, and C. E. PHILLIPS,‡ A.C.G.I., D.I.C.

SYNOPSIS.

A summary is given of the results of an investigation on the influence of small amounts of titanium on the mechanical properties of some commercial aluminium casting alloys. This influence is found to be small with amounts of titanium up to 0·1 per cent.

THE work described below has been carried out at the National Physical Laboratory for the Metallurgy Research Board of the Department of Scientific and Industrial Research.

At the time this work was undertaken certain processes for removing dissolved gases from molten aluminium casting alloys introduced small amounts of titanium into the metal; also, it had been observed that small additions of that element to molten aluminium alloys caused grain refinement in castings. It became desirable, therefore, to investigate the effect, if any, of titanium on mechanical properties of cast alloys for which British Standard Specifications were in use.

The present note deals with the influence of titanium up to about 0·1 per cent. on the mechanical properties of " Y," 7 per cent. copper–aluminium (L11) and copper–zinc–aluminium (L5), alloys, in the form of 1 in. diameter bars chill- and sand-cast, respectively. The materials used in the preparation of the alloys were aluminium containing 99·6 per cent. aluminium, copper and nickel–aluminium hardeners containing about 47 per cent. copper and 20 per cent. nickel, respectively, and high-purity magnesium and zinc. Titanium was introduced by bubbling the vapour of titanium tetrachloride through the melt.

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* Manuscript received November 26, 1936.

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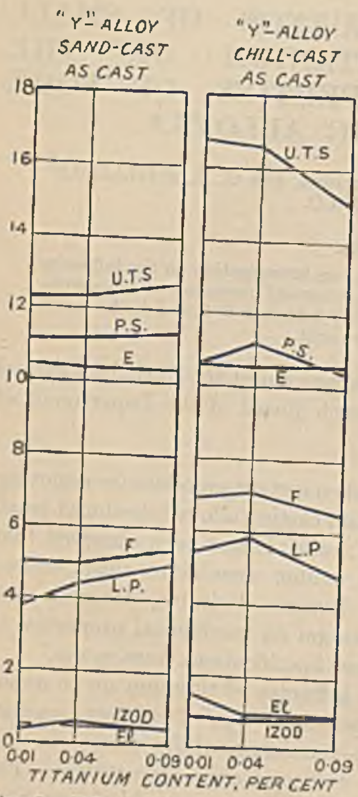

FIG. 1.—Effect of Titanium on Mechanical Properties of "Y" Alloy.

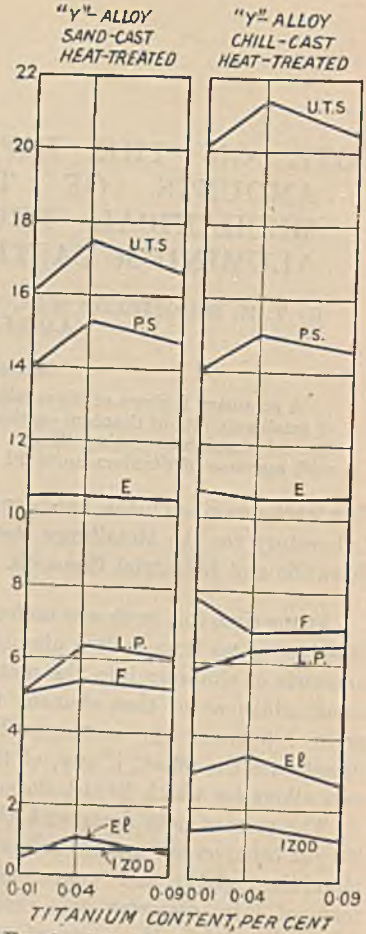

FIG. 2.—Effect of Titanium on Mechanical Properties of "Y" Alloy.

U.T.S. = Ultimate Tensile Stress, tons/in.^{2}.
E. = Modulus of Elasticity, 10^6 lb./in.^{2}.
P.S. = 0·1 Per Cent. Proof Stress, tons/in.^{2}.
L.P. = Limit of Proportionality, tons/in.^{2}.
F. = Endurance Fatigue Limit (20×10^6 cycles), ± tons/in.^{2}.
El. = Elongation, Per Cent. on 2 in. Gauge-Length.
Izod = Izod Impact Value, ft.-lb. (Energy Absorbed).

Owing to practical limitations, it was not possible to prepare from one melt the whole of the bars required for a complete series of mechanical tests, and as it was necessary that the composition of each alloy should be uniform the following procedure was adopted. Three melts of each alloy each of 27 lb. were prepared in a Salamander pot in a gas-fired furnace; no titanium was introduced into the first melt, but about 0·05 per cent. and 0·1 per cent. was introduced into the second and third melts, respectively. The melts were cast in the form of notched ingots. Each batch of ingots was divided into two equal parts; each part was remelted in an iron (Silal) pot, dressed with a mixture of china clay and silicate of soda, in an electric (metal resistor) furnace. The molten alloys were treated for removal of gas by a method similar to that

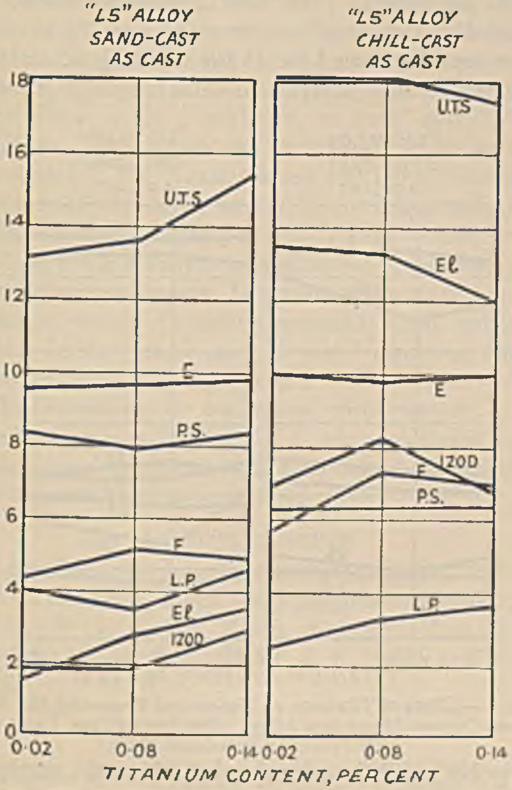

Fig. 3.—Effect of Titanium on Mechanical Properties of L5 Alloy. (See key to Figs. 1 and 2.)

developed by the British Non-Ferrous Metals Research Association, in which the metal is covered with a flux and stirred in an atmosphere of dry nitrogen.

From each melt six 1 in. diameter chill-cast and six standard 1 in. diameter sand-cast bars were made; thus for each composition there were available for tests 12 chill- and 12 sand-cast bars. The chills were open-ended and made of cast iron and were 7¼ in. long with a wall thickness tapering from ½ in. at the top to ⅝ in. at the bottom. They were dressed with a mixture of china clay and silicate of soda and heated to 150°–160° C. and inclined at 30° to the vertical on a dry sand base. The sand moulds were made according to the British Standards Specification for aluminium casting alloys. The method of casting was briefly as follows: The charge of treated alloy was retained in the furnace and a small dressed iron ladle full of molten alloy was removed for casting each bar. A slow and uniform rate of pouring was maintained, the average time taken for one chill- or sand-casting being 12–16 seconds. No feeder head was used for the chills, but the castings were fed. The casting temperature was 725° ± 5° C. for the chill- and 675° ± 5° C. for the sand-cast bars.

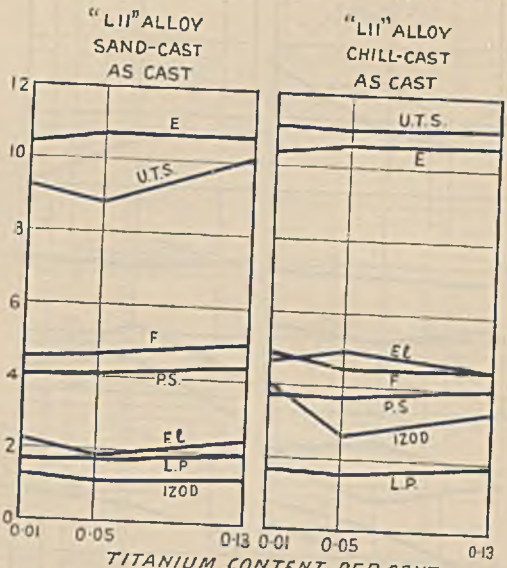

Fig. 4.—Effect of Titanium on Mechanical Properties of 7 Per Cent. Copper–Aluminium Alloy. (See key to Figs. 1 and 2.)

The densities of the cropped bars were determined, and one sand-cast bar from each melt was sectioned longitudinally through the middle and carefully machined. If the machined section was free from visual porosity and the densities of the batch of bars were consistent, it was assumed that the whole were satisfactory for the preparation of test-pieces. The median sections were etched; the grain-size of all the bars examined was small, consequently the influence of titanium was not easily detected but appeared to be slight.

Tensile, standard notched-bar (Izod) impact, and rotating bending fatigue tests (on a basis of 20 million cycles) were carried out on each of the three alloys in the " sand-cast, as cast," and " chill-cast, as cast " conditions. In the case of " Y " alloy similar tests were also made on material in the " heat-treated and aged " condition. This treatment consisted of soaking at 520° C. for 6 hrs. and quenching in boiling water, followed by ageing at least 7 days at room temperature.

Figs. 1–4 show the variation in mechanical properties of each alloy with change in titanium content. In general, the variation in mechanical properties due to change of titanium content is small, and is in no case marked. Bars in the " sand cast, as cast " condition tend to show improvement in mechanical properties with increase of titanium content. The variations in mechanical properties with change of titanium content of heat-treated " Y " alloy, chill-cast L5 and L11 are not of significant magnitude. The mechanical properties of chill-cast bars are superior to those sand-cast.

ACKNOWLEDGMENTS.

The authors desire to acknowledge the help and encouragement given by Dr. C. H. Desch, F.R.S. (Superintendent, Metallurgy Department) and Dr. H. J. Gough, F.R.S. (Superintendent, Engineering Department), and the assistance of Mr. A. E. Bacon and Mr. R. C. A. Thurston, B.Sc.

CORRESPONDENCE.

MR. G. F. COMSTOCK,* A.B., Met.E. (Member): Although it is interesting to note that a general improvement in properties was found from the treatment of the sand-cast alloys with titanium tetrachloride, it should be kept in mind that the paper really shows the results of the use of this compound, including both chlorine and titanium, instead of the effect of titanium alone, as is implied by both the title and the conclusions. It would have been still more interesting had the effect of titanium alone been reported, in amounts between 0·1 and 0·2 per cent. Perhaps some results on these lines, from American practice, may appropriately be submitted in this discussion. The effect of titanium was segregated from other influences in this work by using a master alloy known as " TAM Webbite " as the source of the element, this alloy being composed of aluminium and 6–7 per cent. titanium,

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with unimportant amounts of impurities. An average analysis is: titanium 6·36, iron 0·7, silicon 0·4, copper 0·4, manganese 0·11 per cent. Other factors, such as size of casting, pouring temperature, &c., were kept as closely similar as possible in this work, and all the results were obtained from sand-cast bars, most of them being the average from two to four tests.

One series of tests showed the effect of increasing amounts of titanium on an aluminium alloy containing copper 7·46, iron 0·3, silicon 0·2, and manganese 0·1 per cent., as given in Table A.

TABLE A.

TAM Webbite Added, Per Cent.	Titanium Content, Per Cent.	Yield-Point, Lb./in.^{2}.	Tensile Strength, Lb./in.^{2}.	Elongation on 2 in., Per Cent.	Grains Per mm.^{2}.
None	0·015	13,000	17,700	2·1	2·4
1·5	0·105	13,400	19,950	3·0	6·25
2·5	0·144	14,300	20,150	2·5	8·2
3	0·182	14,130	21,630	2·8	156
4·5	0·224	13,480	22,350	2·8	156
6	0·243	13,420	21,700	2·8	156

With over 0·18 per cent. titanium the tensile strength was increased about 23 per cent., which would seem to be a reasonably well marked improvement, and the grain-size was decreased enormously by that amount of titanium. With the larger additions of TAM Webbite the titanium content of the alloy did not increase proportionately, because without increasing the pouring temperature not more than about 0·25 per cent. titanium can be absorbed.

Tests on another alloy of lower purity, containing copper 6, silicon 1·2, iron 0·5, manganese 0·3, magnesium 0·7, tin 0·3, and nickel 0·4 per cent., gave the results shown in Table B. This shows about 16 per cent. improvement in strength, with the grain-size depending on the titanium content, rather than on the amount added.

TABLE B.

TAM Webbite Added, Per Cent.	Titanium Content Per Cent.	Yield-Point, Lb./in.^{2}.	Tensile Strength, Lb./in.^{2}.	Elongation on 2 in., Per Cent.	Grains Per mm.^{2}.
None	0·02	19,120	19,600	0·8	0·08
2·5	0·095	21,300	22,800	0·9	1·1
2·5	0·138	21,650	22,300	1·0	3·3

Although these tests were carried out carefully in the laboratory, they have been checked in regular foundry practice. Instances of such practical results are given in Table C, the alloy used being the common aluminium casting alloy containing about 8 per cent. copper:

TABLE C.

TAM Webbite Added, Per Cent.	Titanium Content, Per Cent.	Yield-Point, Lb./in.^{2}.	Tensile Strength, Lb./in.^{2}.	Elongation on 2 in., Per Cent.	Brinell Hardness.	Grains Per mm.^{2}.
None	...	14,000	16,800	1·5	47·5	6·25
2·5	...	15,300	22,500	2·2	52·5	44·35
None	0·075	18,000	19,800	2·5	...	...
2·5	0·183	18,550	22,600	2·5	...	...

In some instances in the laboratory an advantage has been derived from the use of a little titanium tetrachloride, probably as a degasifier, in addition to the TAM Webbite for refining the grain; in regular foundry practice in America, however, the latter form of titanium is much more widely used because of its convenience and the consistent and definite benefits obtained with it in soundness and strength.

It may be mentioned in this connection that a patent on aluminium–copper–titanium alloys, which expires in September 1937, has disclosed numerous other advantages due to the small titanium content, namely low crystallization shrinkage, high resistance to wear, fine grain, and good bearing qualities.

The AUTHORS (*in reply*): Some of the results given by Mr. Comstock relate to an alloy very similar in composition to L11 (Table A): the values obtained for ultimate tensile stress and elongation of castings containing titanium additions agree substantially with the authors' results.

The effects of titanium tetrachloride and flux in assisting the removal of gas lead to the production of sound castings and a reliable indication of the influence of varying titanium content on the properties. Titanium tetrachloride was used by the authors mainly because it does not contain impurities which are generally present in titanium-bearing hardeners, and is especially convenient for the addition of small amounts of titanium.

* U.S. Pat. 1,352,322.

STRESS-STRAIN CHARACTERISTICS OF COPPER, SILVER, AND GOLD.*

754

By J. McKEOWN,† M.Sc., Ph.D., MEMBER, and
O. F. HUDSON,‡ A.R.C.S., D.Sc., MEMBER.

SYNOPSIS.

A study has been made of the stress-strain characteristics of gold and silver of a very high degree of purity, and also of two coppers, one oxygen-free but containing a small amount of silver (about 0·003 per cent.), the other containing 0·016 per cent. oxygen but free from silver, both having little more than traces of other impurities. Stress-strain curves were obtained to determine limit of proportionality, 0·01 per cent. proof stress, and Young's modulus. The materials were tested in the fully-softened condition, after slight tensile overstrain (less than 1 per cent.) and after definite larger amounts of tensile overstrain (5–15 per cent.), and after re-heating the overstrained specimens at different temperatures.

It is generally considered that copper in the fully-annealed condition has no elastic limit, and the present tests have shown, as was expected, that pure gold and pure silver, when fully annealed, also show no proportionality of stress to strain in any part of the stress-strain diagram.

The elastic properties induced by cold-working were retained in large measure in all three metals after re-heating for short periods at moderately elevated temperatures, when the amount of cold-working (tensile overstrain) had been small. Low-temperature annealing, as used in the tests described, did not, however, result in raising the limit of proportionality of pure gold and silver and of oxygen-free and oxygen-containing coppers, to the same extent as in other cases, *e.g.* other kinds of copper.[1, 3] The tests have shown that, when any of the metals, fine gold, fine silver, oxygen-free and oxygen-containing coppers, has been subjected to a small tensile overstrain, the effect of this small overstrain is evident in the stress-strain characteristics, even after re-heating to relatively high temperatures.

The tests have shown that the value of Young's modulus (E) for this oxygen-free copper is decreased by a small (5 per cent.) tensile overstrain to $15 \cdot 7 \times 10^6$ lb./in.^{2} (mean value). Larger amounts of overstrain appear to result in a recovery in the value of E, with 15 per cent. overstrain the value of E found being $17 \cdot 6 \times 10^6$ lb./in.^{2}. This is in agreement with the results of Kawai's previous work.

Annealing of the overstrained copper tended to restore the value of E lowered by previous overstrain, and by suitable treatment a value of $18 \cdot 2 \times 10^6$ lb./in.^{2} was obtained. Similar effects of re-heating after overstrain were found in the cases of fine gold and of fine silver, although the raising of the modulus by heat-treatment was less marked than in the case of copper. Gold, which had a value of E of $10 \cdot 3 \times 10^6$ lb./in.^{2} when overstrained 5 per cent., gave $11 \cdot 3 \times 10^6$ lb./in.^{2} when re-heated for ½ hr. at 300° C.

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* Manuscript received June 27, 1936. Presented at the Annual General Meeting, London, March 10, 1937.

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Some time ago the authors had the opportunity to carry out tensile tests on standard 0·564 in. test-pieces of fine gold and fine silver, the materials being very kindly lent for this purpose by Messrs. Johnson, Matthey and Co., Ltd., at the suggestion of Professor R. S. Hutton. The original object of the tests was to obtain full load–extension diagrams for these two metals when in a state of high purity and in the annealed condition. It was felt, however, that while the specimens were available it would be of interest to examine the stress–strain characteristics of gold and silver after overstrain and after overstrain followed by heat-treatment. Later the tests were extended to include copper, and for this purpose a sample of copper of high purity (oxygen-free) was kindly supplied by Messrs. Thos. Bolton & Sons, Ltd., who also supplied some otherwise exceptionally pure copper containing 0·016 per cent. oxygen.

I. PREVIOUS WORK.

The effect of cold-work alone and followed by heat-treatment on the elastic properties of metals has been the subject of numerous investigations, and only the more recent work is reviewed. In 1929 Hudson, Herbert, Ball, and Bucknall [1] dealt at some length with the effect of heat-treatment on the hardness and on the elastic properties, particularly the limit of proportionality, of copper containing small percentages of various added elements. In 1931 Jones, Pfeil, and Griffiths [2] dealt with the effect of heat-treatment on the elastic limit of nickel–copper alloys, while in 1932 the present authors [3] in a paper dealing with the effect on copper at low stresses of cold-work, heat-treatment, and composition referred particularly to the influence on the stress–strain characteristics of these variables.

All these investigations showed that cold-work produces in most materials a definite range of proportionality of stress to strain where none exists in the materials in the fully-annealed state, and that this range is generally increased by suitable low-temperature heat-treatment. These investigations were mainly confined to the determination of limit of proportionality and proof stress, the determination of Young's modulus being as a rule considered as a subsidiary matter.

On the other hand, W. Kuntze [4] in 1929 gave evidence to show that the value of Young's modulus was dependent on the previous history of the specimen tested. He concluded that cold-working decreased the value of the modulus while heat-treatment subsequent to cold-working increased it.

Batson and Hyde [10] state that if the limit of proportionality is exceeded the value of Young's modulus (E) for steel may be decreased, in some cases by as much as 20 per cent. Recovery, however, is effected by rest or immersion in boiling water. The same authors quote the results of tests made at the National Physical Laboratory to determine the effect of heat-treatment on the value of E. The maximum effect due to heat-treatment alone (4 per cent.), was found in the case of the 2·75 per cent. nickel, 0·25 per cent. carbon steel.

An example of cold-work followed by precipitation-hardening as effecting a change in the value of E is given by beryllium–copper.[5] Fully-annealed (water-quenched) sheet containing 2 per cent. beryllium has a value of E of $15{\cdot}2 \times 10^6$ lb./in.^{2}, for the same sheet rolled 6 Nos.* hard $E = 16{\cdot}0 \times 10^6$ lb./in.^{2} and heat-treated after rolling $E = 17{\cdot}9 \times 10^6$ lb./in.^{2}. With 2·5 per cent. beryllium the sheet rolled 6 Nos. hard gave $E = 16{\cdot}3 \times 10^6$ lb./in.^{2}, and when heat-treated $E = 19{\cdot}0 \times 10^6$ lb./in.^{2}.

Kawai [6] carried out an investigation on Armco iron, mild steel, nickel steel, copper, aluminium, and nickel to determine the effect produced on the modulus by cold-working with and without subsequent heat-treatment. He found that in iron and steel the modulus always decreases with cold-working and that in the other metals it decreases for a small degree of working, but increases for a large degree of working. The effect of annealing iron and steel subsequent to cold-working was to increase the modulus again; thus, in the case of mild steel drawn with 36 per cent. reduction annealing at 900° C. returned the modulus to the original value of the soft material.

In the case of copper, aluminium, and nickel, previously cold-worked, the modulus increased rapidly as the annealing temperature was increased, a maximum being reached at 300°, 200°, and 350° C., respectively, at which temperatures recrystallization began to become noticeable; from this point the modulus decreased up to about 650°, 500°, and 900° C., respectively, where it had returned to the initial value before cold-working.

In the 1911 May Lecture to the Institute of Metals, Beilby [7] quoted the results of acoustical tests on the changes in elasticity due to annealing at various temperatures, the test being carried out on vibrating tongues of gold, silver, copper, and iron. The pitches of the hardened tongues were raised by annealing treatments, the increase being of the order of 5 per cent. by annealing at the crystallizing temperature. Since the frequency of vibration is proportional to the Young's modulus, it follows that the modulus was increased by the heat-treatments.

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* 50 per cent. reduction.

II. Experimental.

A. *Materials.*

The gold, assayed by the makers, was 999·999 fine and the silver 1000·000 fine. In each case the metals were cast in $1\frac{1}{4}$-in. diameter bars and then rolled to a diameter of 0·8 in. in steel rolls. The bars were then annealed for 10 minutes at 500° C., and standard British Standard 0·564-in. diameter specimens were machined from them. After the machining operation, the finished specimens were given another anneal for 10 minutes at 500° C.

The oxygen-free copper was of high purity, the oxygen content being less than 0·0005 per cent. A spectrographic analysis gave the following results :

	Per Cent.
Bismuth . . .	less than 0·0001
Arsenic . . .	,, ,, 0·001 (if any)
Lead . . .	0·001 (approx.)
Iron	0·005
Nickel . . .	0·0005
Silver . . .	0·003
Antimony . . .	not detected (less than 0·002 if any)
Tin	,, ,, (less than 0·005 if any)
Silicon . . .	,, ,,

This material was supplied in the form of hard-drawn $\frac{7}{8}$-in. diameter bar. It had been hot-rolled in the ordinary way to (nominal) $1\frac{5}{32}$ in. diameter from an imported, vertically cast, 250-lb. wire-bar of O.F.H.C. (non-guaranteed) quality, and drawn to $\frac{7}{8}$ in. diameter on a draw-bench, being given an intermediate annealing of approximately $\frac{1}{2}$ hr. at 650° C. at 1·0 in. diameter. Specimens were machined to the British Standard 0·564 in. size.

The oxygen-containing copper was supplied in the hard condition in the form of machined bar 7 mm. in diameter. It was made from copper of unusual purity, hot-rolled from an ordinary horizontally-cast 250 lb. wire-bar to $\frac{9}{16}$ in. diameter, annealed, pickled, cold-drawn on a block to No. 000 S.W.G. approximately, and finished on a draw-bench without intermediate annealing to $\frac{5}{16}$ in. diameter; it was finally machined to 7 mm. in diameter. Specimens having a diameter of 0·1784 in. (area $\frac{1}{40}$ sq. in.) on the 2-in. gauge-length were machined from the bar. This copper contained 0·016 per cent. oxygen, and in a careful spectrographic analysis the only other impurities detected were iron (0·001 per cent.) and lead (0·0002 per cent.). It should be borne in mind throughout the subsequent discussion of results that, whereas the oxygen-free copper contained about 0·003 per cent. silver, this specially pure copper, while containing a small amount of oxygen, was apparently entirely silver-free; several independent spectrographic and chemical analyses, carried out to detect silver, completely failed to do so.

B. *Testing Methods.*

Two different testing machines were used in this investigation, a 5-ton Avery lever machine and the 5-ton range of a 20-ton Amsler hydraulic machine. The Amsler machine was calibrated against standards before the tests were made, and a cross-check of the two machines was made using a standard steel specimen, elastic to loads greater than 5 tons, and an extensometer. The test showed that the calibration of the machines agreed to within less than 0·5 per cent.

The extensometer used in the determination of the elastic properties of the materials was a Lamb's roller extensometer designed for a gauge-length of 2 in. The scale distance used was such that 1 cm. on the scale represented a strain of 1×10^{-4} on the specimen. The scale was graduated in mm., and a reading could be estimated to 0·2 mm. with an accuracy of at least ± 0·2 mm., *i.e.* the strain was estimated to $\pm 2 \times 10^{-6}$. With such a high sensitivity as this, it is important, of course, that temperature variations should be very small. The tests were made in a basement laboratory where temperature was constant to ± 1° C. during the period of the test. In addition, the specimen and extensometer were left for at least 1 hr. after being assembled in the testing machine, to allow them to attain a steady temperature before any testing was proceeded with.

For accurate testing of elastic properties the greatest care is necessary to ensure axial loading of the specimen, and this was secured by using grips of the Robertson type. These grips were made on the lathe that was used to produce the copper specimens.

All the determinations of elastic properties were made on the Avery machine, on which the load could be read directly to 0·01 ton and by vernier to 0·001 ton. In most of the tests on gold and silver, the load was increased in increments of 0·025 ton, and this increment could be read to ± 0·001 ton. Thus, for an increment of stress on the specimen of 0·100 ton/in.^{2}, the probable error was ± 0·004 ton/in.^{2}. Taking a mean value of E for gold and silver as $10{\cdot}5 \times 10^6$ lb./in.^{2}, then the strain corresponding to $\pm 0{\cdot}004$ ton/in.$^2 = \pm \dfrac{0{\cdot}004 \times 2240}{10{\cdot}5 \times 10^6} = \pm 0{\cdot}85 \times 10^{-6}$, a measurement approximately half the sensitivity of the strain measurement. It follows from this that the measurement of stress was about twice as sensitive as the measurement of strain. Attempts were made to increase the sensitivity of strain measurements by reading the scale to ± 0·1 mm., but it was considered after experience of this that the increase in sensitivity was not fully justified in all cases, and it was decided to adhere to the former method where the strain was measured to a sensitivity of $\pm 2 \times 10^{-6}$.

Where the value of Young's modulus is calculated from a stress-strain curve showing a very low limit of proportionality of stress to strain, the sensitivity of strain measurement becomes important. As an example, take the case of a specimen having a limit of proportionality of 0·4 ton/in.^{2} and a modulus of $10{\cdot}0 \times 10^6$ lb./in.^{2}. The calculated strain at 0·4 ton/in.^{2} is 90×10^{-6}, and this may be read as 92 or 88×10^{-6}. The former value would give $E = 9{\cdot}74 \times 10^6$, while the latter would give $E = 10{\cdot}18 \times 10^6$ lb./in.^{2}, *i.e.* a total variation of $0{\cdot}44 \times 10^6$ on a mean value of $10 \times 10^6 = 4{\cdot}4$ per cent. On this account the values of E given in this paper and derived from specimens having a limit of proportionality of only about 0·4 ton/in.^{2} and a value of E of the order of 10×10^6 lb./in.^{2} may be in error by about ± 2¼ per cent. When the limit of proportionality is 1 ton/in.^{2}, on the other hand the value of E will vary only by ± 1 per cent., and as the limit of proportionality increases the probable error in E will decrease.

C. *Annealing.*

Annealings at temperatures of 500° C. and over were carried out in an electric muffle furnace, and heat-treatments at 250°–400° C. in an electric tubular furnace in air. Heat-treatment at 200° C. was given in an oil-bath.

D. *Stress–Strain Curves.*

The stress–strain curves were plotted to a strain scale such that 1 mm. on the paper represented a strain of 2×10^{-6} on the specimen. From the straight-line portions of the curves, the limit of proportionality and Young's modulus were determined. The proof stress was determined by drawing, parallel to the elastic line, a line distant from it 1×10^{-4} strain or 0·01 per cent. and noting the stress at which it cut the stress–strain curve.

In a number of cases the early part of the stress–strain curve consisted of two straight-line portions having different slopes. The first part up to a stress of about 0·3 ton/in.^{2} was followed by a much longer straight length on which the experimental points lay very well. In such cases the limit of proportionality and E were determined from the second straight-line portion and the first part was ignored. The reason for this peculiar form of stress–strain relationship, present in some cases and absent in others, is not known, but it is interesting to compare the finding with that of Chalmers[8] on lead specimens using an interference extensometer by which strain was read to 10^{-7}. Chalmers obtained from lead specimens a new type of closed stress–strain loop. The early part of the loading line was curved, and that was followed by a straight portion which was found to persist up to the elastic limit. If the elastic limit was not exceeded, the unloading line was an exact reproduction of the loading line starting with a curve and continuing on a straight line. It may be mentioned that in the loops obtained by Chalmers the straight lines were parallel.

In practically every case in the present work, the return line from the maximum stress down to the initial stress was determined, the rate of unloading being the same as the rate of loading. Except for the case of the severely worked materials, which had been overstrained during the test by only a small amount, the return line was curved for all of its length (see typical stress–strain curves in Figs. 1 and 2). This resulted in the permanent set being less than the apparent inelastic extension at the maximum load. In all three materials, and particularly in the silver, the limit of restitution or elastic limit was much greater than the limit of proportionality; in some cases it was observed to be greater by as much as 100 per cent.

A study was made of the effect of rate of stressing in the case of the fully-annealed materials by increasing the stress in equal increments each 10 minutes and taking readings of the scale at 1 minute, 5 minutes, and 10 minutes after each stress was applied. The creep occurring at the higher stresses was clearly shown by the curves obtained. The curves were plotted in such a way that the creep occurring during the period 1–10 minutes at any stress was eliminated from the strain reading for 1 minute after stressing at the next higher stress and similarly for 5 minutes. This enabled curves to be obtained on the one specimen as if it had been subjected to three separate tests simultaneously—in which the stress was increased at 1-, 5-, and 10-minute intervals, respectively. It is, of course, possible that the curves obtained in this way for the 1- and 5-minute intervals are affected slightly by the strain-hardening due to the small amount of creep occurring during the 10-minute interval. A very interesting feature of the curves obtained was that the return lines, while curved, were parallel for the three rates of stressing. This appears to indicate that the curvature of the unloading line is not a time effect; in other words, is not a phenomenon connected with negative creep.

E. *Load–Extension Diagrams to Fracture.*

Most of these tests were made at a slow rate on the 5-ton range of the 20-ton Amsler machine. In a test on the Avery machine the gauge-length, 2 in., was marked on the specimen using small centre punch marks, and the machine was operated at its lowest speed. Dividers were set to 2·05 in., and when the gauge-length had extended to this amount the load was read off the beam and the time noted. The dividers were now set to 2·10 in., and the load corresponding to this gauge-length noted as before. This process was continued until just past the maximum load. It should be noted that the pulling of the specimen was continuous, not a series of steps, movement of the poise on the beam being stopped only for the short time necessary to read the load.

In the case of the tests on the Amsler machine, the gauge-length was measured by dividers at intervals of time, and the corresponding loads noted.

In each case the rate of testing (given in the tables) was calculated by dividing the final extension per in. of original gauge-length at fracture by the time taken for the test.

III. Results of the Tests.

The results of the tests are given in Tables I–XVII, and typical stress–strain curves obtained are illustrated in Figs. 1 and 2.

A. *Gold.*

(1) *Annealed (as received) material (Table I).*—None of the specimens gave a limit of proportionality, but from the figures given in Table I for strain at maximum stress applied in the test and for permanent strain it would appear that there was some variation in initial condition of the specimens, although they were received in a nominally fully-annealed condition.

(2) *Effect of overstrain on the annealed material (Table II).*—The overstrain in these tests was produced by pulling the specimens in the testing machine until the gauge-length had increased by the desired amount. The effect of 5 per cent. overstrain was to give the material a definite limit of proportionality of 1·3 ton/in.^{2} and a 0·01 per cent. proof stress of 3·6 tons/in.^{2}, the value of Young's modulus being $10{\cdot}3 \times 10^6$ lb./in.^{2}.

(3) *Effect of heat-treatment after* 5 *per cent. overstrain (Table II).*—The effect of heat-treatment following 5 per cent. overstrain is set out in Table II, from which it is seen that annealing at 200° and 300° C.

reduced the limit of proportionality and the proof stress but increased the modulus.

(4) *Effect of speed of testing on ultimate tensile strength and elongation of annealed specimens.*—The results of these tests are given in Table III, where it is seen that reducing the speed of testing causes a reduction in ultimate tensile strength.

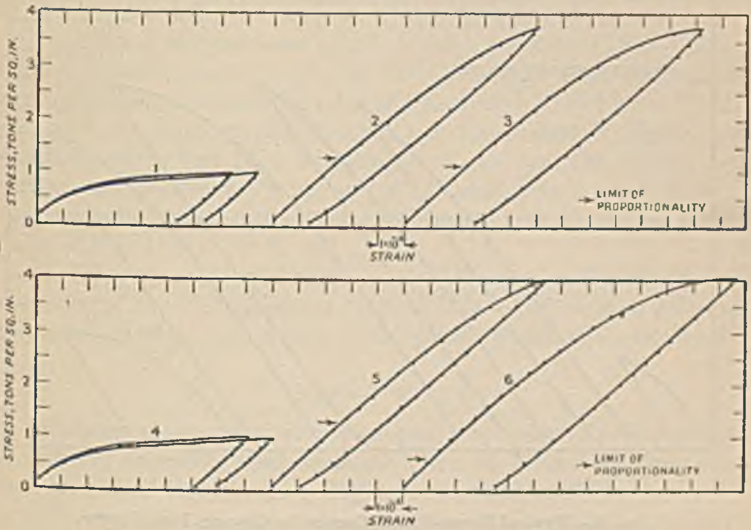

Fig. 1.—Typical Stress–Strain Curves for Silver and Gold.

Curve 1. Silver specimen No. 3, annealed (as received). Curves for 0·1 and 0·01 ton/in.^{2}/minute rates of stressing.

Curve 2. Silver specimen No. 3, annealed (as received) + 5 per cent. tensile overstrain.

Curve 3. Silver specimen No. 3, annealed (as received) + 5 per cent. tensile overstrain + ½ hr. at 350° C.

Curve 4. Gold specimen No. 4, annealed (as received). Curves for 0·1 and 0·01 ton/in.^{2}/minute rates of stressing.

Curve 5. Gold specimen No. 4, annealed (as received) + 5 per cent. tensile overstrain.

Curve 6. Gold specimen No. 5, annealed (as received) + 5 per cent. tensile overstrain + ½ hr. at 300° C.

(5) *Effect of overstrain and heat-treatment on the ultimate tensile strength and elongation* (*Table IV*).—The effect of 5 per cent. tensile overstrain was to increase the ultimate tensile strength slightly and to reduce the elongation slightly. The effect of 5 per cent. overstrain followed by treatment for ½ hr. at 200° C. was to give a further increase in the ultimate tensile strength, the effect on the elongation being very slight.

B. *Silver.*

(1) *Annealed (as received) material (Table V).*—Extensometer tests made on "as received" specimens showed some variation. Two of the specimens gave a possible small limit of proportionality, while the other four gave no proportionality of stress to strain. As in the case of the gold specimens, the greatest differences between the specimens were shown by the strain at 1 ton/in.^{2} and the permanent set. From the results of the tests it would appear that the final heat-treatment of 10 minutes at 500° C. given by the makers did not produce material in the fully-annealed condition, this treatment being insufficient completely to remove all effect of the slight overstrain, which may have occurred in machining. To investigate this matter further, specimen No. 2 was given two further treatments, first 1 hr. at 500° C., and

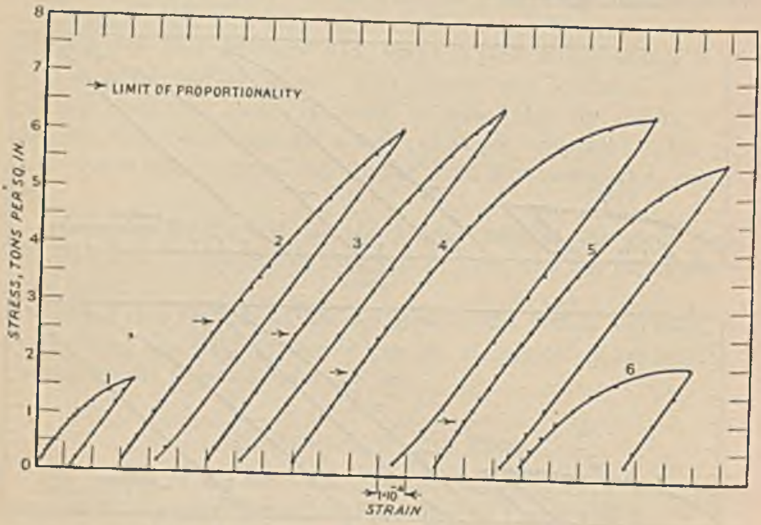

Fig. 2.—Typical Stress–Strain Curves for Oxygen-Free Copper.

Curve 1. Hard-rolled and annealed 1 hr. at 500° C. (Specimen No. 15.)
Curve 2. Hard-rolled, annealed 1 hr. at 500° C. + 5 per cent. tensile overstrain. (Specimen No. 1.)
Curve 3. Hard-rolled, annealed 1 hr. at 500° C. + 5 per cent. tensile overstrain + 1 hr. at 200° C. (Specimen No. 3.)
Curve 4. Hard-rolled, annealed 1 hr. at 500° C. + 5 per cent. tensile overstrain + 1 hr. at 400° C. (Specimen No. 5.)
Curve 5. Hard-rolled, annealed 1 hr. at 500° C. + 5 per cent. tensile overstrain + 1 hr. at 500° C. (Specimen No. 6.)
Curve 6. Hard-rolled, annealed 1 hr. at 500° C. + 15 per cent. tensile overstrain + 1 hr. at 500° C. (Specimen No. 13.)

secondly 1 hr. at 700° C. The first treatment failed to remove the small limit of proportionality induced by the overstrain produced in the initial testing, while the second treatment appeared to produce full annealing.

(2) *Effect of overstrain on the annealed (as received) material (Table VI).*—The effect of 5 per cent. overstrain was to give the material a limit of proportionality of the order of 1½ tons/in.², a 0·01 per cent. proof stress of 3½ tons/in.², and a Young's modulus of 10·1 × 10⁶ lb./in.².

(3) *Effect of heat-treatment after* 5 *per cent. overstrain (Table VII).*—After 5 per cent. overstrain ½ hr. at 200° C. had little effect on the limit of proportionality and left the value of E unaltered, while ½ hr. at 350° C. decreased the limit of proportionality and increased E slightly. A specimen which had been overstrained 5 per cent. in tension and subsequently heated for 1 hr. at 700° C. still gave a small limit of proportionality on the stress–strain diagram, with the much higher value of $E = 11{\cdot}3 \times 10^6$ lb./in.².

(4) *Effect of speed of testing on the ultimate tensile strength and elongation of annealed specimens (Table VIII).*—The effect of reducing the speed of testing was to reduce the ultimate tensile strength slightly.

C. *Oxygen-Free Copper.*

(1) *Effect of annealing the (as received) hard material.*—The results of different annealing treatments are given in Table IX. Annealing for 1 hr. at 500° C., although giving material which would be considered as fully annealed, did not completely remove all traces of elasticity, and it was possible to determine the value of Young's modulus after this treatment. Annealing the material for ½ hr. at 650° C. did not appear to produce any further annealing effect. The effect of a treatment of 1 hr. at 200° C. was to increase the limit of proportionality and the proof stress of the "as received" material. It may be noted that the effect of the higher temperatures of annealing was to produce a decrease in the value of the modulus.

(2) *Effect of overstrain on the annealed material.*—The annealed material was that which had received 1 hr. at 500° C., and the results of the overstrain tests are shown in Table X. The effect of 5 per cent. overstrain was to give the material a definite limit of proportionality of the order of 2·5 tons/in.² and a proof stress of the order of 5·5–6 tons/in.². An overstrain of 10 per cent. gave a slightly lower limit of proportionality but a high proof stress of the order of 8 tons/in.². An overstrain of 15 per cent. gave a limit of proportionality of 2 tons/in.² and a proof stress of about 8·4 tons/in.², a value higher than that of the original hard material. The effect of overstrain on Young's modulus

may be noted: the original material in the hard condition had a value of E of $18{\cdot}3 \times 10^6$ lb./in.^{2}, while for the annealed material, overstrained 5 per cent., E was $15{\cdot}7 \times 10^6$ lb./in.^{2}. Overstrain of 10 and 15 per cent. gave values of E of $16{\cdot}5 \times 10^6$ lb./in.^{2} and $17{\cdot}5 \times 10^6$ lb./in.^{2}, respectively. The value for the fully-annealed material could not be directly determined, but from the evidence given by specimens 15 and 16 in Table IX, it is of the order of $17{\cdot}5$ to 18×10^6 lb./in.^{2}. The results seem to point to the conclusion that a small amount of overstrain produces a considerable decrease in the value of Young's modulus, while a larger overstrain gives a value which is higher than that produced by the small overstrain but lower than that of the annealed material. This, it should be noted, is in complete agreement with the results of Kawai,[6] who showed that for copper with increasing amounts of cold-work produced by stretching, the value of E at first decreased, reached a minimum at approximately 5 per cent. elongation and then increased again.

(3) *Effect of heat-treatment after overstrain.*—The effect of heat-treatment after overstrain is shown in Table XI. The effect after 5 per cent. overstrain may be summarized as follows:

(a) *Limit of proportionality.*—Treatments for 1 hr. at various temperatures up to 500° C. produced at first a slight increase, followed by a gradual decrease of the limit with increasing temperature of treatment. Treatment for 1 hr. at 500° C. left a limit of about 1·0 ton/in.^{2}.

(b) *Proof stress.*—The changes in proof stress corresponded with the changes in the limit of proportionality.

(c) *Young's modulus.*—Treatments for 1 hr. at 100°, 200°, and 300° C. produced little effect on the modulus, but such effect as there was appeared to indicate a definite small increase; while treatments for 1 hr. at 400° and 500° C. produced a further and decided increase.

The effects of treatments for 1 hr. at various temperatures up to 500° C. after 15 per cent. overstrain was to decrease gradually the limit of proportionality, the last treatment removing all traces of proportionality of stress to strain. The value of Young's modulus was again increased by increasing temperature of treatment.

(4) *Load–extension diagrams to fracture.*—The results of the tests on the copper specimens are given in Table XIII, and typical curves of stress and extension are shown for this material (and also for the gold and silver) in Fig. 3. It should be noted that, in accordance with usual practice, in these curves the stress in each case is the load divided by the area of cross-section of the specimen at the commencement of the

test, in other words the "nominal stress." Attention may be directed to the tendency for slight increase of the ultimate tensile strength by low-temperature annealing after the 5 per cent. overstrain in the copper specimens.

The load-extension curves for the materials in the fully-annealed condition have been re-plotted as curves of true stress and strain, the cross-sectional area of the specimen at any extension being determined by assuming constant volume of the gauge-length portion of the specimen. Attempts have been made in the manner indicated by G. I. Taylor [9] to determine suitable parabolas to fit these curves, but no true fits were obtained. The equations of the parabolas which fitted the curves best in the region of 0·1–0·2 strain were as follows, S being the stress in tons per sq. in. and s the strain.

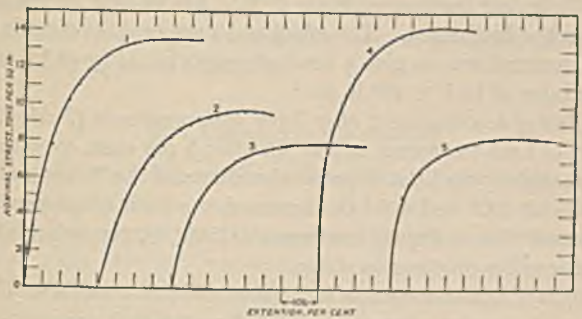

Fig. 3.—Typical Load–Extension Curves.

Curve 1. Oxygen-free copper specimen. Hard rolled and annealed ½ hr. at 650° C.
Curve 2. Silver specimen. Annealed (as received).
Curve 3. Gold specimen. Annealed (as received).
Curve 4. Oxygen-free copper specimen. Hard rolled, annealed ½ hr. at 650° C. + 5 per cent. tensile overstrain + 2 hrs. at 350° C.
Curve 5. Gold specimen. Annealed (as received) + 5 per cent. tensile overstrain + ½ hr. at 200° C.

Pure gold . .	$S = 19{\cdot}1 \sqrt{s}$
Pure silver . .	$S = 19{\cdot}4 \sqrt{s}$
Oxygen-free copper .	$S = 33{\cdot}6 \sqrt{s}$

D. *High-Purity Silver-Free Copper Containing* 0·016 *Per Cent. Oxygen.*

(1) *Effect of annealing the (as received) hard material (Table XIV).*—The effect of annealing the "as received" material at 500° or 600° C. was to remove completely all traces of proportionality of stress to strain. The effect of heat-treatment of the "as received" material

for 1 hr. at 200° C. was to reduce the limit of proportionality from about 2 to 1·27 tons/in.², the proof stress from 9 to 7 tons/in.², and to increase the modulus very slightly.

(2) *Effect of overstrain on annealed material* (*Table XV*).—The effect of 5 per cent. overstrain on the annealed material was to give it a limit of proportionality of 1 to 1·25 tons/in.² and a modulus of 16·6 × 10⁶ lb./in.², compared with 19·9 × 10⁶ lb./in.² in the original material in the hard state. The effect of 15 per cent. overstrain on the annealed material was to give a limit of proportionality of 1·4 tons/in.² and a modulus of 18·1 × 10⁶ lb./in.².

(3) *Effect of heat-treatment after 5 per cent. overstrain* (*Table XVI*).—The effect of heat-treatment at 200° C. after 5 per cent. overstrain was to increase slightly the limit of proportionality and the Young's modulus. Treatments at 300° and 400° C. decreased the limit of proportionality and increased the modulus, treatment at 500° C. removing all traces of proportionality of stress to strain.

(4) *Effect of heat-treatment on ultimate tensile strength* (*Table XVII*).—The effect of overstraining the annealed material 5 per cent. was to increase the ultimate tensile strength slightly, and annealing treatments up to 400° C. did not reduce the value appreciably. 1 hr. at 500° C., however, caused a considerable reduction in ultimate tensile strength. The effect of 15 per cent. overstrain on the annealed material was to increase the ultimate tensile strength from 15 to 17·25 tons/in.².

A large number of specimens broke at or close to the gauge-mark, and consequently it is not possible to reach very definite conclusions as to the effect of overstrain and heat-treatment on the elongation.

IV. COMPARISON OF THE OXYGEN-FREE AND OXYGEN-CONTAINING COPPERS.

A. *Elastic Properties.*

In the annealed condition (up to 650° C.) the oxygen-free copper tended to retain some small range of proportionality of stress to strain, whereas the oxygen-containing copper showed no such range.

The effect of 5 per cent. overstrain in the case of the oxygen-free copper was to give it a limit of proportionality of the order of 2·5 tons/in.², whereas in the case of the oxygen-containing copper the limit was only of the order of 1 ton/in.². On the other hand, the Young's modulus was higher in the case of the oxygen-containing copper than the oxygen-free copper after this amount of overstrain. After 15 per cent. overstrain, the oxygen-free copper had a limit of proportionality of 2 tons/in.² and a modulus of 17·65 × 10⁶ lb./in.², the corresponding figures for the oxygen-containing copper being 1·4 tons/in.^{2} and 18·1 × 10^6 lb./in.^{2}.

In both coppers heat-treatment following overstrain produced a lowering in the limit of proportionality and an increase in the Young's modulus. In the case of the oxygen-free copper, however, treatment for 1 hr. at 500° C. following 5 per cent. overstrain produced a limit of proportionality of the order of 1 ton/in.^{2}, whereas similar treatment in the case of the oxygen-containing copper removed all traces of proportionality of stress to strain.

B. *Ultimate Tensile Strength.*

In the fully-annealed condition the ultimate tensile strength of the oxygen-containing copper was more than 1 ton/in.^{2} higher than that of the oxygen-free copper, and throughout the various treatments this difference in the strength was approximately maintained. It may be noted that the reduction in area is greater for the oxygen-free than for the oxygen-containing copper.

The effect of oxygen in slightly increasing the ultimate tensile strength of copper is well known, but its effect on the elastic properties of the copper has not been very fully investigated. In the present work it is not clear, however, whether the superior elastic properties of the oxygen-free copper are due to the absence of oxygen alone or in part to the presence of the small amounts of other impurities, *e.g.* silver (0·003 per cent.).

V. THE EFFECT OF VERY SMALL AMOUNTS OF OVERSTRAIN.

The effect of a very small amount of overstrain on the stress–strain characteristics of the materials tested has been considered for the two cases:

(1) When the specimen is re-tested without any intermediate treatment.

(2) When the specimen is re-tested after treatment.

In the case of the oxygen-free copper the results of some tests are given in Table XII, and from these it will be seen that the application of a very small overstrain produced a considerable increase in the limit of proportionality. If such overstrain is now followed by a heat-treatment at 500° or 600° C., the limit of proportionality is reduced but is still higher than the original limit. The effect on the modulus is the reverse, the small overstrain producing a small, but apparently definite, decrease of the value of E, which is more or less completely restored by the subsequent heat-treatment.

A specimen of gold in the "as received" annealed condition which had been slightly overstrained to the extent of 0·147 per cent., and then heat-treated for 10 minutes at 500° C., had a limit of proportionality of 0·4 ton/in.^{2}, the value of E being $10{\cdot}7 \times 10^6$ lb./in.^{2}. A similar silver specimen which had been overstrained 0·0368 per cent. and heated for 1 hr. at 500° C. gave a limit of proportionality of 0·4 ton/in.^{2} and a Young's modulus (E) of $10{\cdot}7 \times 10^6$ lb./in.^{2}.

These results illustrate the importance of slight overstrains in their effect on the stress–strain characteristics and also the retention of some of the effects of the overstrain after treatment at comparatively high temperatures.

ACKNOWLEDGMENTS.

The authors desire to express their thanks to the Council of the British Non-Ferrous Metals Research Association for permission to publish this paper. In addition to the acknowledgments made in the text, the authors' best thanks are due to Dr. W. E. Alkins for his personal interest in the work and his assistance in the provision of the specially pure coppers tested.

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APPENDIX.

TABLE I.—*Gold.* *Properties of Annealed (As Received) Material (Extensometer Tests).*

Specimen No.	Rate of Stressing, Tons/in.^{2}/minute.	Limit of Proportionality, Tons/in.^{2}.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
1	0·6	nil	1·0	30·20	28·4
2	0·1	nil	0·8	22·40	20·80
6	0·1	nil	1·0	18·30	16·32
3	0·01	nil	0·8	16·30	14·70
4	0·01	nil	1·01	8·98	6·90
5	0·01	nil	1·0	26·14	24·10

TABLE II.—*Gold.* *Effect of Heat-Treatment after 5 per Cent. Overstrain (Extensometer Tests).*

Specimen No.	Heat-Treatment.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
4	...	1·30	3·60	10·3	4·03	10·36	1·12
6	½ hr. at 200° C.	0·75	2·65	10·7	3·365	9·02	1·40
5	½ hr. at 300° C.	0·60	2·85	11·3	4·045	12·60	3·40

TABLE III.—*Gold.* *Effect of Speed of Testing (Tests to Fracture).*

Specimen No.	Condition.	Rate of Pulling, In./in./minute.	Ultimate Tensile Strength, Tons/in.^{2}.	Elongation, on 2 in., Per Cent.	Reduction in Area, Per Cent.
1	Annealed as received	0·05	7·89	73	90
2	,, ,, ,,	0·05	7·88	72·5	90
3	,, ,, ,, + 10 minutes at 500° C.	0·009	7·56	68	92

TABLE IV.—*Gold.* *Effect of Overstrain and Heat-Treatment (Tests to Fracture) Rate of Pulling in all tests* 0·05 *in./in./minute.*

Specimen No.	Condition.	Ultimate Tensile Strength, Tons/in.^{2}.	Elongation, on 2 in., Per Cent.	Reduction in Area, Per Cent.
1	Annealed as received	7·89	73	90
4	,, ,, ,, + 5 per cent. tensile overstrain	7·97	65	87
6	,, ,, ,, + 5 per cent. tensile overstrain + ½ hr. at 200° C.	8·20	64·5	93·5

TABLE V.—*Silver. Properties of Annealed (As Received) Material (Extensometer Tests).*

Specimen No.	Condition.	Rate of Stressing, Ton/in.^{2}/minute.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
1	Annealed as received	0·1	0·3	0·7	10·3	1·0	14·16	12·06
5	,, ,, ,,	0·1	nil	...	...	1·0	11·50	9·40
6	,, ,, ,,	0·1	0·3	0·65	11·1	1·0	22·02	19·90
2	Annealed as received	0·01	nil	...	...	1·0	5·76	3·68
3	,, ,, ,,	0·01	nil	...	...	1·0	8·42	6·40
4	,, ,, ,,	0·01	nil	...	...	1·0	5·28	3·30
2	1 hour at 500° C.	0·01	0·4	0·9	10·7	1·0	3·70	1·70
2	1 hour at 700° C.	0·01	nil	...	...	1·0	23·38	21·40

TABLE VI.—*Silver. Effect of 5 per Cent. Overstrain on Annealed Material (Extensometer Tests).*

Specimen No.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
2	1·90	3·70	10·1	3·76	9·12	0·80
3	1·30	3·30	10·1	3·76	10·00	1·34

TABLE VII.—*Silver. Effect of Heat-Treatment after 5 per Cent. Overstrain (Extensometer Tests).*

Specimen No.	Heat-Treatment.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
2	½ hr. at 200° C.	1·80	3·5	10·1	3·34	7·70	0·48
2	½ hr. at 350° C.	1·20	3·15	10·3	3·76	11·24	2·62
5	1 hr. at 700° C.	0·30	0·5	11·3	0·63	6·12	5·02

TABLE VIII.—*Silver. Effect of Speed of Testing (Tests to Fracture).*

Specimen No.	Condition.	Rate of Pulling, In./in./minute.	Ultimate Tensile Strength, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction in Area, Per Cent.
1	Annealed as received	0·05	9·61	65	91·5
4	,, ,, ,,	0·01	9·19	60	90
6	,, ,, ,,	0·01	9·16	67·5	91

Table IX.—*Oxygen-Free Copper. Effect of Annealing (Extensometer Tests).*

Specimen No.	Condition.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
0	As received (hard) . . .	2·2	8·1	18·3	8·0	10·4	0·62
14	,, ,, + 1 hr. at 200° C.	3·4	9·0	18·7	9·2	11·78	0·55
0·2	,, ,, + 1 hr. at 500° C. A.C.	0·6	1·4	15·3	2·0	7·80	5·26
0·3	,, ,, + ½ hr. at 650° C. A.C.	0·6	1·3	15·7	2·0	7·40	5·00
7	,, ,, + 1 hr. at 500° C. F.C.	0·6	1·4	16·4	2·0	6·85	4·58
15	,, ,, + 1 hr. at 500° C. F.C.	0·36	1·5	17·3	1·6	3·36	1·20
16	,, ,, + ½ hr. at 650° C. F.C.	0·37	1·48	17·9	1·625	3·40	1·40

A.C. = Air-cooled. F.C. = Furnace cooled.

Table X.—*Oxygen-Free Copper. Effect of Overstrain on Material Annealed 1 Hr. at 500° C.F.C. (Extensometer Tests).*

Specimen No.	Amount of Overstrain, Per Cent.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
1	5	2·64	5·7	15·8	6·08	9·60	1·20
17	5	2·20	5·95	15·7	6·00	9·20	0·68
8	10	2·16	7·9	16·5	9·54	14·32	1·06
9	15	2·00	8·4	17·7	10·20	14·42	0·78

Table XI.—*Oxygen-Free Copper. Effect of Heat-Treatment after Overstrain (Extensometer Tests).*

Specimen No.	Amount of Overstrain, Per Cent.	Heat-Treatment.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
...	5		2·42	5·8	15·7	...	...	...
2	5	1 hr. at 100° C.	2·62	6·1	16·2	6·84	10·76	1·44
3	5	1 hr. at 200° C.	2·44	5·7	16·2	6·49	10·12	1·16
4	5	1 hr. at 300° C.	1·80	5·2	16·5	6·04	9·94	1·76
5	5	1 hr. at 400° C.	1·80	5·1	17·3	6·42	12·42	3·58
6	5	1 hr. at 500° C.	1·00	4·7	17·8	5·62	10·00	2·22
24	5	1 hr. at 500° C.	0·73	4·2	18·2	5·36	12·32	4·42
9	15		2·00	8·4	17·7	10·20	14·42	0·78
12	15	1 hr. at 200° C.	1·88	8·5	17·7	9·36	13·04	0·64
18	15	1 hr. at 300° C.	1·55	7·2	17·9	8·82	12·32	0·56
19	15	1 hr. at 400° C.	0·88	6·2	18·5	8·76	12·46	0·70
13	15	1 hr. at 500° C.	nil	...	...	1·975	5·88	3·60

TABLE XII.—*Oxygen-Free Copper. Effect of Very Small Amounts of Overstrain (Extensometer Tests).*

Specimen No.	Overstrain, Per Cent.	Treatment after Overstrain.	Limit of Proportionality, Tons/in.^{2}.	Young's Modulus. Lb./in.^{2} $\div 10^6$.	Permanent Set, Per Cent.
20	nil	nil	0·37	18·4	0·033
	0·033	nil	1·24	17·7	0·0358
	0·0358	1 hr. at 500° C.	0·62	18·3	0·0412
	0·0358 + 0·0412	nil	1·03	17·3	0·0452
	0·0358 + 0·0452	1 hr. at 600° C.	0·54	18·1	0·0420
	0·0358 + 0·0452 + 0·0420	nil	0·86	17·6	0·0468

TABLE XIII.—*Oxygen-Free Copper. Effect of Overstrain and Heat-Treatment (Tests to Fracture).*

(Rate of Pulling in all Tests 0·05 in./in./minute.)

Specimen No.	Condition.	Ultimate Tensile Strength, Tons/in.^{2}.	Elongation, on 2 in., Per Cent.	Reduction in Area, Per Cent.
...	As received	18·5	29	85·5
14	1 hr. at 200° C. F.C.	18·2	28·5	86
7	1 hr. at 500° C. F.C.	13·65	58	86
15	1 hr. at 500° C. F.C.	13·73	62	90
10	½ hr. at 650° C. F.C.	13·68	62	88·5
16	¼ hr. at 650° C. F.C.	13·76	63	90
1	1 hr. at 500° C. F.C. + 5 per cent. overstrain	14·15	58	87
17	1 hr. at 500° C. F.C. + 5 per cent. overstrain	13·82	58·5	88
2	1 hr. at 500° C. F.C. + 5 per cent. overstrain + 1 hr. at 100° C.	14·47	58·5	88
3	1 hr. at 500° C. F.C. + 5 per cent. overstrain + 1 hr. at 200° C.	14·55	60	86·5
4	1 hr. at 500° C. F.C. + 5 per cent. overstrain + 1 hr. at 300° C.	14·40	59	85·5
5	1 hr. at 500° C. F.C. + 5 per cent. overstrain + 1 hr. at 400° C.	14·25	60·5	87·5
6	1 hr. at 500° C. F.C. + 5 per cent. overstrain + 1 hr. at 500° C.	14·48	63	87
22	1 hr. at 500° C. F.C. + 5 per cent. overstrain + 1 hr. at 500° C.	14·3	61	89
8	1 hr. at 500° C. F.C. + 10 per cent. overstrain	14·75	54	86
9	1 hr. at 500° C. F.C. + 15 per cent. overstrain	15·43	46	85·5
12	1 hr. at 500° C. F.C. + 15 per cent. overstrain + 1 hr. at 200° C.	15·72	49	88
18	1 hr. at 500° C. F.C. + 15 per cent. overstrain + 1 hr. at 300° C.	15·18	*	87·5
19	1 hr. at 500° C. F.C. + 15 per cent. overstrain + 1 hr. at 400° C.	14·80	48·5	88
13	1 hr. at 500° C. F.C. + 15 per cent. overstrain + 1 hr. at 500° C.	13·70	66·5	91

* Broke at gauge-mark.

TABLE XIV.—*Oxygen-Containing Copper of Very High Purity. Effect of Annealing (Extensometer Tests).*

Specimen No.	Condition.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
1	As received	1·97	9·2	19·9	12·5	15·84	0·96
10	,, ,, + 1 hr. at 200° C. .	1·27	6·9	20·4	9·07	10·92	0·41
2	,, ,, + 1 hr. at 500° C. F.C.	nil	...	...	2·68	8·48	5·08
8	,, ,, ,, ,, ,, ,, ,,	nil	...	...	1·21	4·00	2·70
3	,, ,, + 1 hr. at 600° C. F.C.	nil	...	...	2·98	5·17	1·50

TABLE XV.—*Oxygen-Containing Copper. Effect of Overstrain on Annealed Material (Extensometer Tests).*

Specimen No.	Annealing Treatment.	Amount of Overstrain, Per Cent.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
7	1 hr. at 600° C. F.C.	5	1·0	...	16·6	2·46	3·30	0·18
9	,, ,, ,, ,,	5	1·04	4·65	17·0	6·35	10·52	1·60
11	1 hr. at 500° C. .	5	1·27	6·3	16·7	7·25	12·04	1·84
13	1 hr. at 500° C. .	15	1·40	6·6	18·1	8·97	12·92	0·91

TABLE XVI.—*Oxygen-Containing Copper. Effect of Heat-Treatment after 5 per Cent. Overstrain (Extensometer Tests).*

Specimen No.	Annealing Treatment.	Heat-Treatment.	Limit of Proportionality, Tons/in.^{2}.	0·01% Proof Stress, Tons/in.^{2}.	Young's Modulus, Lb./in.^{2} ÷ 10^6.	Maximum Stress Applied, Tons/in.^{2}.	Strain × 10^4 at Maximum Stress.	Permanent Strain, × 10^4.
9	1 hr. at 600° C. F.C.		1·04	4·65	17·0	6·35	10·52	1·60
4	,, ,, ,, ,,	1 hr. at 200° C.	1·25	4·46	17·6	6·0	9·46	1·20
5	,, ,, ,, ,,	1 hr. at 300° C.	0·90	4·25	18·6	6·28	10·52	1·90
6	,, ,, ,, ,,	1 hr. at 400° C.	0·36	1·61	18·4	2·15	4·96	2·30
7	,, ,, ,, ,,	1 hr. at 500° C.	nil	....	....	2·46	3·30	0·18
12	,, ,, 500° C. .	1 hr. at 300° C.	0·91	4·50	17·8	6·38	10·70	1·92

TABLE XVII.—*Oxygen-Containing Copper.* (*Tests to Fracture.*)

(Rate of Pulling in all Tests 0·05 in./in./minute.)

Specimen No.	Condition.	Ultimate Tensile Strength, Ton/in.^{2}.	Elongation, on 2 in., Per Cent.	Reduction in Area, Per Cent.
1	As received (hard)	23·8	*	58·5
10	" " " + 1 hr. at 200° C.	23·6	9†	64·7
2	" " " + 1 hr. at 500° C. F.C.	15·0	50·5	83·6
8	" " " " " " "	15·0	43†	80·5
3	" " " " 600° C. "	15·05	42·5	83·3
9	As received + 1 hr. at 600° C. F.C. + 5 per cent. overstrain	15·55	38†	77
4	As received + 1 hr. at 600° C. F.C. + 5 per cent. overstrain + 1 hr. at 200° C.	15·6	40·5	82·7
5	As received + 1 hr. at 600° C. F.C. + 5 per cent. overstrain + 1 hr. at 300° C.	15·5	41·0	79·8
6	As received + 1 hr. at 600° C. F.C. + 5 per cent. overstrain + 1 hr. at 400° C.	15·4	36·0	79·8
7	As received + 1 hr. at 600° C. F.C. + 5 per cent. overstrain + 1 hr. at 500° C.	13·8	43·5	79·2
11	As received + 1 hr. at 500° C. F.C. + 5 per cent. overstrain	15·75	*	77
12	As received + 1 hr. at 500° C. F.C. + 5 per cent. overstrain + 1 hr. at 300° C.	15·8	*	80
13	As received + 1 hr. at 500° C. F.C. + 15 per cent. overstrain	17·25	22	74·5

* Fractured at gauge-mark. † Fractured close to gauge-mark.
F.C.—Furnace cooled.

DISCUSSION.

MR. J. C. CHASTON,* B.Sc., A.R.S.M. (Member): Table IV records the interesting result that, after tensile overstrain and re-annealing, the tensile strength of the gold annealed "as received" increased from 7·89 to 8·2 tons/in.^{2}. Have any observations been made on grain-size and was it different after the second anneal? Such observations as these become of much greater interest if mechanical results can be correlated with microscopic structure.

DR. HUDSON (*in reply*): With regard to the precise definition of sensitivity of measurements of properties such as the limit of proportionality, it should be realized that the limit of proportionality in non-ferrous metals is, after all, an arbitrary value and must be defined very closely in the way suggested in this paper.

In reply to Mr. Chaston, I would say that the specimens of gold and silver, which were sent to us already machined, were lent for the purpose of tensile testing, and we did not feel at liberty to cut them up and make an extensive general examination. We agree, however, that the correlation of mechanical test results with structure is an extension of the work which should be undertaken.

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CORRESPONDENCE.

Dr. E. W. Fell,* M.Sc. (Member): I wish that the authors had given more information about the specimens they describe.

I desire to discuss the question of the interpretation of stress–strain characteristics, that is, why the curves have the shape they do. In general, a stress–strain curve may be compared to a function of several independent variables, thus:

x_1, the chemical analysis of the specimen;
x_2, the metallographic structure of the specimen;
x_3, the temperature of the specimen;
x_4, &c., stress conditions, in which, for brevity, the rate of stress application may be included.

Whereas chemical analysis and rate of stress application have been carefully determined and recorded in the paper, as is very desirable, there is no reference to the dimensions of the individual crystals of which the specimens are comprised (x_2). This is unfortunate, as I believe that the study of stress–strain characteristics would be much assisted if such data were given in papers of this kind. The characteristics for the same metal may differ owing to variation of crystal size alone. This may have a remarkable influence in the case of zinc and iron. Zinc is an extreme example, however, as the stress–strain curve for the single crystal may lie very near the strain axis, whilst that for the annealed polycrystalline metal lies near the stress axis. Thus, for zinc and other metals, it should be possible to construct a family of curves, each curve being defined by a corresponding crystal size, other conditions being equal.

Another illustration is the well-known and general relation, resembling a parabolic one, between grain-size (in crystals per mm.^{2}) and hardness, which in the case of electrolytic copper subsequently cast, rolled, and annealed, is shown by Angus and Summers.† Thus, if the hardness varies, as measured by ball-penetration methods, it may be concluded that the stress–strain characteristics will vary also.

The working and heat-treatments used by the authors may have influenced the crystalline structure, and the crystal size of the original material used may modify the effects of the subsequent working and heat-treatments to some extent.

On p. 116, the authors refer to some variation in initial condition of the gold specimens, although they were received in a nominally fully-annealed condition. To what is this to be attributed?

For the oxygen-free copper, the curves 1, 5, and 6 of Fig. 2 differ remarkably, and the annealing temperature and time seem considerable. What is the cause of this? It seems that the material may be also largely recrystallized and annealed.

I wished to compare curve 1 of Fig. 3 with Taylor's curve for polycrystalline copper referred to subsequently. Can data be given for crystal size in the specimens? In view of the fundamental nature of the curves in Fig. 3, it seems desirable and necessary to give the actual stress and strain figures from which they are derived, for avoidable error may result if an attempt were made to obtain the figures direct from the curves, due partly no doubt to reduction in reproduction. Several of the dots on the curves, which represent actual observations, are rather indistinct.

Reference is made on p. 121 to work of Taylor in finding parabolas to fit

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* Lecturer in Metallurgy, Manchester University.

† *J. Inst. Metals*, 1925, **33**, Fig. 7 on p. 124.

similar curves. On p. 389 of his paper, a stress–strain curve of "polycrystalline copper" is given and a parabola fits it very well in the lower part of the curve. Unfortunately, no other details of the copper are given. Variations introduced by omission of these details may be considerable and may affect the choice of his parabola.

Regarding the authors' equations of the parabolas given on p. 121, the coefficient in front of the square root sign may, for any one of the metals in the pure and annealed state, be regarded to some extent as dependent on crystal size, that is, as a variable parameter for an associated group of stress–strain curves, provided that the equation does not alter otherwise. This is quite general as a similar comment would apply to temperature (x_3), for example, if it alone were allowed to vary instead of crystal size.

I do not wish to give undue prominence to the effect of crystal dimensions in the interpretation of stress–strain characteristics, because I feel that other considerations such as the nature of the metal itself will be of more significance ultimately.

The AUTHORS (*in reply*): The work has shown that the presence of very small amounts of cold-working can be detected by examination of the stress–strain relationship for the material. In the preliminary preparation of the gold specimens, as described on p. 112, it is probable that some slight working produced in the machining operations was not completely removed during the final anneal of 10 minutes at 500° C. The probability of this is indicated by the test recorded on p. 124, where a specimen of gold overstrained by only 0·147 per cent. was found to have a limit of proportionality of 0·4 ton in.^{2} after a treatment of 10 minutes at 500° C.

The difference between the curves 1, 5, and 6 of Fig. 2 for oxygen-free copper may be explained in a similar manner. The effect of annealing is more pronounced after a large amount of cold-work than after a small amount. Curve No. 5 of Fig. 2 suggests that annealing for 1 hr. at 500° C. after only 5 per cent. overstrain is insufficient to give fully-annealed material.

It is not possible, nor in fact desirable, in a paper of this description to give all the details of data from which the results are obtained. In order to meet Dr. Fell's wish for the actual stress and strain figures used in plotting the curves in Fig. 3 the authors have forwarded to the Institute tables giving these figures.*

Although no detailed metallographic examination has been carried out and no grain-size determination made, some idea of the structure of the materials examined is given by the photographs shown in Figs. A–E (Plates XVI–XVII).

* These tables will be preserved in the Institute's archives and may be consulted on application to the Librarian.

A. Oxygen-Free Copper Cold-Rolled + 1 Hr. at 500° C. × 100.
B. Oxygen-Free Copper Cold-Rolled + 1 Hr. at 500° C. + 5% Over-Strain + 2 Hrs. at 350° C. × 100.
C. Oxygen-Free Copper Cold-Rolled + 1 Hr. at 500° C. + 5% Over-Strain + 1 Hr. at 500° C. × 100.

[*To face p.* 132.

PLATE XVII.

D

D. Fine Gold. Annealed (As Received). × 100.

E.

E. Fine Silver. Annealed (As Received). × 100.

768

THE EFFECT OF MANGANESE ON THE "ANNEALING BRITTLENESS" OF CUPRO-NICKEL.*

By B. K. BOSE,† M.Sc., D.I.C.

SYNOPSIS.

An investigation has been made of the effect of manganese on the brittleness which may appear in the cupro-nickel alloy (copper 75 : nickel 25 per cent.) when annealed at temperatures exceeding 700° C. Previous observations that this brittleness, in the absence of manganese, is caused by the precipitation of graphitic carbon at the grain boundaries have been confirmed.

The elimination of this tendency to brittleness by the addition of manganese has been investigated by measurements of its effect on the physical properties as determined by elongation, tensile strength, and impact tests. These tests have been supplemented by chemical analyses and by an examination of the microstructure.

INTRODUCTION.

THE phenomenon of "annealing brittleness" in certain nickel-copper alloys has long been observed, and attempts have been made from time to time to explain it and to discover the best remedy. It is now accepted that the cause of this peculiar behaviour lies in the fact that nickel absorbs a considerable amount of carbon, which under certain conditions separates out in such a manner as to cause brittleness. F. C. Thompson and W. R. Barclay [1] were probably the first to offer an explanation of this phenomenon, from a study of the microstructure and from the analysis which indicates the presence of free carbon in the alloy after annealing. They showed that this brittleness was due to precipitation of free carbon at the grain boundaries, forming an intercrystalline network, which took place on annealing within a certain range of temperatures. A total carbon content of less than 0·04 per cent. was found to be rarely harmful. The exact conditions for this absorption and precipitation of carbon will not be clearly understood, however, until the equilibrium diagram of the nickel-copper-carbon system has been established. T. Mishima [2] claimed to have established this diagram, but, apart from this statement, unfortunately no further information about his work is available in the English language. This brittleness appears in the cupro-nickel alloys only when they are annealed at a

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* Manuscript received November 25, 1936.

† The Mint, Bombay.

temperature above 700° C., and reaches a maximum at about 800° C., provided, of course, that there is present in the alloy a certain minimum percentage of total carbon.

PRELIMINARY INVESTIGATIONS.

Several instances of such "annealing brittleness" in the case of 75 : 25 cupro–nickel coinage alloy came to the author's notice. In all these cases the cast bars rolled well, but the blanks developed extreme brittleness after annealing. It was found on analysis that all the brittle blanks contained large amounts of graphitic carbon, although none or little was present before annealing. Other blanks which were annealed at the same time, but which were not brittle, were found to be free from graphite. The brittleness was thus assumed to be due to the presence of free graphitic carbon in the metal. It should be noted that although the annealing temperature for cupro–nickel blanks is normally kept below 700° C., in the several instances under review it was certainly increased accidentally to much above 700° C. The good blanks were re-annealed at 800° C., but still showed no evidence of brittleness, and no separation of free graphite. The total carbon content of these blanks was 0·052 per cent. and, therefore, that amount of carbon must be within the safe limit.

The brittle blanks were re-melted with twice the usual amount of cupro–manganese, which is always added as a deoxidizer in an amount corresponding to about 0·1 per cent. manganese. Annealed blanks from this re-melt showed a distinct improvement as regards brittleness, although they were still not satisfactory. The total and the free carbon in these were less than before, as will be seen from Table I. It was thought at the time that the extra amount of manganese added might have helped to eliminate some of the harmful carbon and thus improved the metal, and it was argued that a sufficient amount of manganese might eliminate all the carbon. Although subsequent investigation belied this assumption, as will be seen later, it led to some interesting observations. Fig. 1 (Plate XVIII) shows the microstructure of a brittle blank without etching.

TABLE I.

Description.	Total Carbon, Per Cent.	Graphitic Carbon, Per Cent.
Good blank	0·052	nil
Brittle blank	0·104	0·084
Remelted brittle blanks (annealed) . . .	0·079	0·038

PRESENT INVESTIGATION.

The present investigation was undertaken to discover whether manganese has any influence on the absorption of carbon by cupro–

nickel alloy and on the subsequent deterioration of the alloy on annealing at a moderately high temperature. The investigation was confined to the 75 : 25 copper-nickel alloy. The scheme of the work consisted in preparing a number of alloys of copper and nickel in the exact proportion of 75 : 25 containing about 0·1 per cent. carbon and varying amounts of manganese from 0 to 1 per cent. Some specimens containing 5 per cent. manganese were also prepared. The alloys so prepared were annealed at 800° C., the temperature at which the maximum brittleness takes place, and the carbon contents and the physical properties of the alloys before and after annealing were then determined and compared.

The influence of manganese on the absorption of carbon and on the precipitation of free graphite on annealing was found by estimating the amounts of the total carbon and of the free graphitic carbon before and after annealing for each of the alloys.

As regards the degree of deterioration or brittleness suffered by the specimen after annealing, some difficulty arose about the best method of comparison. Thompson and Barclay[1] took the number of bends endured by a strip as the measure of its brittleness. Although that method was perfectly satisfactory in giving comparative results when performed under strictly identical conditions, it has the disadvantage that it is not a standardized method. The Brinell hardness number was found to give no indication of the degree of brittleness. The Izod impact test, which is in fact a measure of toughness, may, under certain conditions, be also a measure of brittleness, but it gives misleading results under others. Thus, although a work-hardened material does not become more brittle on annealing, it may sometimes show a lower Izod impact value. The percentage elongation in the tensile strength test was considered to be the best available measure for the kind of brittleness under investigation. A further advantage of the test was that the tensile strength was also obtained at the same time, thus giving further important data for comparison. Izod impact tests were carried out, however, in the case of a number of specimens, and gave valuable results.

Finally, the structure of the alloys was examined microscopically in an endeavour to correlate their physical properties with the structural constituents, and if possible to find a plausible explanation for the results of the observations.

Experiments and Their Results.

The purest materials obtainable in large quantities were used in making up the alloys. Pure electrolytic copper and small pellets of

Mond nickel (0·04 per cent. carbon) were used; the manganese was 98 per cent. pure, the rest being mostly iron. The small amount of iron thus introduced with the manganese was not likely to have any appreciable effect on the properties of the alloy. Carbon was introduced in the form of finely powdered graphite. A sufficient amount of carbon —about 0·1 per cent.—which would ordinarily cause the alloy to become brittle on annealing was introduced in the alloys. Difficulties were at first encountered in always introducing the desired amount of carbon simply by melting the metals mixed up with graphite powder. It was found necessary to prepare an alloy of nickel and carbon and to use this carboniferous alloy in making up the cupro–nickel alloy in requisite amounts. This nickel–carbon alloy was prepared by melting nickel pellets mixed with a large excess of graphite powder in a high-frequency induction furnace. The alloy thus prepared contained about 2 per cent. carbon.

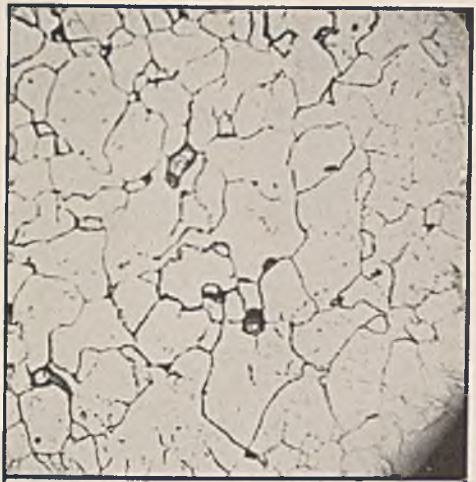
Attempts were made at first to melt the cupro–nickel alloys in the high-frequency induction furnace, but these were unsuccessful. The failure was due to the large differences in the electrical resistivity of the different materials in the charge, and it was found that one spot might be intensely hot while some metal remained unmelted at another. It was also found difficult to control the temperature of the melt and the pouring temperature, thus giving unsound castings. A gas-fired furnace with an air blower was also tried, but was subsequently abandoned in favour of the ordinary coke-fired wind furnace. By using good-quality coke there is less danger of contamination with undesirable furnace gases in a coke furnace than in a gas-fired furnace. The coke-fired furnace, when once properly heated, gave a more evenly distributed heat and was more reliable, amply compensating for the extra care in manipulation.

Deep piping running through a great length of the castings was at first a great source of trouble, but it was overcome by very careful regulation in the rate of pouring, a too rapid rate giving the maximum piping and a too slow one giving a discontinuity in the metal. The alloys were melted in Salamander crucibles, well covered with charcoal, and were poured through a jet of flame in order to prevent oxidation while pouring. Manganese was added, shortly before pouring, in the form of a coarse powder wrapped in copper foil; the molten alloy was thoroughly stirred with a graphite rod. The alloys were chill-cast in an iron mould dressed with graphite powder and heated to about 200° C. before pouring. The pouring temperature was kept at about 1250° C. The castings were in the form of cylindrical bars 16 in. long and of about 1¼ in. diameter

Each cast bar was cut into two, one half was kept in the "as cast"

PLATE XVIII.

1



2

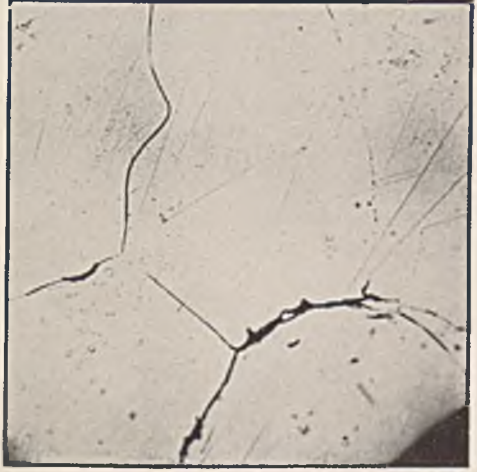


FIG. 1.—Brittle 75:25 Copper-Nickel. Unetched. × 500

FIG. 2.—Sample No. 1A. Unetched. × 1000

To face p. 136.

condition, and the other was annealed. In order to obtain strictly comparable results, test-pieces were made from the same bar for "before annealing" and "after annealing" tests. The annealing was at first carried out in an electric tube furnace in an atmosphere of nitrogen, to avoid any oxidation. Nitrogen from a cylinder, which often contains traces of oxygen, was purified by passing over a heated coil of copper and was then passed through the annealing furnace. It was feared that on annealing under charcoal the bars would absorb carbon and thus vitiate the results, but on careful analysis no such absorption of carbon was detected, at least not beyond the outer skin, which was always removed before taking a sample for analysis. The bars were, therefore, later annealed in an ordinary furnace after being tightly packed in powdered charcoal. The annealing temperature was maintained at 800° C. for 2½ hrs. and the bars were allowed to cool slowly with the furnace.

British standard tensile test-pieces of 2 in. gauge-length were prepared from the annealed and unannealed portions of the bars. The ease or difficulty with which the specimens were machined was exactly in accordance with their degree of brittleness as subsequently revealed—those which were later found to be brittle required an extra amount of care in machining, especially at the finishing stages. The turnings from the brittle bars crumbled up into small pieces, whereas those from the good ones were in the form of spirals several inches long.

The ultimate tensile strength and elongation are given in Table II.

TABLE II.

Specimen No.	Manganese, Per Cent.	Elongation on 2 in., Per Cent.		Loss in Elongation on Annealing, Per Cent.	Ultimate Tensile Strength, Tons/in.^{2}.		Loss in Ultimate Tensile Strength on Annealing, Per Cent.	Izod Value, Ft.-lb.		Brinell Number (2 mm. Ball, 30 kg. Load).
		As Cast.	Annealed.		As Cast.	Annealed.		As Cast.	Annealed.	
1	nil	21·5			19·32			24		106
1A	,,		8·5	13·0		11·36	7·96		5	88
2	0·1	30·5			19·84			24		100
2A	,,		17·5	13·0		14·52	5·32		14·5	94
3	0·25	30·5			19·80					100
3A	,,		13·5	17·0		13·60	6·20			97
4	0·5	29·5			18·56					104
4A	,,		26·5	3·0		16·44	2·12			101
5	1·0	30·5			16·84			34		100
5A	,,		30·0	0·5		16·76	0·08		53	96
6	5·0							38		104
6A	,,								42	97

Several round standard test-pieces (0·45 in. diam.) for notched-bar Izod impact test were also prepared. The results of the Izod tests are given in the same table. Brinell hardness numbers, using a 2 mm. ball and 30 kg. load in a Firth's Hardometer, are also included.

Samples for analysis were taken from the turnings from the specimen and were thoroughly washed with ether to remove any trace of oil, &c. The total carbon content was estimated by combustion in a stream of oxygen. Asbestos impregnated with ferric oxide was introduced into the combustion tube next to the boat to ensure complete oxidation of any carbon monoxide formed. For the determination of free graphitic carbon, weighed quantities of samples were dissolved in warm dilute nitric acid (1 : 4). The separated carbon was filtered and washed through asbestos in a platinum filtering boat, dried at 110° C. and the carbon estimated by combustion. The carbon contents found by analysis are shown in Table III.

TABLE III.

Specimen No.	Manganese, Per Cent.	Total Carbon, Per Cent.	Graphitic Carbon, Per Cent.		Combined Carbon, Per Cent. (By Difference).
			As Cast.	Annealed.	
1	nil	0·108	0·004		
1A	,,	,,		0·044	0·064
2	0·1	0·109	trace		
2A	,,	,,		0·054	0·055
3	0·25	0·081	trace		
3A	,,	,,		0·060	0·021
4	0·5	0·139	trace		
4A	,,	,,		0·087	0·052
5	1·0	0·111	nil		
5A	,,	,,		0·079	0·032
6	5·0	0·121	0·007		
6A	,,	,,		0·052	0·069

Discussion of Results.

From Table II it will be seen that the addition of manganese to the extent of 1 per cent. had no marked effect on the physical properties of the alloy in the " as cast " condition, except that there was an improvement in the elongation on the first addition of 0·1 per cent. manganese. This was most probably due to the deoxidizing effect of manganese. The remarkable effect of the addition of manganese is at once apparent, however, when the physical properties of the annealed specimens are considered. Specimen 1A containing no manganese became extremely brittle on annealing, the percentage of elongation being only 8·5, the actual loss in ductility as compared with that in the unannealed condition being 13·0 per cent. There was no great improvement in the metal until about 0·5 per cent. of manganese had been added. Beyond that there was a rapid increase in ductility, the maximum improvement being reached with a manganese content of 1 per cent. at which stage the percentage of elongation after annealing is practically the same as that before annealing. The beneficial effect of manganese on the alloy in the annealed state is also reflected in the ultimate tensile strength which increases with increasing content of manganese. The effect is more pronounced in the loss in strength caused by annealing, the loss being practically nil with 1·0 per cent. manganese. In the case of impact tests also there was a very marked improvement on the addition of manganese. One rather interesting observation was that with 1 per cent. manganese the toughness of the alloy was actually increased on annealing, the Izod value being increased from 34 to 53 ft.-lb. There was also a similar increase in Izod value with 5 per cent. manganese, but to a smaller extent. The Brinell hardness numbers show a remarkable uniformity and are not much affected by annealing or addition of manganese.

Table III shows that the total amount of carbon taken up by the alloy bears no relation to the amount of manganese added; thus, contrary to the original assumption that it inhibits the absorption of carbon, it was found that manganese had no effect on the total amount of carbon present in the alloy. In spite, however, of the fact that all the alloys were melted under precisely the same conditions, excepting that different amounts of manganese were added, carbon was taken up by the alloys in variable quantities, the reason for which could not be ascertained. In each case, however, the amount of carbon was well above that which would, in ordinary circumstances, cause brittleness on annealing.

The specimens before annealing contained either little or no free graphitic carbon, but after annealing all the specimens contained varying amounts of free carbon. Here again, no relation could be established between the amount of manganese added and the amount or proportion of free carbon separated on annealing. Thus, there was the difficulty that although by the addition of manganese in a sufficient amount there was a remarkable decrease in the harmful effect produced by the carbon precipitated on annealing the copper–nickel alloy, there was no change in the amounts of either the total carbon absorbed or the free carbon precipitated on annealing.

Microstructure.

The explanation, therefore, must lie in the way in which this separation of carbon takes place in the alloy on annealing. A microscopic study was made to elucidate this point. Samples were examined in the polished condition without etching, to endeavour to get evidence of the mode of separation of carbon. Great care had to be taken in preparing and polishing the specimens for microscopical examination, owing not only to the softness of the alloy but also to the smallness of the amount of carbon looked for; both factors increased the danger of the metal flowing over and effectively masking the minute particles or plates of graphite, if any. The unannealed specimen showed no structure on the polished surface, but on etching showed the usual cored structure. Fig. 2 (Plate XVIII) shows the microstructure of the annealed specimen containing no manganese (No. 1A unetched) and is similar to that obtained by Thompson and Barclay[1] with brittle strips. The grains are very large owing to the prolonged annealing at a high temperature. The dark lines round the polygonal grains show the separation of graphite at the crystal boundaries. Specimen 2A also showed a similar structure. Specimen 5A, however, failed to show any structure whatsoever on the polished surface. No microscopical evidence could be obtained of the presence of free graphite either at the grain boundaries or elsewhere, even after repeated and careful polishing and under a 2 mm. oil-immersion lens. The absence of graphite at the grain boundaries explained the freedom from brittleness of the metal, but the presence of a large amount of free carbon in the metal, as revealed by analysis, still remained unsolved. Thompson and Barclay found that a brittle strip regained its ductility if reheated to about 1000° C., and in an excellent photomicrograph they showed that this regeneration was due to the carbon which was previously round the grains being now present in isolated patches. No such patches of carbon could be detected in the present case.

SUMMARY AND CONCLUSIONS.

(1) It has been confirmed that the "annealing brittleness" of 75 : 25 cupro–nickel is due to the precipitation of free graphite at the grain boundaries.

(2) About 1 per cent. manganese cures this "annealing brittleness" in 75 : 25 copper–nickel alloys containing about 0·1 per cent. of carbon.

(3) Manganese, up to 1 per cent., has little effect on the amount of carbon absorbed by the alloy or on the amount of graphite subsequently precipitated on annealing.

ACKNOWLEDGMENTS.

The author wishes to acknowledge his indebtedness to Mr. G. C. Mitter, M.Sc., F.I.C., on whose suggestion the work was first commenced and to Dr. M. S. Fisher for his valuable advice.

REFERENCES.

[1] F. C. Thompson and W. R. Barclay, *J. Soc. Chem. Ind.*, 1919, 38, 130T.
[2] T. Mishima, *World Eng. Congress, Tokyo, 1929, Proc.*, 1931, 36, (4), 215.

CORRESPONDENCE.

MR. GEO. F. COMSTOCK,* A.B., Met.E. (Member): Although the author has confined his paper to the effect of manganese on cupro-nickel, he may be interested in another method of overcoming the trouble which he describes as due to the formation of graphitic carbon. This other method involves the addition of titanium, either as low-carbon ferro-titanium, or if iron is not permissible, as nickel-titanium or cupro-titanium. Titanium is not only a deoxidizer, but has a strong affinity for carbon, and is used effectively for eliminating the influence of carbon on stainless and chromium steels. Titanium carbide is very stable and does not break down nor dissolve in steel or nickel alloys at ordinary heat-treating temperatures. It requires four times as much titanium as carbon to form the compound, and if titanium is added in an amount equal to about six times the carbon content of the melt, and not lost by oxidation, practically all the carbon is held in combination with titanium and neither free carbon nor other carbides can be formed in the alloy.

This effect of titanium on Monel metal and cupro-nickel is described by J. A. Duma † who reported not only the absence of graphite in titanium-treated nickel alloys, but also an improvement in strength and machinability compared to the alloys without titanium. Titanium, therefore, may be used to eliminate free carbon from nickel alloys, instead of merely causing a better distribution of the graphite as is shown by the author to be the effect of manganese.

The AUTHOR (*in reply*): I thank Mr. Comstock for the information regarding the effect of titanium on the elimination of the influence of carbon on nickel alloys. I shall await with interest the publication of Mr. Duma's paper on the subject.

* Metallurgist, Titanium Alloy Manufacturing Company, Niagara Falls, N.Y., U.S.A.

† J. A. Duma, "Effect of Titanium on Some Cast Ferrous and Non-Ferrous Metals," *Amer. Soc. Metals Preprint*, **1936** (Oct.).

THE RESISTANCE OF SOME SPECIAL BRONZES TO FATIGUE AND CORROSION-FATIGUE.*

By H. J. GOUGH,† M.B.E., D.Sc., F.R.S., MEMBER OF COUNCIL,
and D. G. SOPWITH,‡ B.Sc.Tech.

SYNOPSIS.

Fatigue and corrosion-fatigue tests on four types of special bronzes have been carried out to ascertain the suitability of these materials for special aircraft purposes. The materials tested were: phosphor–bronze, aluminium bronze (9 per cent. aluminium), beryllium bronze (2·25 per cent. beryllium), and Superston L189 bronze. The results show that the corrosion-fatigue resistance of the bronzes compares favourably with that of stainless steels, the beryllium bronze in particular having the highest corrosion-fatigue resistance of any material so far investigated by the authors. The fatigue resistance in air of Superston is exceptionally high for a non-ferrous material but the material appears to be somewhat susceptible to stress–concentration effects.

I. INTRODUCTION.

THE fact that several bronzes have been shown by McAdam and others to have corrosion-fatigue resistances but little inferior to their fatigue resistance in air renders an investigation of these properties in the case of several special bronzes of interest. Whilst these materials must be regarded as "heavy" metals, sufficiently high resistance to corrosion-fatigue would entitle them to serious consideration as materials for use in certain parts of aircraft construction. In particular, claims have been put forward for beryllium–copper which render the further investigation of this material desirable, particularly as no data have been published concerning its resistance to corrosion-fatigue, while the available knowledge of its ordinary fatigue properties is extremely meagre.

In a useful summary by H. W. Gillett [2] of the information hitherto available as to the fatigue-resisting properties of bronzes it is stated that:

"Phosphor–bronze is relatively immune to corrosion-fatigue in salt- or fresh-water, but does not have a very high endurance limit to

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* Manuscript received June 30, 1936. Presented at the Annual General Meeting, London, March 10, 1937.

† Superintendent, Engineering Department, National Physical Laboratory, Teddington.

‡ Scientific Officer, Engineering Department, National Physical Laboratory, Teddington.

TABLE I.—*List of Special Bronzes.*

Item.	Material.	Specification No.	Composition,* Per Cent.					Heat-Treatment.
			Aluminium.	Zinc.	Iron.	Nickel.	Other Elements.	
A	Beryllium bronze	...	...	...	...	...	Be 2·4–2·55	(1) Fully heat-treated. (2) Solutionized.
B	Aluminium bronze	D.T.D. 160	9·0–9·8	...	...	...	$\ngtr$ 0·75	(1) Water quenched and tempered. (2) Water quenched.
C	Al–Ni–Fe bronze	D.T.D. 164	9–10	...	0·5–2·5	1–3	$\ngtr$ 0·75	(1) Water quenched and tempered. (2) Water quenched.
D	"P.M.G." metal	...	...	2	...	...	"Hardener" 10	(1) As drawn. (2) Annealed.
E	High-tensile aluminium brass	I.N.O.	3	37	1	...	Mn 2	
F	Phosphor-bronze	B.S.S. 369A.	...	...	...	...	Sn 3·5–5 P 0·1–0·4	
G	Superston L189	D.T.D. 197	8–12	...	4–6	4–6	$\ngtr$ 0·3	

* Remainder copper in all cases.

1

2

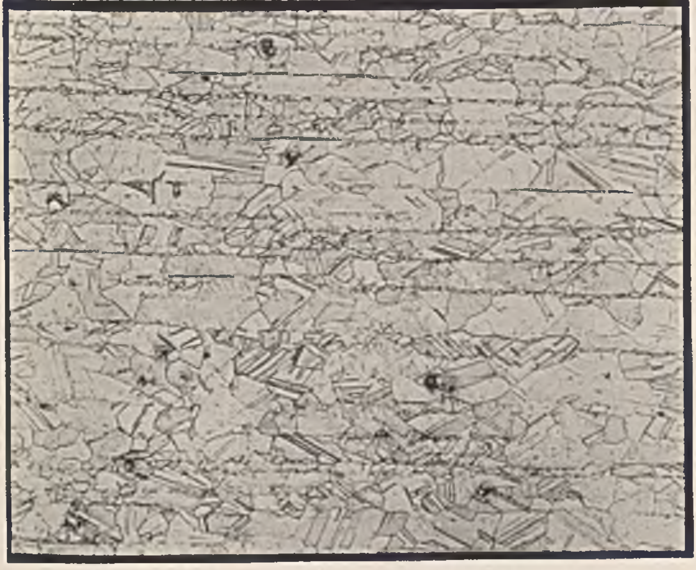


FIG. 1.—Phosphor-Bronze Etched in a Solution of Ferric Chloride. × 100.
FIG. 2.—Beryllium Bronze Etched in a Solution of Ferric Chloride. × 100.

[*To face p.* 144.

PLATE XX.

3

4

FIG. 3.—Aluminium Bronze Etched in a Solution of Ferric Chloride. × 100.
FIG. 4.—Superston Bronze Etched Electrolytically in a 2 Per Cent. Solution of Hydrofluoric Acid in Water. × 500.

start with. Aluminium bronze is outstanding for endurance limit and for corrosion-fatigue resistance, among commercial materials. Copper–beryllium alloys, with a precipitation-hardening treatment, appear to be, on incomplete data, of outstanding possibilities. Their high copper content should give them good corrosion-fatigue properties, though this of course needs experimental verification."

In view of the above-mentioned considerations, the programme of investigation into corrosion-fatigue now in progress at the National Physical Laboratory, on behalf of the Aeronautical Research Committee, was extended to include tests on some special bronzes.

A list is given in Table I of seven special bronzes which would appear to deserve investigation; of these, the following four were considered to be of particular interest:

(1) Phosphor–bronze (B.S.S. 369 A).
(2) Aluminium bronze (D.T.D. 160).
(3) Beryllium bronze (British manufacture).
(4) Superston bronze (D.T.D. 197).

The present paper deals with the results of tests carried out on these four materials. In each case, rotating-beam tests have been carried out both in air and in salt-spray.

II. PARTICULARS OF MATERIALS.

The materials were supplied in the form of ¾-in. bar, except in the case of the beryllium bronze, in which case the diameter was ½ in. The condition of the materials was stated by the makers to be as follows:

Phosphor–bronze—rolled and drawn, normalized for ½ hr. at 275° C.
Aluminium bronze—extruded and drawn (not very much drawing).
Beryllium bronze—extruded and drawn (slight amount of cold-work).
Superston bronze—as forged.

It will be noted that the aluminium bronze and beryllium bronze were not in a heat-treated condition. It was considered desirable, however, to test these materials in the conditions stated prior to testing them in the heat-treated conditions mentioned in Table I, as the condition which produces the highest tensile and air fatigue strengths is not necessarily the best under corrosion-fatigue conditions, and may indeed give very poor results under such conditions. It is intended later to test these two materials in the following conditions:

Beryllium bronze— (1) Fully heat-treated (quenched from 830° to 850° C. in water).
(2) Solutionized (as (1) but age-hardened at 360° C. for 1 hr.).

Aluminium bronze—(1) Quenched from 850° to 900° C. in water.
(2) As (1), tempered at 625°–650° C., followed by slow cooling.

Chemical analyses and microscopic examinations of the materials were carried out in the Metallurgy Department of the Laboratory.

The results are given in Table II and Figs. 1–4 (Plates XIX and XX).

TABLE II.—*Chemical Composition of Materials.*

Per Cent.	Material and Reference Mark.			
	Phosphor-Bronze. HJO.	Aluminium Bronze. HNE.	Beryllium Bronze. HMX.	Superston Bronze. HFP.
Copper .	95·56	89·5	97·26	79·83
Aluminium .	...	8·89	...	9·73
Tin . .	4·23	...	...	...
Nickel . .	...	...	0·30	4·97
Iron . .	...	0·15	0·10	5·42
Beryllium .	...	...	2·25	...
Phosphorus .	0·13	...	...	...
Zinc . .	...	1·40	...	...
Manganese .	...	...	trace	trace

The analyses fulfil the requirements of the specifications (as given in Table I) with the exception of the aluminium bronze, in which the aluminium is slightly low and the total impurities 1·55 per cent. as against the specified maximum of 0·75 per cent. The microstructures shown in Figs. 1–4 (Plates XIX and XX) show that the conditions of the materials agree generally with those stated. The normalizing of the phosphor-bronze (Fig. 1) has not completely removed the effects of cold-work, whilst the amounts of cold-work applied to the aluminium and beryllium bronzes (Figs. 2 and 3, respectively) have not been sufficient to produce visible indications.

Table III gives results of tensile, hardness, and notched-bar tests carried out on the materials. All the materials were found to possess high values of tensile proof stress, although in some cases, particularly Superston, the tensile limit of proportionality was very low.

TABLE III.—*Mechanical Properties of Materials.*

Properties.	Material and Reference Mark.			
	Phosphor-Bronze. HJO.	Aluminium Bronze. HNE.	Beryllium Bronze. HMX.	Superston Bronze. HFP.
Tensile Tests (Mean of 2):				
Ultimate strength, tons/in.^{2}	27·6	35·7	41·8	51·7
Yield-stress, tons/in.^{2}	27·2	...	...	...
Proportional limit, tons/in.^{2}	11·0	7·9	13·7	2·4
0·1 per cent. Proof stress, tons/in.^{2}	25·5	18·6	30·7	32·8
0·15 per cent. Proof stress, tons/in.^{2}	26·2	20·6	33·1	34·7
Young's modulus E, lb./in.^{2} $\times 10^{-6}$	17·7	17·5	16·3	18·8
Elongation on $4\sqrt{A}$, per cent.	32·8	37·0	23·4	10·8
Reduction of area, per cent.	77·5	42·3	61·9	19·4
Notched-Bar Impact Tests (Charpy Type):				
Energy absorbed, ft.lb.	113·6–142·5	19·4–42·6	...	6·7–21·1
Mean value, ft.lb.	123·9	30·3	...	9·6
Brinell Tests:				
Hardness Number	137, 138	150, 151	166, 179	221–233
Mean value	138	150	172	226

III. APPARATUS AND SPECIMENS.

The fatigue tests were carried out in rotating-beam machines of the N.P.L. type, in which a uniform bending moment is applied over the whole length of the test portion by means of equal upward and downward loads at the enlarged outer end of the specimen. The cyclic frequency in all cases was about 2200 stress cycles per minute; all tests were made on an endurance basis of 50 million cycles.

The apparatus used for the fatigue tests in salt-spray has been fully described and illustrated in a previous paper,[3] in which are also discussed the reasons for using cycles of flexural stresses (rotating-bar machine) in preference to cycles of direct stresses. The apparatus, however, may be briefly recalled. The test portion of the specimen is enclosed in an ebonite "spray chamber" provided with holes through which project the ends of the specimen. In the side of the chamber an injector is inserted, so placed that the spray impinges directly on the middle of the test portion of the specimen. The injector is actuated by compressed air (passed through a filter to remove any oil); the solution is a 3 per cent. solution of common salt in distilled water. The resultant spray is in the form of a fine mist.

The form of specimen used is also illustrated in the previous paper, the specimens being of form 1*a* (except the beryllium bronze specimens which, on account of the smaller diameter of the bars supplied, were of form 1*b*), the diameter of the test portion being 0·275 in. in each case.

IV. RESULTS OF FATIGUE TESTS.

The results of the fatigue tests in air and in salt-spray are given in Tables IV–VII; the resulting data are plotted, to logarithmic scales, in Figs. 5–8. The deduced values of the fatigue limits in air and of the endurance limits in salt-spray are summarized in Table VIII.

TABLE IV.—*Results of Fatigue Tests in Air and Salt-Spray on Phosphor-Bronze (Ref. Mark HJO).*

Fatigue Tests in Air.			Corrosion-Fatigue Tests in Salt-Spray.		
Specimen.	Range of Applied Stress, Tons/in.².	Endurance (Millions).	Specimen.	Range of Applied Stress, Tons/in.².	Endurance (Millions).
1A	± 15	4·98	2F	± 20	0·15
1B	± 14	4·06	2G	± 17	1·59
1C	± 13	1·82	2B	± 15	5·18
1D	± 12	8·61	2C	± 13	3·28
1E	± 11	6·05	2E	± 13	11·97
1G	± 10·5	7·67	2A	± 12	25·57
1H	± 10	4·07	2D	± 12	52·10 *
1F	± 10	50·80 *			
1K	± 9·5	53·01 *			
1J	± 9	52·59 *			

TABLE V.—*Results of Fatigue Tests in Air and Salt-Spray on Aluminium Bronze (Ref. Mark HNE).*

Fatigue Tests in Air.			Corrosion-Fatigue Tests in Salt-Spray.		
Specimen.	Range of Applied Stress Tons/in.².	Endurance (Millions).	Specimen.	Range of Applied Stress, Tons/in.².	Endurance (Millions).
1A	± 20	2·37	1G	± 20	0·91
1B	± 16	3·62	1H	± 18	1·75
1D	± 15	3·25	1V	± 16	3·58
1E	± 14·5	29·31	1K	± 14	8·93
1C	± 14	52·52 *	1L	± 12	16·58
			1M	± 11	18·51
			1N	± 10	59·30 *

* Specimens unbroken.

Table VI.—*Results of Fatigue Tests in Air and Salt-Spray on Beryllium Bronze (Ref. Mark HMX).*

Fatigue Tests in Air.			Corrosion-Fatigue Tests in Salt-Spray.		
Specimen.	Range of Applied Stress, Tons/in.^{2}.	Endurance (Millions).	Specimen.	Range of Applied Stress, Tons/in.^{2}.	Endurance (Millions).
1F	± 25	0·70	2H	± 21	2·01
1H	± 25	0·97	2A	± 20	0·75
1A	± 20	5·69	2E	± 20	5·51
1C	± 18	6·58	2G	± 19	11·66
1E	± 17·5	20·32	2D	± 19	19·59
1D	± 17	13·79	2B	± 18	3·76
1G	± 16·5	27·60	2F	± 18	63·47 *
1B	± 16	55·08 *	2C	± 17	21·84

Table VII.—*Results of Fatigue Tests in Air and Salt-Spray on Superston Bronze (Ref. Mark HFP).*

Fatigue Tests in Air.			Corrosion-Fatigue Tests in Salt-Spray.		
Specimen.	Range of Applied Stress, Tons/in.^{2}	Endurance (Millions).	Specimen.	Range of Applied Stress, Tons/in.^{2}.	Endurance (Millions).
1B	± 30	0·46	8A	± 23·1	3·33
4B	± 27	1·32	8B	± 20	6·93
5B	± 25	1·21	8C	± 18	15·93
5A	± 24	9·41	9A	± 15·9	24·69
6B	± 23	6·62	10A	± 14	66·62 *
7B	± 22·5	56·82 *			
1A	± 21·7	50·05 *			

* Specimens unbroken.

Discussion of Results.

The results of the fatigue tests in air are quite reasonably regular; in all cases a fatigue limit has been clearly developed or at least closely approximated to at the fifty million cycles to which the tests were carried. The value of the endurance ratio (ratio of fatigue limit for reversed stresses to ultimate tensile strength) of 0·44 recorded for Superston bronze is extremely high for non-ferrous metals, and the fatigue limit of ± 22·7 tons/in.^{2} for this material is the highest value of which the authors are aware for any material other than a moderately high tensile steel. The material, however, appeared to be very susceptible to stress concentration effects. For instance, when the first few fatigue tests were carried out on specimens 0·3125 in. in

TABLE VIII.—*Summary of Results of Fatigue and Corrosion-Fatigue Tests.*

Material.	Ref. Mark.	Ultimate Tensile Strength, Tons/in.^{2}.	Fatigue Limit in Air, Tons/in.^{2}.	Endurance Limits in Salt-Spray, Tons/in.^{2}.			Stress Ratio.*	Variation Per Cent.	Endurance Ratios.		Ratio of Endurance Limits in Air and Salt-Spray.
				10^7 Cycles.	2×10^7 Cycles.	5×10^7 Cycles.			In Air.	In Salt-Spray.	
		T.	F_B.			f_B.			F_B/T.	f_B/T.	f_B/F_B.
Non-Ferrous Metals :											
Phosphor-bronze .	HJO	27·6	± 9·8	± 13·7	± 12·8	± 11·7	0·79	± 4	0·35	0·42	1·19
Aluminium bronze	HNE	35·7	± 14·3	± 12·8	± 11·4	± 9·8	0·68	± 5	0·40	0·27	0·68
Beryllium bronze .	HMX	41·8	± 16·3	± 18·4	± 18·0	± 17·4	0·92	± 6	0·39	0·42	1·07
Superston bronze .	HFP	51·7	± 22·7	± 18·9	± 16·9	± 14·6	0·68	± 2	0·44	0·28	0·64
Duralumin . .	EXA	28·2	± 9·2	± 4·5	± 4·0	± 3·4	0·67	± 8	0·33	0·12	0·37
Magnesium alloy (2½ per cent. Al)	EXB	16·4	± 6·8	± 1·7	± 1·0	...	0·17	± 12	0·41	(0·10)	(0·25)
Ferrous Metals :											
0·5 per cent. C steel . .	EOY	63·2	± 25·0	± 5·0	± 3·9	± 2·8	0·44	± 12	0·40	0·044	0·11
15 per cent Cr steel . .	FAO	43·3	± 24·8	± 11·2	± 10·3	± 9·1	0·73	± 4	0·57	0·21	0·37
18/8 Cr–Ni steel .	EWZ	66·3	± 23·8	± 17·5	± 16·7	± 15·8	0·87	± 5	0·36	0·24	0·67
17/1 Cr–Ni steel .	FAP	54·5	± 32·8	± 15·0	± 13·8	± 12·3	0·76	± 5	0·60	0·23	0·38

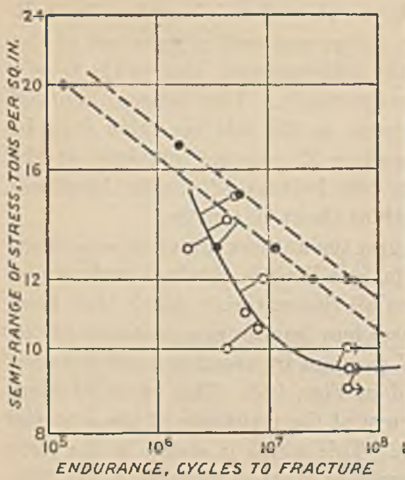
* For tenfold increase of endurance.

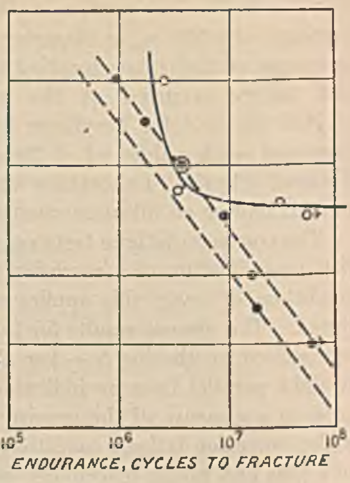
diameter in the test portion, with an enlarged end (carrying the ball-bearings) of 0·375 in. in diameter, failure occurred in three out of five specimens at the collars locating the ball-bearings; also, in the tensile test, failure occurred at the gauge-marks. The fatigue limit of ± 16·3 tons/in.^{2} for beryllium bronze in the soft condition may be compared with values of ± 20 and ± 13 tons/in.^{2} obtained at the National Physical Laboratory on two bronzes of similar beryllium content having an ultimate strength of about 70 tons/in.^{2}.

The corrosion-fatigue tests confirm the authors' previous experience that no indication of a corrosion-fatigue limit is obtained under these conditions of test: this applies to all the materials which they have tested. The present results for these four bronzes can most suitably be represented on the $\log S - \log N$ diagram by areas enclosed between straight parallel lines as indicated in Figs. 5–8. The width of these areas is a measure of the consistency of the resistance of the material under corrosion-fatigue conditions. This width is stated in the form of a plus and minus percentage variation of stress in Table VIII. The variation in the case of Superston is extremely small, and that in beryllium bronze somewhat higher, but still reasonably small. The Superston gives quite a high ratio of corrosion-fatigue endurance limit to air fatigue limit in spite of its high notch-sensitivity, which might be expected to be accompanied by an equally high sensitivity to stress concentration at corrosion pits (see for instance [4]). The corrosion-fatigue resistances of phosphor–bronze and to a smaller degree beryllium bronze are higher, at any rate up to fifty million cycles, than the fatigue resistance in air. This apparent anomaly is explained by some previous work by the present authors,[1] in which it was shown that the intrinsic fatigue resistance of a material may be considerably higher than that developed in normal fatigue tests in air. Thus, the fatigue limit of copper (which McAdam had shown also possesses a corrosion-fatigue resistance higher than that in air) when tested *in vacuo* was 13 per cent. higher than that obtained in normal tests in air.

The data obtained in the present investigation, together with that for the six materials previously investigated, are summarized in Table VIII. In this Table a column headed "Stress Ratio" is included; this denotes the ratio of the stresses for a tenfold increase of endurance, *e.g.* from 10^6 to 10^7 cycles (for the straight portion of the corrosion-fatigue $\log S - \log N$ curve or band). The stress ratio may be regarded as a measure of the damage a material sustains due to corrosion-fatigue, the actual height of the curve being influenced also by the initial fatigue strength.

The bronzes will be seen to compare very favourably with stainless

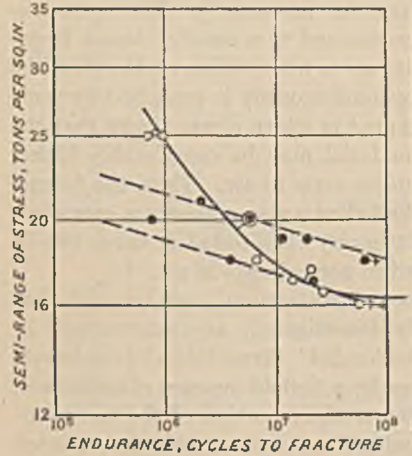


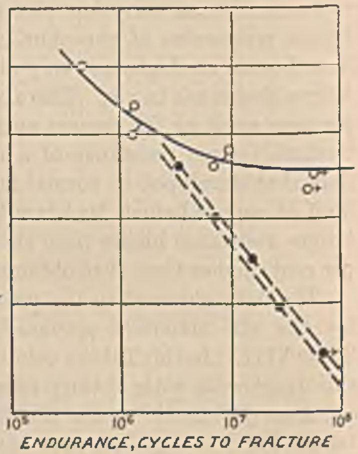


——→ SPECIMEN UNBROKEN
—○— TESTS IN AIR
- -●- TESTS IN SALT SPRAY

Fig. 5.—Phosphor-Bronze.
(Ref. mark HJO.)

Fig. 6.—Aluminium Bronze.
(Ref. mark HNE.)





——→ SPECIMEN UNBROKEN
—○— TESTS IN AIR
- -●- - TESTS IN SALT SPRAY

Fig. 7.—Beryllium Bronze.
(Ref. mark HMX.)

Fig. 8.—Superston Bronze.
(Ref. mark HFP.)

steels. Beryllium bronze * in fact is superior to the best of the stainless steels (18/8 Cr–Ni) investigated, the advantage increasing as the endurance increases, as the stress ratio for beryllium bronze is also the highest recorded. The variation in the case of the bronzes and the stainless steels is also of the same order (± 5 per cent.), and distinctly less than that of the materials—carbon steel, Duralumin, and magnesium alloy—of lower corrosion-fatigue resistances. Superston bronze, though not so good as beryllium bronze, is almost as good as the 18/8 steel. The phosphor–bronze, as stated by Gillett, has, in spite of a low fatigue limit in air, a comparatively good corrosion-fatigue resistance, the ratio of endurance limit in salt-spray to ultimate strength of 0·42 for this material being equalled only by beryllium bronze, the next highest values being 0·28 and 0·27 for Superston and aluminium bronzes, respectively. The particular aluminium bronze tested, although having a moderately high corrosion-fatigue resistance, cannot, at any rate in the condition tested, be considered as justifying Gillett's remarks quoted in the Introduction.

Acknowledgments.

The authors desire to express their indebtedness to the Director of Scientific Research, Air Ministry, for the opportunity to make these experiments and for permission to publish the results; to the Executive Committee of the National Physical Laboratory for the facilities afforded; to Mr. H. Sutton, M.Sc., of the Metallurgy Department, Royal Aircraft Establishment, Farnborough, for assistance in drawing up the programme; also to Dr. L. Aitchison and Mr. S. J. Nightingale of Messrs. Jas. Booth & Co. (1915), Ltd., and to Messrs. J. Stone & Co., Ltd., for their co-operation in the supply of material.

References.

[1] H. J. Gough and D. G. Sopwith, "Atmospheric Action as a Factor in Fatigue of Metals," *J. Inst. Metals*, 1932, **49**, 93.

[2] H. W. Gillett, "The Resistance of Copper and its Alloys to Repeated Stress. Part IV—The Bronzes and Special Alloys," *Metals and Alloys*, 1932, **3**, 275.

[3] H. J. Gough and D. G. Sopwith, "Some Comparative Corrosion-Fatigue Tests Employing Two Types of Stressing Action," *J. Iron Steel Inst.*, 1933, **127**, 301.

[4] D. J. McAdam, Jr., and W. R. Clyne, "Influence of Chemically and Mechanically Formed Notches on Fatigue of Metals," *J. Research Nat. Bur. Stand.*, 1934, **13**, 527.

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* It may be pointed out that at present beryllium bronze is extremely expensive, costing about 16 times as much as the other bronzes here dealt with.

DISCUSSION.

Mr. A. J. Murphy,* M.Sc. (Member): It is perhaps a little unfortunate that references are made in the paper to D.T.D. specifications, since the composition of the aluminium bronze does not comply with D.T.D. Specification No. 160. I think that it will be found that it is not stated in the paper that that sample complied with D.T.D. Specification No. 160, but the impression may be given that it does. The composition of the nickel–iron–aluminium bronze is within the range specified by D.T.D. Specification No. 197, but the elongation is below the minimum of that specification. It is only right to say that the latter material was not supplied as D.T.D. Specification No. 197, and that in normal production bar of so small a diameter as ¾ in. would not be made by forging but would be extruded or rolled. In this case it was a question of supplying a small amount of material for experimental purposes. Those remarks are, I think, to the point, because the low elongation value reported by the authors was probably obtained on the ends of rods, which would be rather cold in the finishing stages of forging. Forged bar of 1 in. diameter and heavier readily satisfies the requirements of D.T.D. Specification No. 197 and gives elongations of the order of 17–20 per cent., the specification minimum being 15 per cent.

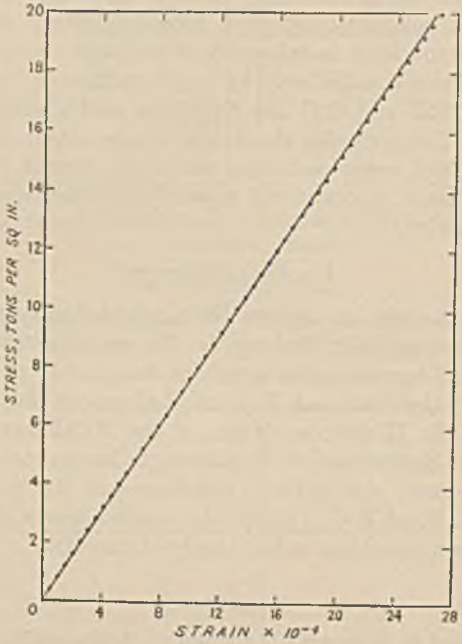

Fig. A.

The fatigue limit in air as found by the authors, namely ± 22·5 tons/in.^{2}

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* Chief Metallurgist, J. Stone and Company, Ltd., Deptford.

on a basis of 50,000,000 reversals, is in good agreement with our own result of ± 21·7 tons/in.².

I suggest, with all deference, that the authors have unduly emphasized their observations regarding the limit of proportionality and notch sensitiveness of this D.T.D. Specification No. 197 bronze, and it would be unfortunate if this created a wrong impression. In Table III a value of 2·4 tons/in.² is given for limit of proportionality, and reference is made to this on p. 146. We have made many determinations of the limit of proportionality of this bronze using the Lamb roller extensometer, and Fig. A shows a typical stress-strain curve obtained in our laboratory. From this we deduce a limit of proportionality of 12·8 tons/in.². The other mechanical properties of this same sample were :

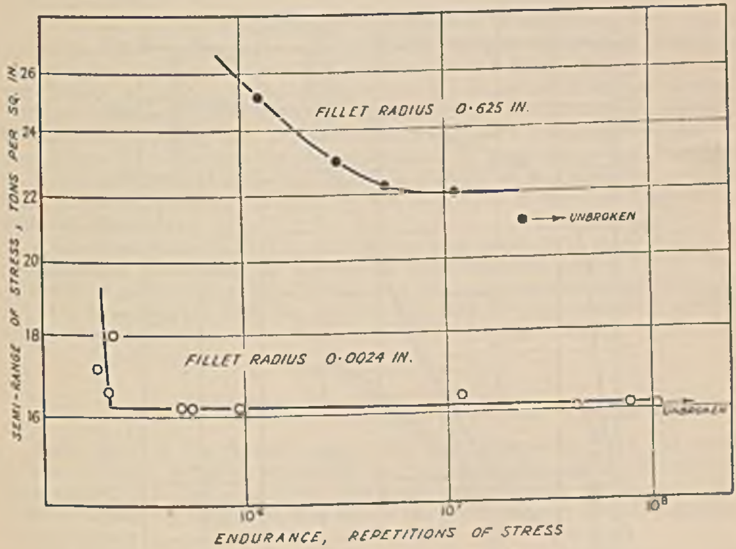

Fig. B.

Ultimate tensile stress, tons/in.²	51·44
0·1 per cent. Proof stress, tons/in.²	30·28
Elongation on $4\sqrt{A}$, per cent.	17·0
Brinell hardness number	212

The value of 2·4 tons/in.² given in the paper is so far removed from anything that we have experienced that we thought at first that there must be some error in the report. I understand, however, that this is not so. I can only say at this stage that it is extremely surprising if a material with a tensile strength of 51 tons/in.² and a 0·1 per cent. proof stress of 30 tons/in.² has a limit of proportionality of only 2·4 tons/in.². The matter is of sufficient interest to warrant a re-examination.

The references on pp. 149 and 151 to notch sensitivity are more important. The evidence on this point appears to be the breaking of a tensile test-piece at the gauge-marks and the failure of three fatigue test-specimens at the collars locating the ball bearings. It would have been useful if the authors had checked their deductions from this purely circumstantial evidence by fatigue tests of specimens provided with a definite notch or sharp change of section. This omission is the more remarkable in view of the authors' comment that the behaviour in corrosion-fatigue is not that which would be expected from a notch-sensitive material.

We have carried out such tests, using single point loading, with specimens having radii of 0·04 in. and 0·0024 in. at the stress fillet. A typical result with the 0·04-in. fillet showed an endurance of 31,400,000 reversals with a range of stress of ±17·1 tons/in.². Fig. B shows a series of results for the fillet radius of 0·0024 in., and for comparison a curve is also given for the normal test-piece having a fillet radius of ⅛ in. These results give a clear indication of an endurance limit of ±16·1 tons/in.² with a fillet radius of 0·0024 in. The reduction of the safe range of stress due to this sharp corner is therefore less than 27 per cent. Comparing these results with observations on other materials of similar tensile strength, we find that in steels having tensile strengths of 40–60 tons/in.² the reduction in fatigue-strength caused by a sharp change of section has been reported at various figures between 30 and 63 per cent. It may safely be concluded, therefore, that bronze, complying with D.T.D. Specification No. 197 is not more notch-sensitive than other materials of similar tensile strength.

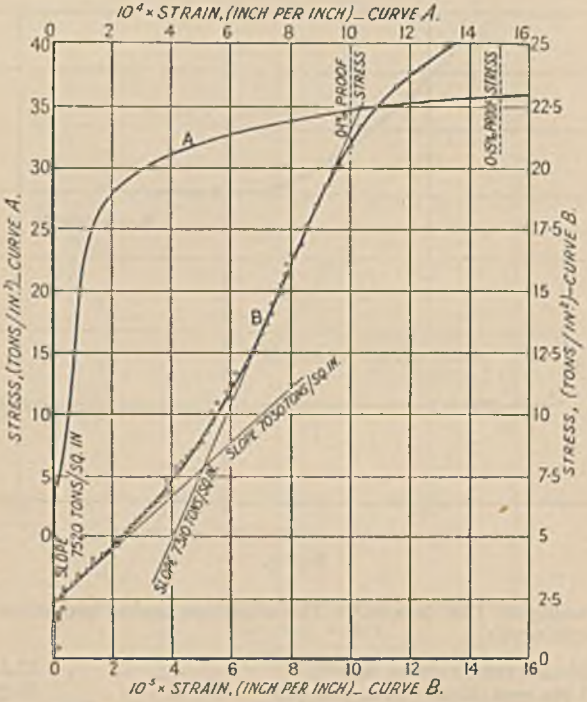

Fig. C.—Stress-Strain Difference Curves for Superston Bronze (HFP1AA).

Mr. Sopwith (*in reply*): The value reported for the limit of proportionality of Superston is admittedly very low. The behaviour of the material was most unusual. There appeared to be a distinct proportional limit at the value of 2·4 tons/in.^{2} mentioned, at which point the slope of the stress–strain curve decreased fairly suddenly from about 7500 to 7300, after which it again rose slightly, and then fell away fairly rapidly at about the value of the proportional limit mentioned by Mr. Murphy. Fig. C is the stress–strain difference curve for this material. There is a quite sudden deviation at about 2·4 tons/in.^{2}, but the 0·1 per cent. proof stress is very high, about 35 tons/in.^{2}. As this behaviour only occurred incidentally in the course of the investigation, it was not pursued further, but a second specimen behaved in a very similar manner.

So far as the notch sensitivity of Superston is concerned, two tensile specimens failed at the gauge-mark and three fatigue test-pieces; that is to say both the tensile test-pieces and three of the five fatigue test-pieces which were tested before it was decided to reduce the diameter of the test portion. On that evidence I think that the comment made in the paper is justified. It is pointed out later that this is not, as might have been expected, accompanied by a low corrosion-fatigue resistance. It is satisfactory to hear that the notch sensitivity is somewhat less than perhaps we had expected, and also that the fatigue limit as obtained by Mr. Murphy is in such good agreement with our own value.

It has been stated that it is unfortunate that reference is made to D.T.D. Specifications, particularly in the case of the aluminium bronze D.T.D. 160. As a matter of fact the particular material mentioned was supplied to the Air Ministry as complying with the specification, and for that reason no analysis was made until some progress had been made with the research.

CORRESPONDENCE.

The Authors (*in further reply to the oral discussion*): We are much interested in Mr. Murphy's statement that ¾-in. Superston rod would normally be extruded or rolled: however, the condition in which the material was actually tested, *i.e.* as forged, was one of the two (cast and forged) suggested by the makers.

The question of the proportional limit of the Superston has already been dealt with, but it may be added that the value of the proportional limit of a material may, in certain cases, depend considerably on the accuracy of the extensometer used and on the amount of the load increments: in the present case, the standard N.P.L. procedure was followed and the order of accuracy should be fairly high.

Mr. J. C. Chaston,* B.Sc., A.R.S.M. (Member): The results described in this paper are extremely interesting, but may I be allowed to suggest that being conducted on materials in the "as received" condition they may be so misleading as to be worthless to the designer. It should not need pointing out at the present time that material as received from the manufacturer after rolling, cold-drawing, or forging is not in a standardized condition. Its properties may vary over a wide range, and if it is to be used—as it most often is—in this condition, scores of tests may be necessary before a fair picture can be presented of the variations likely to be encountered in practice. When only one test is to be made, there can be no virtue in carrying this out on a random sample, produced by an unknown treatment. The authors explain

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that they did not wish to test the materials in the " heat-treated condition," but there can have been no objection to determining and recording the precise mechanical treatment which they received.

The AUTHORS (*in reply*): The reasons for testing some of the materials in the " as received " conditions are stated in the paper, *viz.* that the condition which produces the highest tensile and air fatigue strengths is not necessarily the best under corrosion-fatigue conditions. It is also pointed out that tests on the materials concerned in two heat-treated conditions are to be carried out: these are now in progress. The details of the mechanical treatment of the materials as stated by the makers are also given in the paper.

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DIRECTIONAL PROPERTIES IN ROLLED BRASS STRIP.*

By MAURICE COOK,† M.Sc., Ph.D., Member.

Synopsis.

The tensile properties of brass strip in directions parallel, normal, and at 45° to the rolling direction, have been determined after progressively increasing rolling reductions up to more than 90 per cent. When the rolling reduction has been sufficient to induce a directional effect the greatest strength and least ductility are obtained normal to the rolling direction, while the converse obtains in the rolling direction.

When cold-rolled brass strip is finally annealed, it may show directionality which is revealed both by tensile tests and by the occurrence of ears or waves on the edges of cups cut from the strip. In annealed strip showing directionality, the tensile strength is least and the ductility greatest at 45° to the rolling direction, and it is in this position that ears are formed. The extent to which directionality exists in rolled and annealed strip is largely determined by the conditions of the penultimate and final annealings and by the magnitude of the rolling reduction between these two annealings.

A study of the orientation of twinning planes in rolled and annealed 70 : 30 brass strip showing appreciable directionality in tensile properties and in the tendency to form ears on cups, indicates that the frequency of orientation of the twinning planes is lowest at about 45° to the direction of rolling. The direction of maximum frequency of orientation of twinning planes appears to be fortuitous in strip not showing directionality in other respects.

Introduction.

The occurrence of directional properties in strip or sheet metal is of considerable theoretical interest and practical importance. Apart from directional properties arising out of the development of fibre due to the presence of non-metallic inclusions, recent investigations have shown that in materials where such inclusions are not present to any appreciable extent, directionality may exist in the properties of the metal not only in the rolled condition, but also after annealing. When metal is fabricated into cups by blanking and forming either together in one operation, or separately, the existence of marked directionality manifests itself by the presence of ears or a waviness at the edge or mouth of the cup which may vary in position, and considerably in

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[*] Manuscript received May 9, 1936. Presented at the Annual General Meeting, London, March 10, 1937, and also at a General Meeting in Birmingham, March 23, 1937.

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intensity, according to the rolling and annealing treatments which the strip or sheet has received in the course of its preparation. While a number of investigations have been made on directionality, there still remains much information to be obtained which will not only be of immediate practical use, but which will also help towards a fuller understanding of the subject. The work described in the present paper was undertaken to obtain, in the case of brass, information of this kind, since few results have hitherto been published concerning directional properties in this alloy.

Price and Davidson[1] who determined, after various rolling reductions, the tensile properties of 65 : 35 brass strip, in directions parallel and normal to the direction of rolling, noted that up to reductions of about 50 per cent. in thickness the tensile strength in the two directions was not measurably different, but that thereafter the strength in the transverse direction was greater than that in the longitudinal direction. The reduction in area at the fracture was found always to be greater in the longitudinal than in the transverse direction, while elongation values in the two directions were not sensibly different up to reductions of about 35 per cent., but thereafter higher values were obtained on transverse specimens.

Kaiser[2] studied the causes giving rise to waviness on copper cups and determined the effect of such factors as the temperature of the penultimate and final annealing operations, as well as the magnitude of the final rolling reduction (*i.e.* the rolling reduction between the penultimate and final annealings) on the extent of the waviness. He concluded that, in order to minimize waviness on copper cups, the final rolling reduction should not exceed 60 per cent., the temperature of the final annealing should be as low as possible and the intermediate annealings should be carried out at 700° C. or higher temperatures.

Bauer, von Göler, and Sachs[3] determined the directional properties of copper and some copper–zinc alloys after a 92 per cent. reduction in thickness by cold-rolling, and after annealing at 500° C. Except for copper and the 98 : 2 alloy, they found the tensile strength to increase with increasing angle of the specimen to the direction of rolling, the highest value being obtained on transverse specimens. In the annealed condition the tensile strength was found to decrease, and the elongation to increase with an increasing angle.

Phillips and Bunn,[4] who determined the affect of the final rolling reduction and the temperature of the final annealing operation for tough-pitch and deoxidized copper, concluded that to avoid serious directional properties the final rolling reduction should be limited to about 50–60 per cent. and the final annealing to 500°–600° C., although

FIG. 1.—About Natural Size.

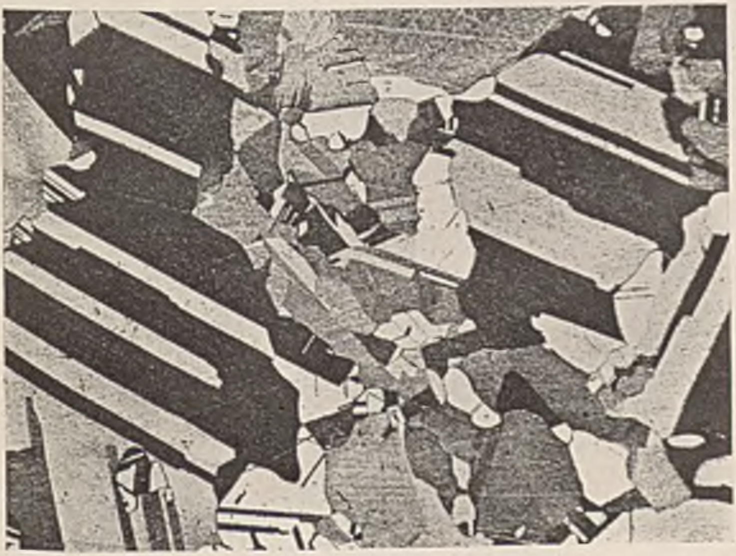

FIG. 3.—Specimen 800° C./10%/525° C. × 75.

[*To face p.* 160.

4

5

6

7

Fig. 4.—Specimen 550° C./50%/525° C.
Fig. 5.—Specimen 550° C./90%/725° C.
Fig. 6.—Specimen 550° C./50%/725° C.
Fig. 7.—Specimen 550° C./90%/525° C.

All × 100.

it should be noted that the results were obtained on material annealed at one temperature only at the penultimate annealing stage.

With a 90 : 10 copper–zinc alloy, Phillips and Samans [5] found that the most pronounced tensile directional properties and the greatest tendency to waviness on cups are obtained by large final rolling reductions and a high temperature in the final annealing operation. Whereas copper was found to exhibit waviness in and at right angles to the direction of rolling, it occurred in the 90 : 10 alloy at 45° to the direction of rolling.

The formation of ears or waviness on cups of cupro–nickel has been studied by Bassett and Bradley,[6] according to whom ears may be formed either at 45° to, or in, and at right angles, to the direction of rolling, their position and size being affected by the magnitude of the final rolling reduction and the temperature of the final annealing.

With mild steel Phillips and Dunkle [7] found that with strip finally rolled less than 40 per cent. ears were formed at 45° to the rolling direction, whereas with strip rolled 50 per cent. or more they occurred in the 0 and 90° positions.

EFFECT OF COLD-ROLLING ON THE PROPERTIES OF 70 : 30 AND 64 : 36 BRASS STRIP.

Brasses of the compositions shown in Table I were obtained at a thickness of approximately 0·3 in. after a number of rolling and annealing operations. The last rolling reduction to bring the strip to this thickness was 50 per cent., and at this stage the strip was annealed at 625° C. for 2 hrs. The annealed strip was then cold-rolled without any intermediate annealing operations, samples suitable for testing being obtained after reductions in thickness of approximately 10, 30, 50, 80, 90, and 95 per cent. Relative to the direction of rolling, samples were cut parallel, normal, and at 45°, and the results of tests made on these specimens are detailed in Tables II and III. The data obtained with the two different compositions of brass show that up to reductions

TABLE I.—*Percentage Composition of Brasses Investigated.*

	64 : 36 Brass.	70 : 30 Brass.
Copper	63·4	70·5
Tin	0·01	Nil.
Lead	0·06	0·01
Iron	0·06	0·009
Nickel	0·03	0·006
Phosphorus	Nil.	0·001
Zinc (difference)	36·44	29·47

of about 50 per cent. the tensile strength is the same in the three different directions, but with greater reductions the strength at 90° is greater than at 45° to the direction of rolling, while the strength in the rolling direction is lowest. These differences in tensile strength values increase in magnitude with increasing rolling reduction. In so far as they are comparable, these results on the effect of rolling on directional tensile strength confirm those of Price and Davidson, and of Bauer, von Göler, and Sachs. A much less pronounced directionality was found in the values for proof stress. With rolling reductions of up to 90 per cent. no appreciable directionality could be detected in limit of proportionality values which were determined with a Lamb roller extensometer, under conditions where strain measurements accurate to $0{\cdot}5 \times 10^{-5}$ in. could be made.

TABLE II.—*Directional Properties of* 64 : 36 *Brass after Progressively Increasing Amounts of Cold-Working.*

Reduction and Direction.		Limit of Proportionality, Tons/in.^{2}.	0·1 Per Cent. Proof Stress, Tons/in.^{2}.	Tensile Strength, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	D.P. Hardness, 10 Kg. Load.	Brinell Hardness, 10 Kg., 1 mm.
Per Cent.	Degrees.							
Nil.	0	4·0	6·2	20·8	66·5	70	64	63
	45	4·1	6·2	20·3	68·0	69		
	90	3·5	5·8	20·6	64·0	62		
10·7	0	8·0	14·2	23·3	48·5	65	105	97
	45	8·0	14·0	22·5	50·0	62		
	90	8·1	14·2	23·0	47·0	56		
29·2	0	12·2	24·5	29·4	20·0	58	141	130
	45	11·9	22·0	28·2	17·0	56		
	90	12·8	23·0	29·1	17·0	49		
50·0	0	15·0	30·1	37·5	8·5	50	176	160
	45	14·5	27·9	37·2	9·0	48		
	90	15·3	27·8	38·0	8·5	40		
79·4	0	17·8	33·3	44·9	4·5	47	200	177
	45	17·6	34·2	46·1	4·5	37		
	90	18·0	34·1	48·2	6·0	28		
89·6	0	18·2	35·0	47·9	3·0	46	216	188
	45	18·3	34·5	49·8	3·0	31		
	90	19·4	37·9	54·8	3·0	19		
96·4	0	...	...	51·1	2·0	46	223	192
	45	...	...	54·2	2·0	30		
	90	...	...	60·7	2·0	15		

Although there were small differences in elongation values in the soft condition, the highest values being at 45°, these quickly decreased, and after rolling reductions of the order of 20–30 per cent., up to reductions in excess of 90 per cent., the elongation values in the three directions were not sensibly different. At all rolling reductions the reduction in area values at 90° to the rolling direction were lowest. In the other two directions they were not very different up to reductions of about 60 per cent., but thereafter increasingly higher values were obtained in the rolling direction than at 45°.

TABLE III.—*Directional Properties of* 70 : 30 *Brass after Progressively Increasing Amounts of Cold-Working.*

Reduction and Direction.		Limit of Proportionality, Tons/in.^{2}.	0·1 Per Cent. Proof Stress, Tons/in.^{2}.	Tensile Strength, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	D.P. Hardness, 10 Kg. Load.	Brinell Hardness, 10 Kg. 1 mm.
Per Cent.	Degrees.							
Nil	0	2·6	5·1	20·6	74	73	60	58
	45	2·3	3·9	19·7	82	73		
	90	2·6	4·6	20·2	75	69		
10·8	0	7·3	14·2	23·1	54	66	98	89
	45	6·9	12·7	21·5	60	68		
	90	8·0	13·2	22·5	55	55		
30·3	0	10·8	23·0	29·3	23	59	146	135
	45	10·5	22·0	28·2	21	64		
	90	12·0	22·3	29·2	22	54		
50·5	0	15·5	30·2	37·6	11	49	175	159
	45	14·4	27·5	37·6	11	50		
	90	15·3	28·4	39·0	11	43		
79·4	0	17·8	34·4	44·6	5	47	207	181
	45	17·4	31·9	46·3	6	43		
	90	18·8	33·9	49·1	6	31		
90·2	0	19·1	35·5	48·6	3	47	219	190
	45	20·0	35·4	49·8	3	35		
	90	19·8	40·6	55·1	2	22		
95·6	0	...	...	51·7	2	39	224	192
	45	...	...	52·2	2	29		
	90	...	...	59·5	1	12		

DIRECTIONAL PROPERTIES IN ANNEALED STRIP.

For the determination of directional properties in annealed strip and the conditions necessary for producing strip which would yield flat-topped cups, specimens of 70 : 30 brass strip, all from the same ingot, were obtained at thicknesses of 0·041, 0·074, and 0·370 in. One set of specimens was annealed at 550° C. for 1 hr. and another set at 800° C. for 1 hr. They were then all rolled to a final thickness of 0·037 in. Thus at this thickness were obtained six different samples representing final rolling reductions of 10, 50, and 90 per cent. in thickness and penultimate annealings of 1 hr.'s duration at 550° and 800° C. Each of the six samples was divided into three pieces, which were annealed finally at 525°, 625°, and 725° C. for half an hour, making a total of 18 different treatments.

Cups measuring approximately 0·50 in. in diameter and 0·42 in. in height were made in one operation from each of the 18 samples, and pieces of the strip cut in three directions were also tested. The results of these tests, together with the heights of ears or waves on the cups, are given in Tables IV and V, and a series of cups illustrating a range of earing or waviness is shown in Fig. 1 (Plate XXI).

TABLE IV.—*Mechanical Properties of Annealed* 70 : 30 *Brass. Penultimate Annealing Temperature* 550° *C.* (1 *Hr.*)

Final Annealing Temperature. (½ Hr.), ° C.	Tensile Strength Tons/in.².			Elongation on 2 in., Per Cent.			Reduction of Area, Per Cent.			Height of Ears, Inch.	Grain-Size, Mm.
	0°.	45°.	90°.	0°.	45°.	90°.	0°.	45°.	90°.		
					Final Rolling Reduction 10 Per Cent.						
525	22·6	22·0	22·2	58	60	53	75	76	69	0·006	0·03
625	21·4	20·8	21·8	59	61	58	74	74	69	0·011	0·05
725	20·3	18·7	20·1	61	63	60	74	74	73	0·023	0·08
					Final Rolling Reduction 50 Per Cent.						
525	24·9	24·4	24·7	52	54	47	71	71	66	0·005	0·02
625	21·8	21·0	21·8	58	66	61	69	70	68	0·009	0·045
725	20·0	18·7	20·5	60	70	63	68	71	68	0·015	0·08
					Final Rolling Reduction 90 Per Cent.						
525	26·1	24·8	25·3	46	50	46	67	74	67	0·015	0·02
625	22·5	21·2	22·0	59	65	61	73	76	71	0·022	0·04
725	19·8	18·9	20·8	63	69	66	68	74	66	0·027	0·08

The tensile test results given in Tables IV and V show that at 45° to the direction of rolling the tensile strength is least and the ductility greatest, which agrees with the observation that the ears on the cups invariably occur in this position. With regard to the intensity of the earing effect, or the height of the ears, the values given in Tables IV and V indicate that with a given penultimate annealing temperature the height of the ears increases with the temperature of the final anneal. In other words, in order to avoid undue development of directional properties, the final annealing should not be carried out at high temperatures. The connection between height of ears and directionality in respect of tensile strength is shown in Fig. 2, where heights of ears are plotted against a value obtained by dividing the difference in tensile strength between that at 45° and that of the average tensile strength at 0° and 90°, by the product of the two.

TABLE V.—*Mechanical Properties of Annealed* 70 : 30 *Brass. Penultimate Annealing Temperature* 800° *C.* (1 *Hr.*)

Final Annealing Temperature (¼ Hr.), ° C.	Tensile Strength Tons/in.².			Elongation on 2 in., Per Cent.			Reduction of Area, Per Cent.			Height of Ears, Inch.	Grain-Size, Mm.
	0°.	45°.	90°.	0°.	45°.	90°.	0°.	45°.	90°.		
				Final Rolling Reduction 10 Per Cent.							
525	19·6	18·2	19·8	45	51	49	63	74	72	0·027	0·05–0·50
625	18·8	18·2	19·1	51	60	52	70	72	68	0·017	0·10–0·50
725	18·4	18·1	18·6	61	65	62	68	72	67	0·014	0·08–0·20
				Final Rolling Reduction 50 Per Cent.							
525	23·7	23·4	23·9	47	53	52	70	70	68	0·007	0·025
625	21·0	20·7	21·6	63	63	58	72	73	70	0·011	0·045
725	18·6	18·0	18·7	71	73	60	69	72	63	0·012	0·10
				Final Rolling Reduction 90 Per Cent.							
525	26·1	24·9	25·3	48	48	46	74	74	72	0·007	0·02
625	21·6	21·3	22·1	53	61	55	74	74	71	0·009	0·045
725	19·4	18·5	19·6	61	64	60	68	72	65	0·016	0·10

TABLE VI.—*Height of Ears* (*Inch.*)

Penultimate Annealing Temperature, ° C.	Final Annealing Temperatures.								
	525° C.			625° C.			725° C.		
	Rolling Reduction (Final Stage).								
	10 Per Cent.	50 Per Cent.	90 Per Cent.	10 Per Cent.	50 Per Cent.	90 Per Cent.	10 Per Cent.	50 Per Cent.	90 Per Cent.
400	0·014	0·007	0·027	0·033	0·031	0·047	0·051	0·046	0·058
500	0·010	0·007	0·027	0·024	0·016	0·040	0·039	0·029	0·052
600	0·009	0·006	0·022	0·011	0·009	0·030	0·019	0·018	0·033
700	0·019	0·007	0·010	0·008	0·008	0·013	0·016	0·013	0·017
800	0·035	0·007	0·012	0·009	0·008	0·013	0·014	0·011	0·012

The only exception to the generalization that the height of the ears increases with the temperature of the final annealing is in the group subjected to a penultimate anneal at 800° C. and finally rolled 10 per cent. This reduction does not break up the large structure sufficiently for normal recrystallization and grain-growth to occur in the final annealing. This is well shown by the structure of the strip finally annealed at 525° C., which is illustrated in Fig. 3 (Plate XXI). In this particular group the height of the ears, the size of the crystals, and the extent of non-uniformity decrease as the final annealing temperature is increased. Apart from the material subjected to a penultimate annealing at 800° C. and rolled with a 10 per cent. reduction, which gave rise to abnormal structural features, the height of the ears for any given penultimate annealing temperature and rolling reduction, increases with the grain-size. Without, however, so connecting it to a particular set of conditions, the height of the ears produced is not related to the grain-size. Fig. 4 (Plate XXII) shows the structure of a brass which gave practically flat-topped cups, while from the brass, the structure of which is shown in Fig. 5 (Plate XXII), cups with ears 0·027 in. high were produced. On the other hand, both of the brasses, the structures of which are shown in Figs. 6 and 7 (Plate XXII, produced cups having ears of approximately the same height, namely 0·015 in., in spite of the large difference in grain-size. The microsections illustrated in Figs. 3, 4, 5, 6, and 7 were taken parallel to the direction and in the plane of rolling.

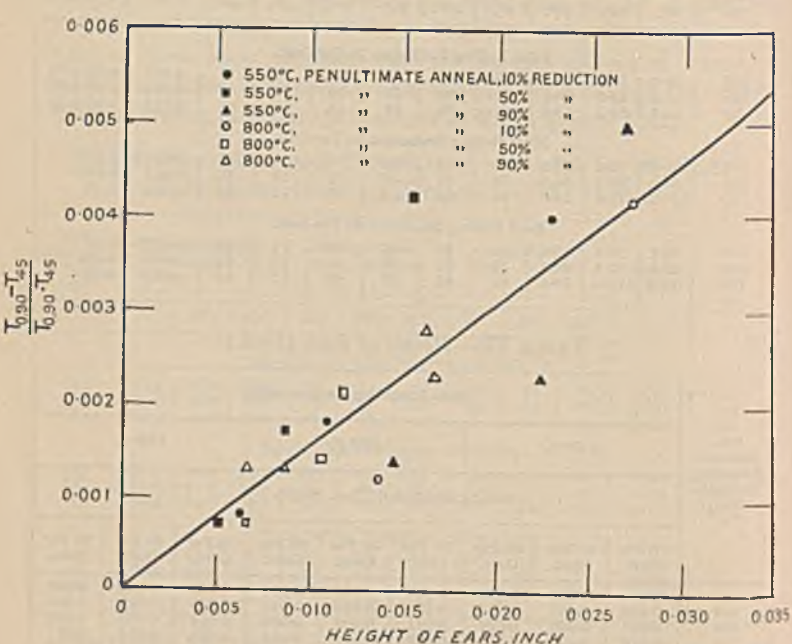

Fig. 2.

To obtain further evidence on the effect of the penultimate annealing temperature, this operation was carried out at 400°, 500°, 600°, 700°, and 800° C. instead of only at 550° and 800° C., as previously. The same three final rolling reductions and three final annealing temperatures were adhered to, and cups of the same dimensions as those cut from the earlier strips were made from the 45 different strips so produced. The heights of the ears on these cups were measured, and the results obtained are given in Table VI.

With the exception of the strip rolled 10 per cent. and finally annealed at 525° C., the effect of increasing the penultimate annealing temperature from 400° to 800° C. is, generally, to decrease the height of the ears. This applies to the three rolling reductions and the three final annealing temperatures which have been dealt with. According to these experiments, strip yielding cups with the least amount of waviness at the mouth is obtained with a final rolling reduction of 50 per cent. in thickness and a low final annealing temperature, *i.e.* 525° C.

With this combination the effect of the temperature of the penultimate anneal on the waviness is apparently insignificant, but immediately either of these conditions is departed from, and either the magnitude of the final rolling or the temperature of the final annealing is increased, then the effect of increasing the penultimate annealing temperature in reducing the extent of waviness, becomes increasingly apparent.

CRYSTALLOGRAPHIC EVIDENCE OF DIRECTIONALITY.

A visual examination of the microstructure of annealed brass does not suggest the existence of any directional features or preferred orientation, but recently attempts have been made to demonstrate the existence of directionality by more detailed examination of the microstructure. One of these consists of classifying the longest diameters of individual grains by plotting the direction which they make with a fixed direction, *e.g.* the direction of rolling. From a point on this fixed line, radii are marked off of lengths representing the frequency of each class. If no directionality exists the plotted radii will be more or less equal in length, while, on the other hand, any directionality would be revealed by a lengthening of the lines in preferred directions. The maximum diameter of the crystal is not definitely related to the crystal structure, and, therefore, this method for determining directionality is an arbitrary one. Twinning, which as shown by Phillips [8] takes place on the octahedral planes in alpha brass, is a real property of crystals and, therefore, the measurement of the orientation of twinning planes should serve as a means of ascertaining the existence of preferred orientation.

This interesting method of investigation, *i.e.* the determination of directionality by measuring the frequency of orientation of twinning planes, appears to have been first explored by Johnston,[9] [10] who

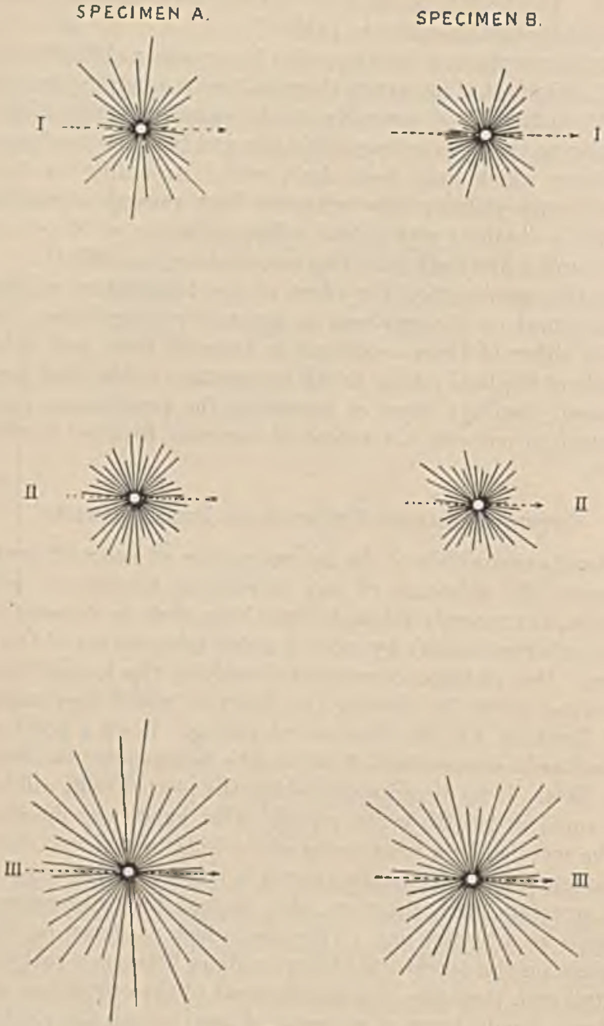

Fig. 8.

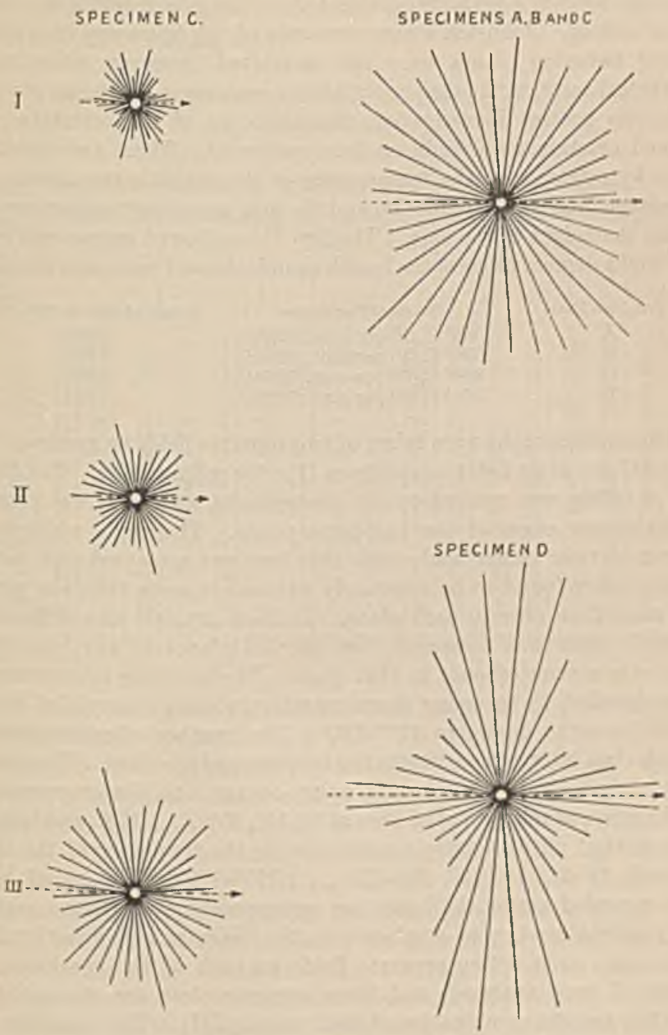

Fig. 9.

concluded that "quite strong directionality persists in the visible structure, even after strong over-annealing," and that the directionality takes the form of a preferred orientation of the grains across the direction of rolling. Johnston's measurements of the frequency of orientation of twinning planes were not correlated, however, either with mechanical tests on the strip, or with the occurrence of ears on cups.

In the present investigation measurements of the orientation of twinned crystals were made on four specimens. These are indicated below by reference to the temperature of the penultimate anneal, the percentage final rolling reduction and the final annealing temperature, as well as the height of the ears. The first three showed earing only to a very slight degree, whereas the fourth sample showed pronounced earing.

Specimen Mark.	Details of Preparation.	Height of Ears on Cups, Inch.
A	550° C./10 per cent./525° C.	0·006
B	550° C./50 per cent./625° C.	0·009
C	800° C./90 per cent./625° C.	0·009
D	550° C./90 per cent./725° C.	0·027

Photomicrographs were taken of two separate fields on specimens A, B, and C and of six fields on specimen D in the rolling plane. The direction of rolling was marked on the photographs, so that it was parallel to the longer edges of the half-plate prints. The angle which each system of twin bands made with this line was measured and noted. Crystals were found to be commonly twinned in more than one plane, and more than once in each plane. In these crystals each differently oriented plane was measured, but parallel planes in any one grain were only accounted once in that grain. The resulting measurements were classified by grouping them together in class intervals of 0°–9°, 10°–19°, and so on up to 170°–179°. The number of measurements in each class interval constitutes the frequency of the class. The results were plotted by drawing from a point, on an initial line representing the direction of rolling, radial lines at 5°, 15°, 25° . . . 175°, and lengths were marked off on them proportionate to the frequency of the class intervals 0°–9°, 10°–19°, 20°–29° . . . 170°–179°. The radial lines were extended across the basis line symmetrically, this being merely an expedient serving to emphasize in the diagram any directionality which may exist. Two separate fields on each of the specimens A, B, and C were analyzed, and these separate plots are shown in (I) and (II), and the combination of each pair in (III) in Fig. 8 and on the left portion of Fig. 9. The combination of all six fields from specimens A, B, and C is shown in the upper right part of Fig. 9, while the combined results obtained from the six separate fields on specimen D is shown in the lower right portion of the same figure. The number of measurements made in each of the two fields on specimens A, B, and C varied between 366 and 555, the total number being 2929. More than four hundred measurements were made in each of the six fields on specimen D, totalling 2654.

TABLE VII.—*Measurements of the Frequency of Twinning Directions.*

Orientation of Twin Bands to Direction of Rolling.	Specimen A.			Specimen B.			Specimen C.			A, B, & C.	Specimen D.						
	Field.			Field.			Field.			Field.	Field.						
	I.	II.	I & II.	I.	II.	I & II.	I.	II.	I & II.	All 6.	I.	II.	III.	IV.	V.	VI.	All 6.
0– 9°	15	28	43	22	17	39	22	22	44	126	25	26	31	33	32	24	171
10– 19°	23	28	51	19	19	38	18	25	43	132	27	16	29	24	16	19	130
20– 29°	21	25	46	22	24	46	13	21	34	126	17	18	11	14	12	20	92
30– 39°	34	22	56	25	20	45	11	28	39	140	8	16	18	15	15	14	86
40– 49°	45	34	79	30	39	69	19	36	55	203	11	13	9	14	10	13	70
50– 59°	29	36	65	36	33	69	18	34	52	186	19	14	15	16	10	22	96
60– 69°	19	36	55	33	27	60	19	30	49	164	25	27	24	27	26	37	166
70– 79°	25	27	52	39	19	58	33	21	54	164	45	46	36	40	48	34	249
80– 89°	54	38	92	16	27	43	20	27	47	182	47	37	46	47	37	44	258
90– 99°	41	38	79	19	23	42	15	28	43	164	43	47	34	29	48	45	246
100–109°	15	23	38	28	33	61	29	43	72	171	47	41	41	36	35	42	242
110–119°	46	32	78	32	23	55	21	30	51	184	29	32	24	28	42	21	176
120–129°	34	29	63	26	27	53	28	23	51	167	26	19	11	13	23	11	103
130–139°	53	26	79	40	32	72	23	28	51	202	23	10	11	21	19	12	96
140–149°	36	33	69	34	42	76	17	32	49	194	9	12	12	16	17	11	76
150–159°	22	25	47	17	34	51	17	30	47	145	14	15	24	22	15	17	107
160–169°	24	27	51	13	21	34	19	32	51	136	20	15	24	22	15	23	119
170–179°	19	31	50	21	25	46	24	23	47	143	20	26	37	28	27	33	171
Total.	555	538	1093	472	485	957	366	513	879	2929	455	429	437	444	447	442	2654

The plots for the individual fields on A, B, and C suggest that the twin orientation is random and while the combined plot for these specimens is more regular, it is not suggestive of any very marked preferred orientation. This result is not surprising, since these specimens yielded flat-topped cups, and did not exhibit markedly directional properties. On the other hand, the combined plot which was obtained on a sample yielding cups with pronounced waves shows much more evidence of preferred orientation, the twinning planes occurring with greatest frequency at right angles to the direction of rolling and with least frequency at 45° to the direction of rolling. Thus, it would seem that rolled material which possesses directional properties also exhibits a preferred crystalline orientation, as shown by the direction of twinning planes, although no such evidence of directionality can be detected from a visual examination of the structure.

ACKNOWLEDGMENTS.

The author's thanks are due to the Management Board of Messrs. I.C.I. Metals, Ltd., Witton, Birmingham, for permission to publish the results contained in this paper, and he also gratefully acknowledges the valuable assistance which he has had from his colleagues Messrs. C. J. Faulkner, A. Fletcher, and W. G. Tallis.

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[7] A. Phillips and H. H. Dunkle, *Trans. Amer. Soc. Metals*, 1935, **23**, 398.

[8] A. J. Phillips, *Proc. Inst. Metals Div. Amer. Inst. Min. Met. Eng.*, 1928, 429.

[9] R. G. Johnston and W. G. Askew, *Met. Ind.* (*Lond.*), 1934, **44**, 383; 1934, **45**, 27, 219.

[10] R. G. Johnston, *Met. Ind.* (*Lond.*), 1934, **45**, 560, 588, 613.

DISCUSSION AT THE ANNUAL GENERAL MEETING.

DR. C. J. SMITHELLS,* M.C. (Member of Council): I cannot add anything regarding brass, but the problem of directional properties is of such general interest in regard to all metals that I should like to make one or two remarks. My colleague Mr. C. E. Ransley has been investigating a very similar problem in rolled molybdenum sheet, and his results may throw a little light on this problem. Molybdenum, like α iron, has a body-centred cubic lattice, and develops a very pronounced preferred orientation on rolling. A certain amount of trouble was experienced when this sheet was subsequently subjected to cold-pressing operations, since certain sheets developed cracks at 45° to the direction of rolling, as shown in Fig. A (Plate XXIII). This trouble was most pronounced in sheet that had been cross-rolled and then annealed. We studied the development of preferred orientation by X-rays, and the results give a very clear picture of what happens to the crystal grains during rolling. The same kind of thing happens in all metals and is therefore, I think, of general interest.

When rolling is carried out in one direction only, the crystal fragments arrange themselves so that the cube diagonal lies in the direction of rolling, and the diagonal of the cube face lies in the rolling plane. This allows the crystal to have a random orientation in other directions. If it is now rolled at right angles to the first direction, the other diagonals of the cube face are aligned in the surface of the sheet, and now all the crystal fragments must have exactly the same orientation in all respects. (The mechanism was illustrated by a model.) The result is that the 100 planes, which are the cleavage planes in molybdenum, are now all lined up at 45° to the direction of rolling, and so perfectly that the sheet is brittle in this direction, although perfectly ductile in all other directions.

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* Research Laboratories, The General Electric Company, Ltd., Wembley.

FIG. A.—Cross-Rolled Molybdenum Sheet Showing 45° Brittleness. × ½.

[*To face p.* 172.

Bend tests at various angles confirm these results. Annealing does not easily destroy this orientation, and in fact emphasizes the weakness at 45°. I should be interested to know whether Dr. Cook thinks that these results throw any light on his own work. I think it should be possible to correlate his results with the changes in structure which are taking place.

Mr. E. A. G. Liddiard,* M.A. (Member): It is not necessary for me to stress the practical importance of Dr. Cook's paper; the data which have been so carefully collected will be used over and over again for the purposes of reference. In this paper we are also shown the practical means of overcoming the trouble of "earing" in drawn brass. There may still be some doubt in our minds as to whether troubles of earing in brass strip can always be cured by attention to annealing and degree of reduction in the final stages, but Dr. Cook could reassure us on this point if he would tell us to what extent the troubles are, in fact, cured in works practice.

Although there is no doubt from this and earlier work that the formation of ears in drawn cups in α brass is accompanied by directional tensile properties in the strip, I do not think that Dr. Cook has established a linear relationship between those two properties. If we study Fig. 2, we are forced to conclude either that the experimental methods which he has used are not sufficiently sensitive to establish such a relationship or that there is some other uncontrolled variable present. Probably the former is the explanation, but I was rather surprised to see a line drawn through such scattered points.

From a theoretical point of view, it is interesting to have Johnston's statistical method applied in this investigation. It is a laborious method, but the suggestion that preferred crystal orientation accompanies mechanical directional properties is sufficiently important to warrant a good deal of labour to establish it. Dr. Cook has shown that in one sample of 70 : 30 brass sheet exhibiting mechanical directionality there is also preferred orientation of the crystals, and in three other samples which showed no appreciable mechanical directionality there was no appreciable preferred crystal orientation. That suggests a most satisfying explanation of the phenomenon of directionality, but we ought not to be content with just one observation on material showing directional properties. This one observation has entailed some thousands of measurements, but I hope that in the course of time Dr. Cook will be able to carry out one or two tests on other samples which show directionality.

Has Dr. Cook ever observed any directional effects in the Vickers hardness tests on these samples?

Mr. T. H. Turner,† M.Sc. (Member): Dr. Cook, in introducing his paper, referred to wrought iron, and one might, therefore, take his remark as applicable to all materials, but he limits himself, and quite rightly, in the paper to rolled brass strip. If we take sections and not strip, then we must be very careful in speaking of direction, because where a section has a thick part and a thin part the direction of elongation or flow may be quite different from that of rolling. I have taken in what may be regarded as girder sections, with thick heads and thin webs, transverse, longitudinal, and 45° test-pieces, and found very considerable differences in the thick sections and no difference in the thin sections, all in the same piece and within an inch or two of one another. I think that that has not been published, and it is rather an interesting comment, though perhaps not quite applicable to the strip alone.

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† Chief Chemist and Metallurgist, London and North-Eastern Railway, Doncaster.

The **President**: I read this paper with great interest, and with the wish that it had been published in 1915 or 1916 instead of 1937. The problem of ears in cups of brass and cupro-nickel was at that time very worrying, and if in those days we had had the information contained in this paper we should have been saved a great deal of trouble. The difficulties were overcome, but largely by empirical methods, and the want of systematic information was extremely serious at that time. It is curious that it was not until a long time after the War—not, indeed, until 1931 or 1932—that this problem of ears in cups was studied scientifically.

Dr. **Cook** (*in reply*): I have not encountered in brass instances of directionality so pronounced as Dr. Smithells seems to have found in molybdenum. The brass used for the work described in the paper was all rolled in one direction. Dr. Smithells mentioned that with molybdenum annealing did not destroy directionality, but actually emphasized it. This is also the case with brass. For any given set of conditions relating to the temperature of the penultimate annealing operation and the magnitude of the final rolling reduction, the effect of increasing the temperature of the final anneal, as shown by the results contained in Tables IV and V, is to increase the directionality effect. I have deliberately refrained from speculative comment and from discussing the results in any detail for the additional work which I have carried out, subsequent to the preparation of the paper, indicates that there is much more still to be discovered about this interesting subject. As an example I might mention that I have produced strip which yields cups having six ears.

In reply to Mr. Liddiard, there is no doubt that in commercial practice it is possible by attention to rolling and annealing conditions to eliminate directionality from rolled strip to the extent that cups produced from it are substantially free from waviness. This is certainly the case with copper, brasses, and cupro-nickels with which I have had experience, and I imagine that it is likely to be so with other materials. It is not claimed that a precise or quantitative relationship exists, or has been established, between the height of ears on cups and differences in tensile properties of the strip in different directions. The illustration forming Fig. 2 was only included to show that, in a general way, an increase in the directionality effect, as revealed by tensile test results, manifests itself also in the form of more pronounced waviness on the cups, and I think that the results show this very clearly. No evidence has been obtained which would indicate that there is any appreciable difference in the diagonal lengths of diamond pyramid hardness impressions made on brass strip which shows directional effects in tensile test results and on cups cut from it.

Although not related to strip, Mr. Turner's interesting observations indicate yet another application where consideration might usefully be given to the wider subject of directionality in the properties of rolled products.

DISCUSSION AT BIRMINGHAM.

Dr. J. D. **Jevons**,[*] B.Sc. (Member): Controversy (or perhaps we had better say "discussion"), often arises between the supplier and user of drawing- and pressing-quality sheet concerning some condition or effect which the user claims is harmful. All too frequently the supplier adopts a purely defensive attitude. Basing his reply on what, to the non-legal mind, is the amusing formula of the defence in a libel action, he says, in effect: "Don't be silly: this defect of which you complain does not exist, you are imagining it; or, if it does exist, it is negligible; or if it is not negligible it is due to your own tools, certainly not to our sheet; or if it is due to our sheet, send us back the offending metal

[*] Works Metallurgist, Joseph Lucas, Ltd., Birmingham.

and we will replace it and promise that the trouble shall not occur again." Unfortunately no proper investigation is made, the trouble *does* occur again, and no progress results. Dr. Cook has demonstrated admirably how such controversy can be cleared up by properly conducted, and therefore impartial, research. Further, such results, when published, provide information of considerable value which will, or ought to, enable suppliers to improve the quality of their product.

In opening this discussion I shall approach the subject from the point of view of the user, because others here are far more qualified than I am to put forward the point of view of the supplier. Although this paper, and therefore my comments, deal only with directionality attributable to the properties of the crystal, I should like to direct attention to the very harmful directional properties conferred on drawing-quality brass sheet by strings of small crystals, such as are seen in Fig. B (Plate XXIV) often accompanied by β particles in brass of 64 per cent. copper content, or streaks of non-metallic inclusions and lines of phosphorus segregation in steel. Clearly, such strings will possess less ductility (no ductility at all in the case of inclusions in steel) than the surrounding metal, will offer increased local resistance to flow, and may aggravate directional effects arising purely from preferred orientation of the crystals.

Coming to directionality attributable to preferred orientation (and possibly other properties) of the crystals composing an aggregate, Dr. Cook has shown how preferred orientation can influence (1) the tensile properties of an aggregate in sheet form, and, (2) the height and direction (relative to that of rolling) in which ears are formed in a cupping operation. Admirable though the demonstration is, I suggest that a reader of this paper may receive the impression that ears, and even directionality itself, are of merely academic interest. This is most definitely not so, and I will try to indicate, very briefly, the practical significance of directionality to the user of deep-drawing quality sheet.

Directionality manifests itself in three principal ways: (1) thinning of walls, leading in extreme instances to rupture along certain planes in the original sheet; (2) uneven flow in the tools, leading to local thinning or puckering according to the stresses set up, and (3) the formation of ears.

Dealing with the first of these manifestations, the modern tendency in deep-drawing is to utilize the full capacity of sheet for deformation. If, owing to marked directionality, the physical properties of sheet fall below a certain fairly high standard even in certain directions, failure will occur, as is shown in Fig. C, Plate XXV. Here is a simple cup drawn in 0·040 in. thick steel sheet without any interstage annealing. Although at first sight not a remarkably severe draw, this cup fails persistently if the general ductility of the steel falls slightly below the normal value owing to the grain-size being rather small. It is particularly interesting to observe that the splits always occur at approximately 45° to the direction of rolling. The continuous line on the slide marks the direction of rolling of the original sheet, and the dotted lines are marked at 45° to it and through the centre of the cup. The conformity of the splits to the dotted lines is remarkable, and adds practical shop confirmation to the laboratory observations of Dr. Cook with brass, and Phillips and Dunkle with steel, that, after certain rolling and annealing treatment, sheet possesses minimum ductility in a direction lying at 45° to that of rolling.

Although time will not allow me to show other examples of failure attributable to directionality, I can assure you that the one shown in Fig. C is not a freak, but a very typical example. I will go so far as to say that, given sheet of good quality, the success or failure of many severe modern drawing operations depends very largely on the severity of the directional properties existent in the sheet used. The opinion of other users on this view will be interesting.

Regarding the second manifestation, uneven flow in tools, this effect will presumably be most marked in large pressings, such as automobile wings and body panels, with which I have had no first-hand experience. Perhaps some one can enlighten the meeting on this point.

Even in small articles of complicated shape, it is common practice to use blanks of rather irregular shape in an attempt to accommodate localized flow. Bearing in mind that the maxima and minima for various physical properties change their angular relationship to the direction of rolling according to the treatment which the sheet receives toward the end of its travel through the mill, it becomes evident that the present practice of orienting blanks solely with regard to the conservation of metal in the strip form may not produce blanks having maxima and minima lying in the optimum position for the shaping of any given article. Further, since the position of these maxima and minima may vary from batch to batch of sheet, it seems as if it may be desirable to ascertain both the severity and orientation of directional properties in each batch of sheet. Truly a heavy burden on the shoulders of the user unless, due to the assimilation of researches such as that of Dr. Cook, suppliers can reduce the directionality of their sheet to a satisfactorily low value.

The third manifestation, that of ears, is not in itself detrimental unless the height of the ears is considerable and the size of the blank barely adequate. The point is that marked ears indicate the presence of thinning in the walls in line with them. They can, therefore, be regarded as a useful warning to the practical operator that all may not be well with the shells he is producing.

I hope that these remarks will show that the property of directionality can, when pronounced, be a source of real trouble to the user of drawing-quality sheet, and that it is not one of merely academic interest.

Dr. Cook states that, in all his experiments with brass sheet, ears were formed in directions lying at 45° to that of rolling. I think that this is borne out in practice, and Fig. D (Plate XXV) shows typical, but not pronounced, ear formation in a small brass cup. The direction of rolling is indicated by the thick black line, and it will be seen that the ears have formed in the usual 45° direction. Fig. E (Plate XXVI), however, shows a curious example of ear formation, also in a circular brass shell. Again, the black line indicates the direction of rolling, and it will be seen that ears have occurred on only *one* of the 45° planes, and that on the other plane distinct wrinkles have formed. Unfortunately I was unable to obtain a piece of the original sheet, or some interesting directional properties might have been discovered in it.

With steel sheet, the position of ears may be either at 45° or at 0° and 90° in different batches of sheet. Fig. F (Plate XXVI) shows a typical example of the last position, *i.e.* 0° and 90°, the white line showing the direction of rolling. Phillips and Dunkle have shown that the direction of the maxima and minima for certain physical properties of steel sheet varies with the treatment which the sheet received during the final stages of its passage through the mill. I cannot help regretting that Dr. Cook did not make tests in at least one position between 0° and 45°, and also between 45° and 90°, as similar changes comparable to those which occur in steel might have been revealed. Has Dr. Cook any figures, not included in the paper, which throw any light on this possibility?

Gensamer and Mehl have shown that a similar change occurs in the X-ray pictures of steel sheet, and that under certain conditions a six-pole figure is obtained instead of the usual four-pole figure. Can Dr. Cook say whether any comparable phenomena occur with brass, or whether ears *always* form at 45° to the direction of rolling, irrespective of rolling procedure? If so, has he any theory why this should be so?

I would like to suggest that in cold-rolled sheet which has not been annealed, and in which the crystals are therefore elongated, the property of directionality may be due in part to the greater number of crystal boundaries which occur

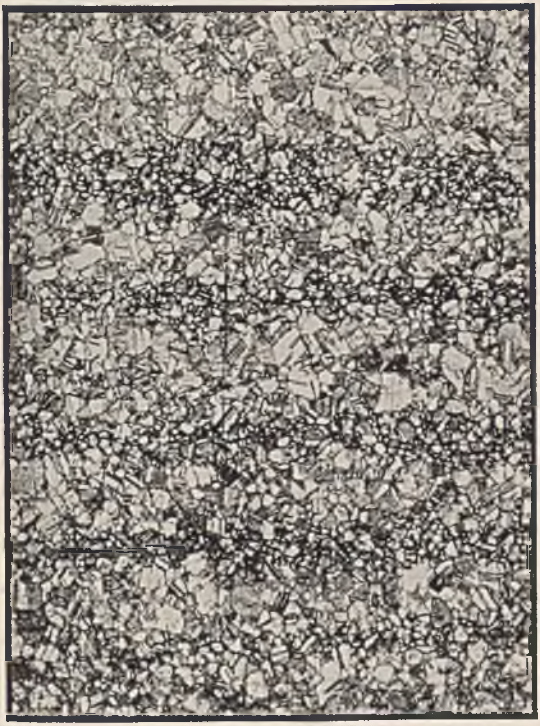

FIG. B.—Stringers of Small Crystals, Accompanied by β Particles, in Brass Sheet of Approximately 64% Copper Content. × 75.

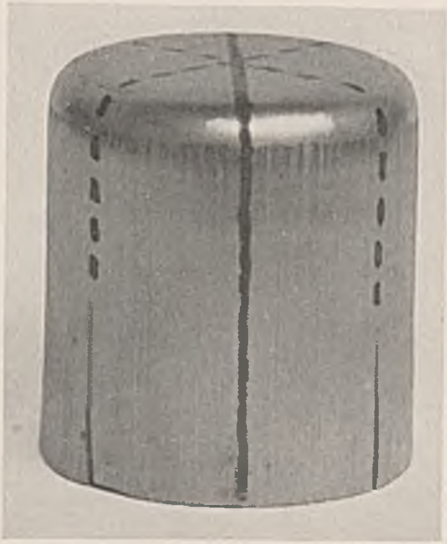

FIG. C.—Steel Cup, Drawn without Interstage Annealing, Showing Formation of Cracks in Directions Oriented at 45° (Marked by Dotted Lines) to the Direction of Rolling (Marked by Continuous Line) in the Original Sheet.

FIG. D.—Ears formed in Brass Cup at 45° to the Direction of Rolling of the Original Sheet (Marked with Thick Line).

FIG. E.—Ears Formed in Brass Cup on One 45° Plane, with Wrinkles on the Other 45° Plane, Relative to Direction of Rolling (Marked with Thick Line).

FIG. F.—Ears Formed in Steel Cup at 0° and 90° to the Direction of Rolling (Marked with Thick Line).

PLATE XXVII.

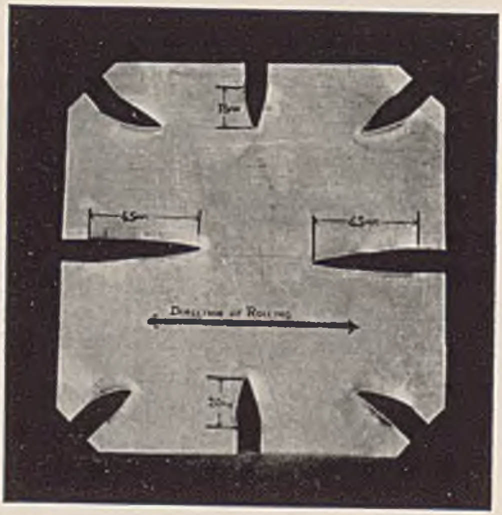

FIG. H.—Directionality in 64% Copper Content Brass Sheet, 0·037 in. Thick, as Revealed by Different Tear Lengths obtained at 0°, 45°, and 90° to the Direction of Rolling (Indicated by Arrow).

per unit length of the aggregate at 90° to the direction of rolling than parallel to it. Our knowledge of the precise atomic structure of crystal boundaries still seems very vague, but I think that it is established that these boundaries offer a greater resistance to slip than the interior of the crystal. Perhaps Dr. Cook and other speakers can give us their views on this possible part cause of directionality.

Statistical examination under the microscope, X-ray pictures, or values obtained on tensile test-specimens cut in a number of directions are seemingly necessary to reveal directionality in a precise manner. Nevertheless, I should like to direct attention to a very simple test, termed the tear length test, which, I believe, originated many years ago in the laboratory with which Dr. Cook is now associated.

A useful refinement of the usual procedure in which a flap 1 cm. wide is cut, gripped with pliers and pulled away from the main sheet, is the use of a slotted rod of 1 cm. diameter on which the flap can be wound back, in the same way as one opens a tin of sardines. (See Fig. G.) With the aid of this rod, sheet too thick to be tested with the aid of pliers can be dealt with easily and, with sheet of any thickness, results tend to be more consistent and reliable than when the crude method of pulling is used.

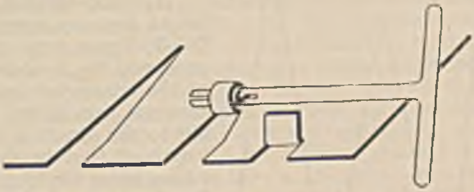

Fig. G.—Diagram Illustrating Tear Length Test by Means of Slotted Winder.

I am not prepared to say exactly what properties the tear-length test measures: probably the combined effect of several, but, if tears are made in different directions in a piece of sheet, one effect produced by directionality is revealed in a very distinct and rapid manner, and I wish that Dr. Cook had made and compared tear length measurements with the other more fundamental measurements that he has made and compared so admirably. If the specimens of sheet still exist, could this be done?

The specimen of brass sheet shown in Fig. H (Plate XXVII) shows tears made at 0°, 45°, and 90° to the direction of rolling. Although this specimen is fairly typical, experience shows that in different sheets the length of tears made at 45° seems to vary in relation to those made at 90° quite appreciably, being less in some and greater in others. In this particular sheet the lengths at 45° and 90° are very nearly equal. Further, in brass as well as steel the *minimum* value may lie in directions *other* than 45° and 90°.

Although I have insufficient evidence to make a definite statement, I am inclined to think that the direction of minimum tear length may not always correspond to that of minimum elongation. It may be that tear length is determined by several properties, including ductility and tenacity, and that for this reason it may be of special significance from the aspect of deep-drawing.

In brass sheet having an apparently equiax microstructure when examined visually, I have known variations up to 300 per cent. to occur between the maximum and the minimum tear length values. Clearly, a variation of this order must indicate directionality of a severity which will influence the behaviour of sheet during deep-drawing operations to an appreciable degree.

Interesting evidence of the effect of directionality is to be found, during the making of tear length tests, in the tendency evinced by tears made in directions other than 0° and 90° to turn into the direction of rolling, a tendency which is often very pronounced. This tendency can be seen in mild form in the 45° tears in the specimen illustrated in Fig. H (Plate XXVII).

I have attempted to discuss directionality from the point of view of the user, and I hope that, with so many suppliers here, this point of view will not be lost sight of. In particular it will be interesting if makers of large pressings will give the meeting their views on the effect of directionality on the flow of sheet in large tools.

Dr. H. W. Brownsdon * (Vice-President) briefly referred to the "tear" test mentioned by Dr. Jevons, and stated that it was 14 years ago since he published some details of this test,† and he showed some lantern slides indicating the directions in which the "tear" test was of interest in the testing of metal strip, that revealing directionality being one of the most important.

He had applied the "tear" length test to a sample of annealed 70 : 30 brass strip giving flat top cups, and Fig. I showed the lengths of the triangular tongues of metal torn out parallel to, at 45° and at 90° to the direction of rolling, the length of that in the direction of rolling being the longest, that at 45° the shortest, and that at 90° intermediate between the other two.

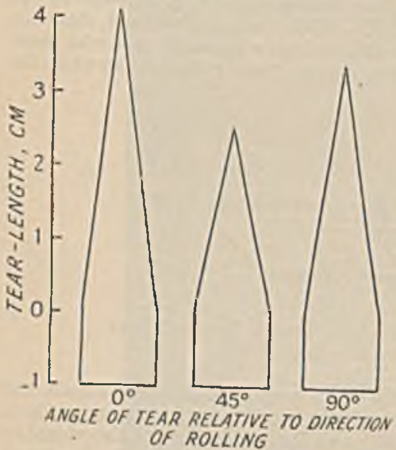

Fig. I.—Angle of Tear Relative to Direction of Rolling.

Dr. Cook had produced evidence to show that these differences in directional properties may be correlated with the frequency of twinning planes, and it was interesting to note if reference be made to Fig. 9 of his paper relating to specimens "A," "B," and "C," that there was an inverse relationship between the frequency of the twinning planes and the tear lengths, the direction of rolling in which the twinning planes were least frequent giving the longest tear length; the direction of 45° in which the twinning planes were most frequent giving the shortest tear length, and the position at 90° was intermediate for both twinning frequency and tear length.

It would be interesting to know whether these directional properties as revealed by the "tear" length test could also be correlated with the structure as revealed by X-ray examination.

Mr. W. F. Brazener‡ (Member of Council representing the Birmingham Local Section): In introducing his paper, Dr. Cook stated that the subject is one of considerable theoretical interest and practical importance. This phraseology considerably under-states the importance of this matter. We in Birmingham know that, on the theoretical side, the subject has created considerable discussion: one, perhaps, would not go so far as to say heated,

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† *Bull. Brit. N.F. Metals Res. Assoc.*, 1923, (9).

‡ General Manager, The Mint (Birmingham), Ltd., Birmingham.

but, nevertheless, it has aroused the keenest interest. That it is of practical importance no one engaged in the production of brass strip will deny. I have in mind at the present time a Company which produces during the course of a month several million cups similar to those which are illustrated in Fig. 1. As is to be expected, there are times when production does not move so smoothly as at others. In accordance with the general trend of modern mass production, all stages of the operations are checked by a costing process. Excessive scrap is very promptly indicated, and this is found to be due, very largely, to the variation in the depth of the cup after pressing. The ideal cup would, of course, press with a level top and require no trimming-up. Prior to the appearance of Dr. Cook's paper it was assumed that the only factors which could govern the amount of trimming-up scrap from the top of the cup were: (1) gauge of metal; (2) grain-size; and (3) the correct size of tools. It is now quite easy to see that the directional properties of the brass are a very serious factor. To my mind the paper does establish that, in practice, what may be regarded as normal process for the production of soft brass strip gives relatively the best results for pressing operations, that is to say, with annealing temperatures of approximately 625° C. with reductions in the neighbourhood of 50 per cent. The paper further emphasizes the importance of control of intermediate processes in the production of soft brass strip. Too often manufacturers may neglect the intermediate processes and be content only with consideration of the final annealing temperature. In the paper a grave warning is given that something considerably further than this is required if satisfactory material is to be obtained. Perhaps it may be mentioned here that the smallness of ears on cupping is not always a measure of the suitability of soft brass for any particular operation. One may have to consider, amongst other things: (1) the depth of the cup required; (2) its shape; (3) whether it is essential to have a completely smooth dome. There are a multiplicity of questions which immediately come to mind after a close study of this paper. A few that have occurred to me are:

(1) Is it likely that any treatment prior to the penultimate annealing will influence the directional properties? For instance, is there any difference between brass which is primarily hot-broken-down as compared with that which receives cold-rolling from beginning to end? Also, is any serious over-heating at any intermediate annealing stage likely to affect the final product?

(2) Are metals or alloys which have more plastic properties than brass likely to be affected in a manner similar to that indicated in the paper? I have in mind, particularly, soft copper which may be used for similar purposes.

(3) In the case of cups which are required to be subjected to deep-drawing and have to undergo an intermediate annealing, what is the effect produced on brasses which have originally: (*a*) pronounced directional properties; and (*b*) no directional properties?

(4) A further question which comes to mind is whether a long-time annealing at a low temperature to produce a large grain-size would remove directional properties where, as is indicated in the paper, the short-period high-temperature annealing leaves pronounced effects.

R. G. Johnston * (Member): As the person more or less responsible for the introduction of statistical methods for showing directionality in the microstructure of annealed materials, I am glad to express my delight at the wonderful results that Dr. Cook has achieved by them. He has carried this

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* Midland Laboratory Guild (1928), Ltd., Birmingham.

work much further than I did, and has been rewarded, very rightly, by results hidden from me.

In my own work in 1934 I connected the type of plot I termed bi-modal with the phenomenon of "ears" on cups. Dr. Cook's plot of his specimen D is clearly bi-modal, with one maximum at 0° and one at 90°. I think that measures of "maximum diameters" such as I used in my work can be regarded also as fundamentally related to the inner structure of the grain. I have often proposed to regard the classes of minimum frequency (avoided directions) rather than those which are preferred, as these are often much more definite. In Dr. Cook's specimen D the groups of avoided classes include 10 out of 18 classes (55·5 per cent.) with only 36·75 per cent. of frequencies in them.

Dr. T. **Lloyd Richards**,* B.Sc. (Member): I have recently had an opportunity to study X-ray photographs of materials such as those considered in this paper. The results afford an interesting confirmation of Dr. Cook's observations on the correlation of the directionality in mechanical properties and frequency of twinning orientation, with ear formation. X-ray photographs were kindly taken by Messrs. Stephen and Barnes, of the Philips Industrial X-Ray Department, of samples of 70 : 30 brass strip produced by the rolling and annealing treatments detailed in Table A.

TABLE A.

Sample.	Penultimate Annealing Temperature, ° C.	Final Reduction, Per Cent.	Final Annealing Temperature, ° C.	Produced Cups Having:
555	500	50	500	No ears.
947	900	40	700	Four ears at 45° to the direction of rolling.

X-ray photographs were taken of these samples, employing cobalt radiation and using back-reflection and Debye–Scherrer cameras with the X-ray beam at normal and at glancing incidence, respectively. Reproduction of these photographs are shown in Plate XXVIII.

A specimen of polycrystalline 70 : 30 brass with a random orientation of the crystals will give reflections of the characteristic K_α doublet, and the K_β line of cobalt at the planes, and making the angles with the incident beam indicated in Table B.

All the possible reflections are recorded on the two photographs taken with sample 555, the first eleven appearing on the Debye–Scherrer photograph and the remaining three on the back reflection photograph. The grains appear to be large enough to produce individual spots, but there is an even distribution of spots on the rings or lines in both pictures. This indicates that sample 555 has grains of the order of 0·02 mm. which are orientated at random.

When comparing the photographs of the two samples it is noticed that in each case the shots are distinct with no evidence of distortion of the crystals; also there are fewer but larger spots on the photographs of sample 947. This means that both samples are fully annealed whilst the grain-size is bigger in sample 947 than in sample 555. Further, it is observed that some of the reflections in the photographs of sample 947 are missing.

In the back-reflection photograph of this sample the rings produced by the reflection of the K_α doublet at the (004) plane are entirely missing. In the Debye–Scherrer photograph it is seen that the central portions of the line

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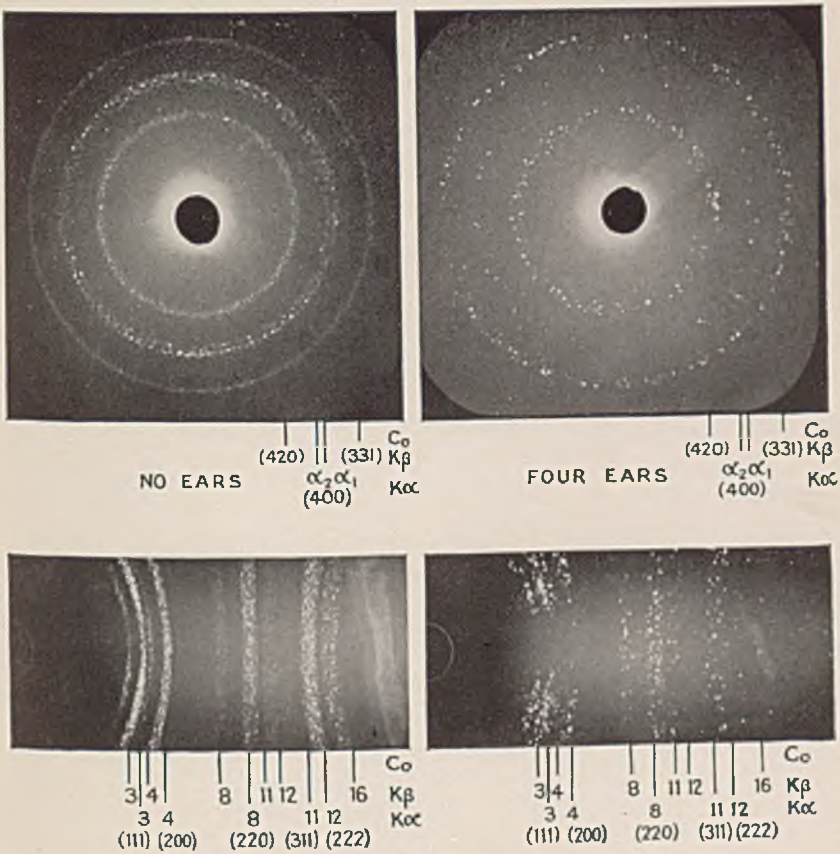
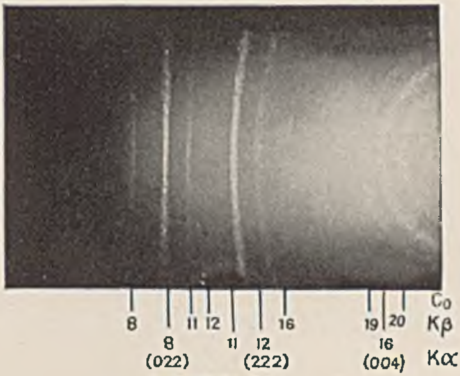


FIG. J.—70 : 30 Brass.

[*To face p.* 180.

PLATE XXIX.



ANNEALED
NO DIRECTIONALITY

NOT ANNEALED
SHOWING PREFERRED ORIENTATION
(110) PLANE IN THE SURFACE

ANNEALED
SHOWING PREFERRED ORIENTATION
(100) PLANE IN THE SURFACE

FIG. K.—70 : 30 Brass.

produced by the reflection of the K_β line and K_α doublet at the (111) and (002) planes are absent, also that the reflection of the K_α doublet at the (222) plane is missing, and, further, there is an increase in intensity in the central portion of the line produced by the reflection of the K_α doublet at the (022) plane.

These observations suggest that for the sample 947 the (100) plane is in the plane of the strip with a (100) direction in the direction of rolling. With such an orientation of the crystal planes, the octahedral or (111) planes which are the slip planes meet the (100) planes in the face of the strip at 45° to the direction of rolling and are also in a position for easy slip in the tensile test samples taken at 45° to the direction of rolling. The observed minimum tensile strength and maximum ductility of the brass strip at 45° to the direction of rolling, and the production of cups having ears in these directions are thus explained. A minimum frequency of twinning directions would also be expected in these directions for crystal growth can take place on the octahedral planes, which meet the face of the strip in these directions without twinning.

TABLE B.

Reflecting Plane.		Radiation.	Angle between Reflected Beam and Incident Beam.	
(*hkl*)	$h^2+k^2+l^2$			
(111)	3	K_β	44° 48′	Recorded on the Debye–Scherrer photograph.
(111)	3	K_α	50° 4′	
(002)	4	K_β	52° 12′	
(002)	4	K_α	58° 34′	
(022)	8	K_β	77° 4′	
(022)	8	K_α	87° 26′	
(113)	11	K_β	93° 46′	
(222)	12	K_β	99° 16′	
(113)	11	K_α	104° 12′	Recorded on the back-reflection photograph.
(222)	12	K_α	115° 27′	
(004)	16	K_β	123° 20′	
(313)	19	K_β	147° 4′	
(004)	16	K_α	154° 0′	
(420)	20	K_β	159° 24′	

It should be pointed out that the orientation observed in the present instance, that is, in the case of cold-rolled brass strip which has been subsequently annealed is different from any of those which have been observed by other workers for metals of face-centred cubic structures which have been cold-rolled without subsequent annealing. When metals having a face-centred cubic structure are cold-rolled without subsequent annealing, it is usual to find either the (112) or (110) planes in the plane of the strip with the [111] or [112] direction in the direction of rolling, respectively.

Apparently in the present case *re-orientation* as well as recrystallization had taken place on annealing. This point was of sufficient interest and importance to investigate further. For this purpose Dr. Wright of Birmingham University very kindly allowed his X-ray apparatus to be used.

Debye–Scherrer photographs of samples of 70 : 30 brass strip in the annealed and cold-rolled condition were taken, using cobalt radiation. Three photographs were taken of each specimen with the X-ray beam, normal, glancing, and at 45° to the plane of the strip and the rolling direction. The samples had the treatments indicated in Table C.

These photographs indicated that in the case of the cold-rolled sample which was not subsequently annealed the (110) plane was in the face of the strip, whilst for the sample 947 the (100) plane was in the face of the strip. Reproduction of the photographs taken with the three samples and with the X-ray beam at 45° to the plane of the strip and direction of rolling are given in Plate XXIX. The different orientation of the crystal in samples 940 and 947 can be observed readily from the photographs.

TABLE C.

Sample.	Penultimate Annealing Temperature, ° C.	Reduction, Per Cent.	Final Annealing Temperature, ° C.
555	500	50	500
940	900	40	Not annealed
947	900	40	700

Mr. A. PINKERTON * (Member): Some years ago, after reading the papers by Phillips and Samans on 90 : 10 brass and by Bassett and Bradley on cupro-nickel, I carried out some similar experiments on 70 : 30 brass. Unfortunately I was not in a position to produce cups from the strip and had to be content with determining the tensile strength and elongation. This was done in five directions, *viz.* 0°, 22·5°, 45°, 67·5°, and 90° to the direction of rolling. The results were not very conclusive, but did seem to point to the fact that a low penultimate anneal, a light reduction, and a low final anneal gave the best results. This seemed to work out fairly well in practice, but it is gratifying to know that with a 50 per cent. reduction and a low final anneal one has more freedom with the penultimate anneal.

I should like to ask Dr. Cook which property of the metal he considers most sensitive in showing the presence of directionality, whether it is the maximum stress, the elongation, or the reduction of area. One would think that the elongation or the reduction of area would be the most sensitive, but I notice that in the paper the author has used a function of the maximum stress in plotting the curve in Fig. 2. Some of the tests recorded in Tables IV and V which show a very uniform tensile strength in the three directions tested vary considerably in the elongation and the reduction of area, and a given variation in these tests does not always result in the same amount of earing in the cups. For instance, in Table IV the specimen which had the 550/50/525 treatment gives a maximum difference in the elongation figures of about 14 per cent. of the average values and gives ears on cupping of 0·005 in., while the specimen which had the 550/90/625 treatment gave a maximum difference in the elongation figures of only 10 per cent. of the average values and the height of the ears was 0·022 in. The difference in the tensile strength in the two cases cited is about 2 and 6 per cent. of the average values. It appears to me that it would be difficult to forecast the performance of strip on cupping from the results of tensile and elongation tests only and that actual cupping tests would be the only satisfactory method to use. The distribution of the points in Fig. 2 bears this out to some extent.

After showing the directionality in cold-worked brass of both 64 : 36 and 70 : 30 qualities, Dr. Cook has confined his tests on the annealed metal to 70 : 30. It would have been interesting to have had a similar series of tests on 64 : 36 brass to see if the same conditions apply to this alloy. It would also have been useful to have had a set of tests included on specimens which were given a final reduction of about 35 per cent. as this is the more usual finishing treatment in works practice.

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* Technical Manager, Earle Bourne and Company, Birmingham.

Mr. H. Hayes * (Member): There are still a great many users of rolled brass strip who attribute the production of "wavy" cups to the composition of the material. One instance came to notice when a user, noting the presence of iron on the analysis report sent to him (the figures being well within the usual amount allowed), stated that it was undoubtedly the cause of waviness as he always had the trouble when producing steel cups, and, therefore, iron being a constituent of steel would cause the same trouble if it got into the brass. This may appear a trivial matter, but it is very difficult to combat these ideas. A paper of this type is of great service in dispelling these notions.

The amount of "waviness" that can be considered to be a serious matter naturally depends on the amount of subsequent drawing to be carried out, and the diameter of the cup itself. In the manufacture of clinical thermometer tubes, "waviness" of more than 0·03 in. is a serious matter because of the difficulty of stripping the drawn tube off the drawing punches. The "ears" from the "waves" thin out during drawing to a marked degree and the strippers fail to hold the tube, with the result that it is drawn back into the die with disastrous effects.

During a fairly extensive series of experiments carried out in order to produce brass strip for the manufacture of cups for the production of clinical thermometer tubes, it was found that in order to keep the "waves" less than 0·03 in. it was necessary to give the material thorough soaking anneals from ¼ in. thick downwards. The temperature was kept to 600° C., except for the penultimate anneal which was at 570° C. and the final anneal at 550° C. The amount of soaking time varied, of course, with the weight of charge, but it was never less than 2½ hrs. On one occasion, a batch of material was reported to be giving "wavy" cups at one end of the strip only; it was found to be due to the fact that the furnace door was left slightly open during annealing, at a stage when the strip was 0·120 in. thick. The finished thickness of the material was 0·013 in. so that it will be seen how important it is that the strip is well annealed at a sufficiently early stage.

With regard to the amount of rolling between the penultimate and the final anneal, it was found in these experiments that provided that the reduction was between 30 and 50 per cent. no effect in the directional properties could be traced, and this was also the case whether the rolling was done in light or heavy reductions.

The Author (*in reply*): Before replying to the discussion I wish to say that my attention has recently been directed to another paper † dealing with X-ray evidence of directionality in rolled copper.

Referring to Dr. Jevons's very interesting remarks, I have not, prior to the completion of the work described in the paper, produced or encountered brass strip which yielded cups having ears in any directions other than at 45° to the direction of rolling. Bearing in mind, however, the fact that it has already been quite definitely shown that ears can be produced at 45° and also at 0° and 90° to the direction of rolling in cupro-nickel, and also in steel, according to the rolling and annealing conditions to which the material has been subjected, it would seem conceivable that in brass, in certain circumstances, ears might possibly be formed in directions other than at 45°. With all the strip with which the paper dealt they occurred at 45° and were all more or less of the same height. By further modifications in the rolling and annealing treatments, however, I have since produced strip which has actually yielded cups with six ears. This result should serve both as an indication that there

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* Birmingham.

† A. Phillips and G. Edmunds, *Proc. Amer. Soc. Test. Mat.*, 1929, 29, (II), 438.

is yet much to be learned about this subject of directionality, and also as a timely warning against premature speculation and theorizing. With the material dealt with in the paper I am inclined to doubt if tests in directions between 0° and 45° and between 45° and 90° would have been particularly informative, but this, of course, would not necessarily be so if the conditions of manufacture were appreciably altered.

It is possible, as Dr. Jevons has suggested, that in material in the rolled condition the directionality so induced may, at least in some measure, be associated with the increase in the number of grain boundaries per unit length at 90° to the direction of rolling, but there is evidence, I believe, which would indicate that some measure of preferred orientation in the crystalline aggregate is actually brought about by rolling without subsequent annealing. Dr. Richards, for example, in the course of his remarks has pointed out that X-ray evidence suggests that in brass the (110) plane becomes orientated parallel to the surface of the strip.

Both Dr. Jevons and Dr. Brownsdon referred to the tear test, and I was very interested to learn of the correlation which Dr. Brownsdon had found between tear length and the frequency of twinning orientation. It was difficult to say just what this tear test did measure, but it seemed clear that in some respects it was extremely sensitive and could show very clearly, in some instances, differences which were not revealed with certainty by other methods. The material dealt with in the paper was 0·037 in. thick, which is too thick to be suitable for a comprehensive series of tear tests with the object of attempting to correlate the results with those obtained by other methods. Thinner material, suitable for the tear test, was not very satisfactory, however, for the cupping experiments, or for the determination of tensile strength values, when relatively small differences were being looked for.

In reply to Mr. Brazener, I have no evidence which would indicate that there is any difference in respect of directionality between material which was originally hot broken down before cold-rolling or between material which had been cold-rolled throughout from the cast ingot. Again, I have no evidence which would indicate that overheating in annealing prior to the penultimate annealing would affect the directional properties of the finished strip. Soft copper tended to exhibit directional properties to a more marked and pronounced degree than brass. Without making a strict comparison, which I have not done, it would not be easy to say what the effect would be of intermediate annealing on brass products which had been produced on the one hand from strip free from directional properties, and on the other from strip which had pronounced directional properties. It would probably largely depend on the amount of cold-work to which the product had been subjected and the conditions of the annealing operation. So far as the work covered by the paper went, all the evidence showed that as a rule for any given set of conditions, relative to the temperature of the penultimate anneal and the magnitude of the last rolling reduction, the tendency towards the development of directional properties was reduced as the temperature of the final anneal was decreased.

The remarks of both Mr. Johnston and Dr. Richards are welcome contributions to the discussion and I am pleased to note that by X-ray examination of some of the materials which I have used in the investigation Dr. Richards has been able to show that, in annealed strip showing directionality, there was a preferred orientation of the crystal planes which would account for the formation of four ears on cups at 45° to the rolling direction, and for the fact that the minimum tensile strength, maximum elongation, and minimum twinning frequency all occurred in this direction.

I am interested to know that Mr. Pinkerton has carried out some tensile test and elongation measurements on samples cut at 22·5° and 67·5° as well as at 0°, 45°, and 90°, but I am not surprised that in the absence of other data the results did not appear to be very conclusive. For indicating the existence of directional properties in strip an actual cupping test would probably be more informative than a tensile test and it would have, moreover, the advantage of being much more easily and quickly carried out. One would not expect the conditions controlling the development of directional properties in 64 : 36 brass to be greatly different from those for 70 : 30 brass and in order to keep the amount of work involved in the investigation within reasonable bounds tests on 64 : 36 were not carried out, and the number of different annealing temperatures and rolling reductions was, for the same reason, limited to those described in the paper. As Mr. Hayes has pointed out, the practical importance of ears depends very largely on the nature and size of the product, and the extent to which it is subsequently drawn, for, in addition to the stripping difficulty, to which he has referred, a pronounced earing effect involves the necessity of increasing the amount of metal cut away in trimming. The question of the presence of iron or any other impurity, or deliberately made addition, being responsible for waviness on cups, to which Mr. Hayes referred, can be readily disposed of, as was done in the work described in the paper, by producing from the same original ingot, strip which yielded flat topped cups, and strip which yielded wavy or eared cups, by varying the rolling and annealing conditions.

A STUDY IN THE METALLOGRAPHY AND MECHANICAL PROPERTIES OF LEAD.*

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By BRINLEY JONES,† M.Met., MEMBER.

SYNOPSIS.

Reference is made to the tendencies to structural change in rolled lead at ordinary temperatures, and it is stated that mechanical tests can have little significance unless these changes can be controlled or prevented.

Experiments dealing with the relationship between deformation, grain growth, and recrystallization in "as rolled" structures are described, and it is shown that grain growth develops as a result of the critical straining of very refined "as rolled" structures. Lead of "medium" refinement is found to be immune from grain growth and to be affected only by strains severe enough to cause recrystallization. The structures which result from grain growth and recrystallization, respectively, after rolling, are shown to be different in type. In the former, the grains are well defined, infrequently twinned, and often associated with intercrystalline cracking; in the latter they are confused and repeatedly twinned.

Heavily twinned, recrystallized structures have been found, from experience, to be desirable, and reference is made to large-scale experiments dealing with the production, on a commercial basis, of sheets having such structures.

INTRODUCTION.

THE studies to be described in this paper are concerned mainly with commercially pure lead in the rolled form, although some of the conclusions derived are equally applicable to extruded products.

There is sometimes a tendency to overlook the fact that lead, one of the softest metals, is largely used as a material for engineering construction. Its mechanical properties, therefore, however much in contrast they may stand from those of the more rigid metals, call for assessment. The short-comings of conventional methods of testing are well-known, and whether figures derived from tensile, hardness, impact, fatigue, and creep tests can always be usefully interpreted is open to question. Provided, however, that a metal possesses, under the stresses and strains of service, the property of mechanical permanence, it will not be denied that information of substantial value can be derived from such tests. During the last few years the mechanical properties of lead have received increasing attention, and a large

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* Manuscript received December 3, 1936. Presented at the Annual General Meeting, London, March 10, 1937.

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accumulation of data, expressed in terms of ultimate stress, hardness, fatigue-resistance, and creep rates is available. Unfortunately, however, lead is an unstable metal in so far as it only possesses the property of permanence in a qualified way. Lead may be lacking, therefore, in the essential feature which gives ordinary test results any significance. Changes in the metallographic structure of lead under normal circumstances of use are common, and our experience has shown that such changes can proceed to extreme degrees. For example, Figs. 5 and 6 (Plate XXXI) illustrate two samples of chemical lead sheet. Both pieces were rolled originally from the same ingot and were stored in the same place for the same time at room temperature. No particular precautions were taken, however, in the handling of these pieces, and a chance examination, some 2 or 3 weeks after rolling, revealed an extraordinary difference in structure between the two. Both samples had lost their original " as rolled " structures, but it is known that recrystallization had occurred in the one case and what has been called " exaggerated grain growth " [1] in the other. Tensile test-pieces, cut from these specimens, when strained at a rate of 0·09 in. /minute, gave results as follows :

	Ultimate Stress, Lb./in.^{2}.	Elongation on 3 in., Per Cent.
" Recrystallized " structure .	2000	60
" Coarse " structure . .	1350	46

In Figs. 1 and 2 (Plate XXX) are shown photographs of the test-piece cut from the coarse-grained metal, before and after straining. It must be obvious, on account of the unequal distribution of strain alone, that structures of this type are extremely weak and totally unsuited for constructional purposes. The percentage of service failures associated with such conditions makes it necessary that any coarseness in structure should be avoided wherever possible.

Since changes in structure imply changes in mechanical properties, it is clear that mechanical tests, when applied to lead, may measure properties which are only temporary, and quite secondary to more fundamental characteristics. Appreciation of the more fundamental values, which govern test figures, would provide a sounder basis for understanding the true nature of the metal.

In this paper it is maintained that it is misleading, in the case of a metal in which structural changes can easily occur, to rely on figures derived from mechanical tests unless these structural changes can be controlled or prevented. The experiments to be described are the result of an attempt to discover whether it would be possible to assess and control the mechanical properties of lead with greater certainty by first understanding the underlying factors upon which these properties depend.

MICROSTRUCTURE OF LEAD.

The microexamination of lead usually reveals that type of structure which would be expected of any pure metal, *viz.* a simple polyhedral structure. A typical field is illustrated in Fig. 7 (Plate XXXI).

Initially, at any rate, a structure such as this is affected by quick and moderate strains in a manner typical of any pure metal. Fig. 8 (Plate XXXI), for example, illustrates the development of slip-bands resulting from compression of material similar to that shown in Fig. 7. It is a common experience that the surface of lead will roughen when strained to an extent depending on its coarseness of grain. It is usually considered, however, that lead cannot be permanently hardened by cold-work; it will in fact, if sufficiently strained, recrystallize Fig. 9 (Plate XXXII), for instance, was observed in less than 10 minutes in spontaneously and rapidly at ordinary temperatures. The field shown after a scratch in the form of a cross was marked on the metal surface.

Since lead is expected to undergo strain in practice, the readiness with which structural change can occur is a characteristic of the first importance. It is in this very particular of structural instability that lead begins to diverge, in practice, from the other commonly used constructional metals, and a specification dealing with its mechanical properties could only be devised on the basis of a full understanding of the laws underlying this instability.

"ABNORMAL" STRUCTURES IN LEAD.

As stated above, the microstructure of lead reveals, in the ordinary way, a simple polyhedral structure. Much improved technique in the polishing and etching process together with a careful scrutiny of many hundreds of specimens have shown that this is by no means always the case. Figs. 10–12 (Plate XXXII) are photographs from various samples of commercially pure lead sheet, all of which contained more than 99·98 per cent. lead and were polished and etched in the usual way.

The structures are the reverse of simple, and seem to the author to be unique. It is not proposed, here, to analyze the peculiar patterns developed in these different sections—which are all manifestations of recrystallization and grain growth—or to discuss their origin. The structures were chosen because they seemed to illustrate in a new way the difficulty of appreciating the physical nature of lead without bearing its metallographic condition continually in mind.

GRAIN GROWTH AND RECRYSTALLIZATION.

Before describing further experimental work it is considered desirable to distinguish, yet again, between the conceptions of recrystallization and grain growth. A study of the research work being carried out on lead and its alloys will show that confusion still exists owing to lack of clear distinction between these two terms. It is difficult to improve on the definitions given by Carpenter and Elam[2] 15 years ago, quoted below:

"By recrystallization, the authors mean the complete re-orientation of a crystal or a group of crystals. The new arrangement starts from new centres and is quite independent of the old system of orientation. This always gives a refined structure."

"By crystal growth, the authors mean the re-arrangement of certain crystals in a crystal aggregate to conform with the orientation of certain other crystals, during which process the latter increase in size by addition of re-orientated material at the same time as the former decrease in size by the same amount."

In Fig. 3 (Plate XXX) is shown a specimen of lead sheet which was treated to illustrate these processes. This sample, carefully preserved in an unstrained condition after leaving the rolling mill, was severely bent in the middle, leaving the ends undisturbed, re-straightened, and subsequently held at a temperature of 50° C. for 12 hrs. The original "as rolled" structure of the extremities of the piece remained unchanged. In the centre, where deformation was severe, complete recrystallization occurred and a new, relatively refined, structure appeared. Separating these two structures were regions in which true grain growth occurred.

EXPERIMENTAL WORK.

Usually, immediately after rolling* commercially pure leads (99·99 per cent. lead) possess structures of extreme refinement. A typical example is illustrated in Fig. 4 (Plate XXX). It has been somewhat surprising to discover that not only are "as rolled" structures usually initially refined, but that, provided that samples are completely preserved from further deformation, such refined structures are apparently indefinitely retained. Not only have specimens kept under observation for more than 1 year shown no sign of structural change, but they have remained stable when exposed for several weeks

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* *I.e.* rolling under the conditions of temperature and reduction obtaining under industrial conditions.

to a temperature of 50° C. Deformation after rolling is an essential precursor, apart from heat-treatment,* to structural change.

In service, however, lead sheet is invariably coiled before leaving the works, and a pure " as rolled " structure is rarely seen.

In order to arrive at some quantitative idea of the relations between deformation, grain growth, and recrystallization, the following experiment was carried out.

Ingots of lead 20-lb. in weight and 2½ in. thick, were cast and cold-rolled into sheets of ⅛ in., the material being 99·99 per cent. pure. From the flat parts of the sheets, strips 6 in. long by 1 in. wide were carefully sawn. Extreme precautions were taken to protect the metal from even the slightest of strains after rolling. Five pieces were selected, inserted in a tensile machine, and elongations of ½, 1, 2, 4, and 6 per cent. applied. After storing for 24 hrs. at 50° C., these specimens together with a sample in the " as rolled " condition were etched, and the various structures resulting from the different treatments are illustrated in Fig. 13 (Plate XXXIII). The " as rolled " sample, apart from slight incipient grain growth along the sawn edges, retained its original structure unchanged. In the ½ per cent. elongated piece, considerable grain growth occurred, but areas of the original refined structure remained unabsorbed. In the 1 per cent. elongated specimen the " as rolled " structure was completely obliterated by coarse grains. The effect of 2 per cent. elongation was to initiate recrystallization, whilst 6 per cent. elongation produced an entirely new and relatively refined recrystallized structure. It is clear from this experiment that recrystallization and grain growth in lead are governed by the same laws as in aluminium, iron, &c., and there is no need to dwell further on the classification and mechanism of formation of the structures since the subject has already received much attention from other workers, notably Carpenter and Elam,[2] Smithells,[3] and Jeffries.[1] It is of the very first importance to realize, however, that the structural changes initiated by deformation proceed, in the case of lead, at moderate or even room temperatures. It follows, therefore, that, whereas phenomena which occur in iron, for example, might be considered to some extent of scientific interest only, they are in lead a matter of immediate and everyday practical concern.

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* It has been found that, in dealing with sheet rolled from the usual brands of virgin pig and refined pig leads, exposure to temperatures up to approximately 65° C., accelerates structural changes which would normally occur at room temperatures, but does not alter their nature or initiate new changes. The effect of temperatures much in excess of 65° C., however, is to introduce fresh factors, *e.g.* two specimens of sheet which, after treatment at 50° C. might emerge with refined and coarse structures, respectively, might after treatment at 100° C. both develop medium structures.

After the above experiment, several attempts were made to produce the same sequence of structures in extruded metal. These were all unsuccessful until it was realized that grain growth could only proceed in structures initially of extreme refinement. A 90-lb. billet of refined pig lead, to which 0·006 per cent. antimony had been added, was accordingly extruded cold into strip 1½ in. wide by ⅛ in. thick. The resulting structure was comparable in refinement to that of rolled sheet. Lengths were carefully cut, preserved as much as possible from further strains and elongated ½, 1, 2, 4, and 6 per cent., in the same manner as previously described. After storing for 24 hrs. at 50° C., the samples were etched and photographed. In Fig. 14 (Plate XXXIV) it is seen that in the ½ per cent. elongated specimen huge grains developed by pure growth; 6 per cent. elongation, as before, produced a relatively refined and completely recrystallized structure.

The experimental difficulties involved in cutting test-pieces and applying small amounts of tensile strain were almost insuperable, and no great accuracy can be claimed for the lower elongation figures quoted. In order to obtain more certainly and conveniently information which could be directly related to works' practice, numerous experiments were carried out using the following technique. Small ingots of various leads were rolled into strips of ⅛ in. thickness, and from the flat parts of each strip 8 in. lengths were immediately cut. Fifteen minutes after rolling different degrees of strain were imparted to the pieces by bending them around radii of 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, and 1¼ in., respectively. Figs. 15, 16, and 17 (Plate XXXV) are photographs of three specimens selected from a series of bent strips rolled from ingots of Broken Hill lead. The material was, as usual, stored for 24 hrs. at 50° C. after straining, and the strips, after examination, were flattened, etched, and immediately photographed. In Fig. 15, a strip bent around a 12 in. radius, the strain was insufficient to cause structural alteration with the exception of limited growth of two or three grains. Substantially the structure remained in the "as rolled" condition. In Fig. 16, a 6 in. bend sample, coarse grain growth developed; whilst bending around a radius of 1¼ in. produced, as shown in Fig. 17, complete recrystallization with a relatively refined structure. It is almost incredible that the same metal, after such simple treatments can assume such diverse forms.

STABILITY OF STRUCTURE IN LEAD.

The ultra-coarse structures mentioned in the previous pages were all developed as a result of slight deformation of metal which was in a state of extreme grain refinement. In spite of repeated attempts,

PLATE XXX.

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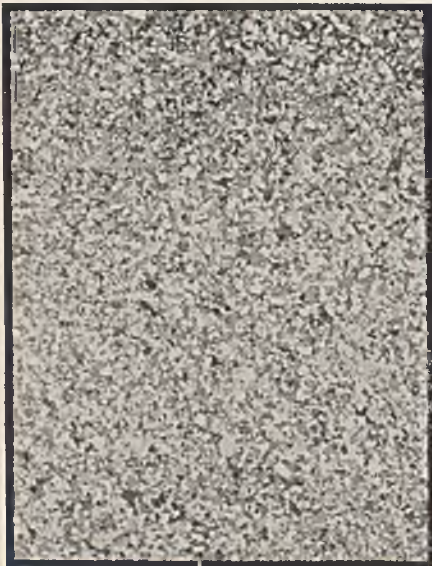
FIG. 1.—Test-Piece Cut from Coarse-Grain Lead Sheet. × 1. Reduced by $\frac{1}{3}$.
FIG. 2.—Test-Piece After Pulling in Tension. × 1. Reduced by $\frac{1}{3}$.
FIG. 3.—Lead Sheet Showing "As Rolled" Structure, Grain Growth, and Recrystallization. × 1. Reduced by $\frac{1}{3}$.
FIG. 4.—Lead Sheet: Refined "As Rolled" Structure. × 1. Reduced by $\frac{1}{3}$.

[*To face p.* 192.

PLATE XXXI.



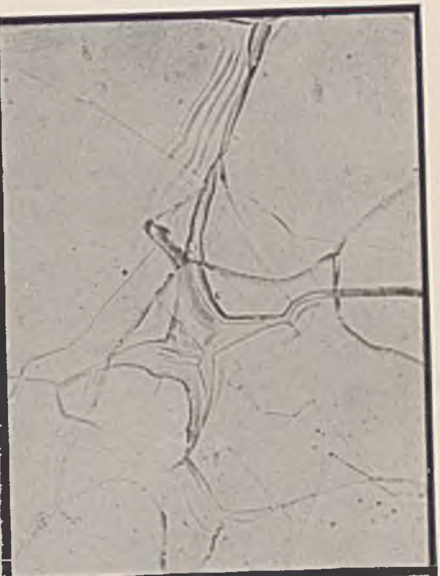
6

8

FIG. 5.—Lead Sheet : Recrystallized. × 1.
FIG. 6.—Lead Sheet : Grain Growth. × 1.
FIG. 7.—Lead : Polyhedral Structure. × 100.
FIG. 8.—Lead : Slip Bands. × 100.

PLATE XXXII.


9


10


11

FIG. 9.—Spontaneous Recrystallization. × 100.
FIG. 10.—" Abnormal " Structure. × 50.
FIG. 11.—" Abnormal " Structure. × 50.
FIG. 12.—" Abnormal " Structure. × 100.

PLATE XXXIII.

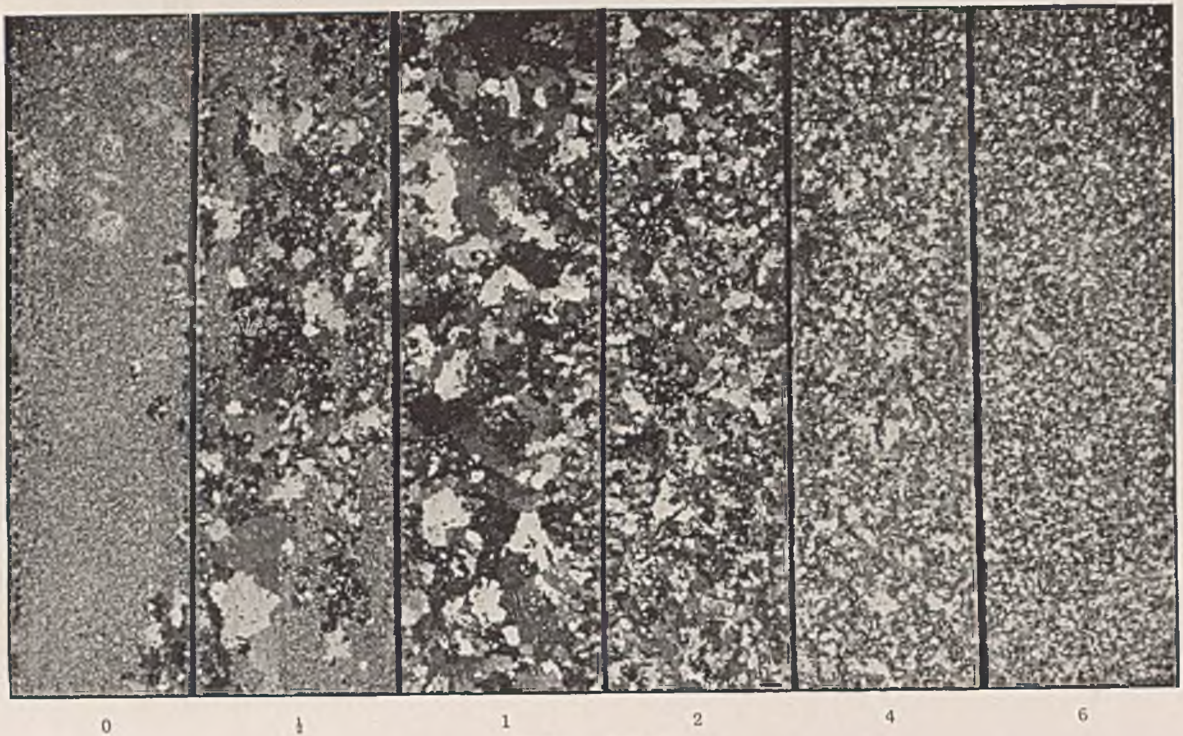


FIG. 13.—Rolled Lead; Strained and Stored 24 Hrs. at 50° C. × 1.

PLATE XXXIV.

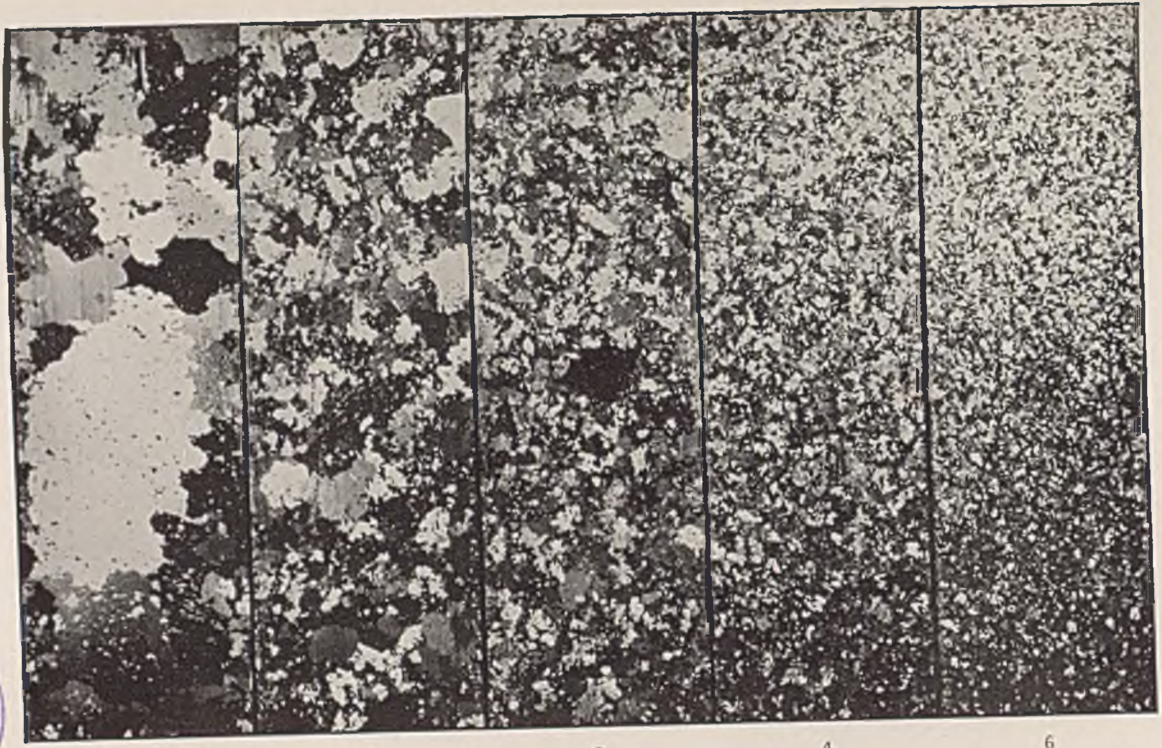
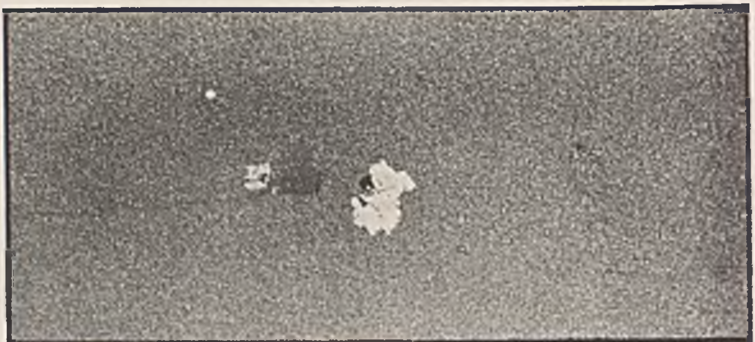


FIG. 14.—Extruded Lead; Strained and Stored 24 Hrs. at 50° C. × 1. Reduced by $\frac{1}{6}$.

15



16

17

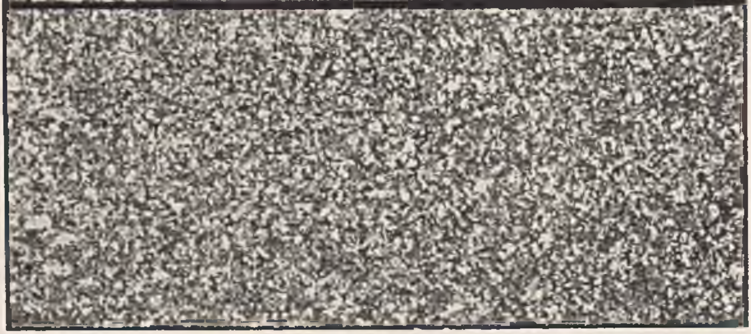
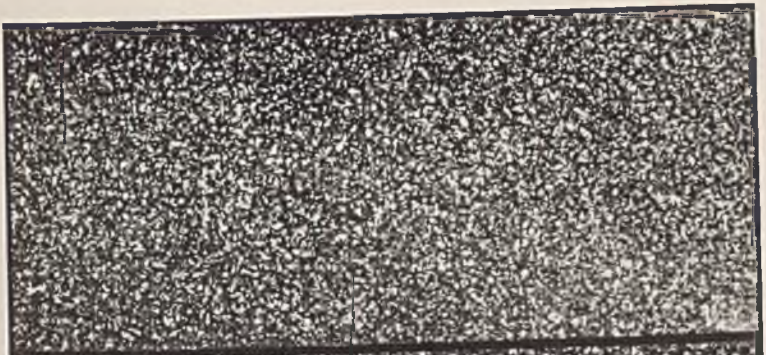
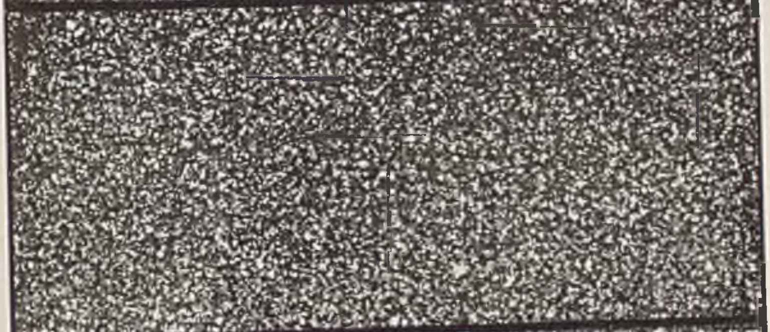


FIG. 15.—Rolled Lead : Bent and Stored 24 Hrs. at 50° C. 12 In. Bend. × 1.
FIG. 16.—Rolled Lead : Bent and Stored 24 Hrs. at 50° C. 6 In. Bend. × 1.
FIG. 17.—Rolled Lead : Bent and Stored 24 Hrs. at 50° C. 1¼ In. Bend. × 1.



18



19

20

FIG. 18.—Rolled Lead: Recrystallized, Then Bent and Stored 24 Hrs. at 50° C. 12 In. Bend. × 1.

FIG. 19.—Rolled Lead: Recrystallized, Then Bent and Stored 24 Hrs. at 50° C. 6 In. Bend. × 1.

FIG. 20.—Rolled Lead: Recrystallized, Then Bent and Stored 24 Hrs. at 50° C. 1¼ In. Bend. × 1.

PLATE XXXVII.

21

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FIG. 21.—Grain Growth in Service. Intercrystalline Cracking. × 2 Diam.
FIG. 22.—Recrystallized Structure. × 5 Diam.

it was never found possible to produce grain growth of this type other than by beginning with refined structures. The sequence of structures, for example, as illustrated in Fig. 14 has never been obtained from hot extruded lead. In view of the fact that the mechanical properties of coarse-grained lead are completely undesirable for almost any purpose, the practical implications of the above statements are of great importance. It is considered, therefore, well worth while to record one of the experiments conducted in the light of this finding.

Ingots of chemical lead of the same quality used for the bending experiment reported were rolled and 8 in. lengths were cut. In order to confer on the material a structure of moderate, in place of extreme refinement, 10 of the lengths were elongated by 4 per cent. in a tensile machine and treated for 1 hr. at 50° C., *i.e.* the metal was completely recrystallized. The specimens were then bent severally around radii of 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, and 1½ in., respectively, and held for 24 hrs. at a temperature of 50° C. The result of this experiment was remarkable, for with two exceptions every sample retained its original structure unchanged. Only the strips bent around the 3 in. and 1½ in. radius showed any alteration. The deformation in these instances was, as would be expected, severe enough to destroy the original structure and promote, by recrystallization, fresh ones exactly similar in type but slightly coarser. Figs. 18, 19, and 20 (Plate XXXVI) are photographs of the 12, 6, and 1½ in. bends, respectively, selected from this series. In order to give full opportunity for any further tendencies to grain growth to proceed, the complete series was maintained at 50° C. for another 4 days. The 6 in. bend specimen was then inserted in a steam oven and kept at a temperature of 100° C. for 1 month; subsequently all samples were kept under observation, at room temperatures, for 8 months. None of these treatments had any effect.

The conclusions which appear to be warranted from this and numerous other similar experiments carried out on rolled and extruded metal are:

(1) Lead, when subjected to those critical degrees of deformation which are liable to cause exaggerated grain growth, is immune from such processes, provided the initial grain-size is above a certain minimum.

(2) Structures in which, at ordinary temperatures, deformation does not promote grain growth, are only affected by strains sufficiently severe to initiate recrystallization. Such structures then recrystallize and are replaced by others similar in type: these in their turn also resist grain growth, provided that strains are not severe enough

to reproduce grain refinement, comparable to that resulting from cold-rolling or cold-extrusion.

As a guide to those who are interested, from a practical point of view, attention at this point is directed to two further photographs. Fig. 21 (Plate XXXVII) shows (×2) a specimen of lead sheet in which grain growth had proceeded in service and which had subsequently failed through intercrystalline cracking. Invariably in such cases, the grains are distinctive, individual, and infrequently twinned. This constitutes an excellent example of what is undesirable and avoidable. In comparison, a sample of a " medium " recrystallized structure (×5) is illustrated in Fig. 22 (Plate XXXVII). Examination shows the grains to be confused, interlocking, heavily twinned, and different in character from those developed as a result of grain growth. Experience has taught us that conditions must be abnormally severe to induce intercrystalline cracking in structures of the confused type—irrespective of their degree of coarseness or refinement.

The question of the effects of small amounts of impurities on the grain growth and recrystallization of lead has not been forgotten during the course of the present investigation. A study of the widespread literature dealing with this aspect, however, fails to reveal much appreciation of the effects of impurities from the point of view of what influences they may have on the wholesale structural alterations which are possible in lead during the ordinary routine of large-scale production and use. Although a great deal of work remains to be done, it is known, for example, that additions such as 0·05 per cent. tin and 0·05 per cent. antimony do not prevent the coarse grain growth which results from the slight straining of refined " as rolled " structures.

DISCUSSION OF RESULTS.

From the point of view of both the user and manufacturer of lead products, an ideal state of affairs would exist if it were possible to provide at will material (*a*) of any desired structural type, and (*b*) which would resist radical transformation under normal conditions of service. It would then no doubt be found that lead of medium grain-size would be used. For one thing, the advantages usually secured by conferring upon metals structures of extreme refinement tend to be offset in the case of lead and lead alloys by a serious decrease in creep resistance, and it is certainly difficult to imagine any important application where coarse structures would be preferred. It has been emphasized that structures of medium grain-size, recrystallized after rolling, such as that illustrated in Fig. 22, possess surprising stability, since they are not susceptible to grain growth and can only be destroyed by strains severe enough to promote recrystallization. The author has never known a case of service failure associated with structures of this type.

In the manufacture of lead sheet, ingots of from 10 to 12 tons in weight and of the order of 6 in. thick are usually hot-rolled into slabs about 1 in. thick. The slabs are then sheared into sections which are afterwards separately rolled into sheet of required gauge with no further re-heating. The finished sheets are coiled into rolls before leaving the mill bed.

It is possible, therefore, that the finishing temperature of the first sheet rolled from any particular ingot may be considerably higher than that of the last sheet. If a mill has been working continuously and rapidly, for a long period, the finishing temperatures of all sheets might be considerably above atmospheric. Certain of the strains involved in coiling are severe enough to destroy refined "as rolled" structures, even when both metal and rolls have been cold. Hence, it is probable that much of the material produced in practice possesses, at the outset, a structure immune from exaggerated grain growth. After coiling, sheets remain comparatively undisturbed for varying periods—and of course at various temperatures depending on the weather—until they are uncoiled by the user. It will be clear from what has been said, that none of these treatments will be deleterious to metal which was initially immune from grain growth. It is possible, however, to conceive a peculiar combination of circumstances in which a roll of sheet, when received by the user, would contain a complete range of structures changing progressively from the inside to the outside. The last section, for example, of the first ingot to be rolled after a weekend break, coiled into a roll, stored possibly in a warm place or despatched on a long sea voyage before uncoiling, might eventually be found to have assumed such a condition. Several methods for preventing this undesirable state of affairs will suggest themselves, but it is not proposed here to discuss the pros and cons of practical ways whereby stable structures could be conferred deliberately on lead sheet.*

A great deal of large-scale experimental work has been carried out in which a number of 10-ton ingots have been rolled under various conditions of temperature and reduction. The "macrostructure" of lead is fortunately very easy to reveal and numerous full-sized sheets (30 ft. × 8 ft.) have been etched over their complete surfaces.

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* Methods for the production of stable structures in lead sheets are the subjects of an application for a British Patent.

The details of these experiments may be explained in some future publication, but it can be stated that the practical difficulties involved in the commercial production of sheets having uniform medium recrystallized structures have been surmounted.

ACKNOWLEDGMENTS.

The author wishes to express his thanks to the Directors of Messrs. Goodlass Wall and Lead Industries, Limited, for permission to publish this paper; to Messrs. R. A. Cookson and W. Eckford for encouragement and help in large-scale work; to Mr. A. Lloyd for much assistance in experimental work; and to Messrs. T. A. Read and E. Morgan for their help in the photography.

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[1] Z. Jeffries, *J. Inst. Metals*, 1920, **24**, 379.
[2] H. C. H. Carpenter and C. F. Elam, *J. Inst. Metals*, 1920, **24**, 83.
[3] C. J. Smithells, *J. Inst. Metals*, 1922, **27**, 107.

DISCUSSION.

DR. J. MCKEOWN,* M.Sc. (Member): This paper raises a number of interesting questions; for example, can the author say whether the fine-grained materials which exhibit marked grain growth after deformation also exhibit marked grain-size contrast before working? Jeffries' view is that grain-size contrast is one of the most important factors in producing growth. The author states that "Lead, when subjected to those critical degrees of deformation which are liable to cause exaggerated grain growth, is immune from such processes, provided the initial grain-size is above a certain minimum." Jeffries has advanced the hypothesis that unstrained grains grow at the expense of strained grains, and I should like to consider an application of this hypothesis to the information given in the present paper. I have tried to visualize how the difference in behaviour of fine and medium or even relatively coarse-grained leads subsequent to deformation can fit in with this hypothesis.

If Jeffries is right, the presence of unstrained grains scattered throughout the sheet of lead in a field of strained grains is essential to grain growth, and in this case why should this condition be more liable to occur in the fine than in the coarse-grained lead? I have been led to conclude that this difference in behaviour is probably due to the difference in the extent of grain boundaries in the two materials. I suggest that even at the fairly rapid rate of straining used in applying the overstrain to the test-pieces, the deformation occurring consists of both intercrystalline and transcrystalline movement, and it is probable that the ratio of the intercrystalline to the transcrystalline increases as the grain-size decreases. The fact that fine-grained lead gives a greater elongation in the tensile tests than coarse-grained lead appears to confirm this statement. If this is so, it will follow that for a given definite amount of overstrain the transcrystalline deformation is smaller in the fine-grained than in the coarse-grained material. The smaller the amount of plastic

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* Investigator, British Non-Ferrous Metals Research Association, London

deformation the greater the tendency to unequal straining which, according to Jeffries' hypothesis, favours grain growth. Again, as the grain-size diminishes so the probability increases that a few grains will have their planes of easiest slip at right-angles to the direction of the component stress applied to those particular grains, and therefore the probability increases of having a few unstrained and comparatively stable grains which are in a condition to grow.

It would appear that the author's failure to produce exaggerated grain growth in grain-sizes above a certain minimum is due to the fact that the smallest amount of overstrain applied by him was too great to bring about uneven straining and thus give rise to a few centres instead of a large number of centres of grain growth.

Mr. F. A. Martin,* B.Sc., A.I.C.: Lead sheet used for building chemical plant is not normally strained in service or erection, to any great extent, so that stabilization of the structure, as described, should be an advantage. Lead sheet used in the building trade, however, is often severely strained in the processes of shaping, usually by beating with mallets and dressers.

Are these conditions likely to destroy altogether the stabilized structure which is taken as the starting point? If so, is there any treatment which might be added to the operative plumber's routine, and which would restore in the severely worked sheet, the desirable properties of a stabilized structure?

Dr. E. Voce,† M.Sc. (Member): In Figs. 10–12 we have three pictures of the abnormal structures referred to on p. 189, and the author states that the specimens were "etched in the usual way." By "the usual way" does he mean by the method suggested in his earlier paper,‡ *i.e.* with the hot etch?

Mr. Brinley Jones: Yes.

Dr. Voce: Then I think that these structures are merely the annealing effect of the hot etching. This etching technique is carried out by the author at 80° C., and by myself at 70° C., and I have seen effects like these very often. With cold-worked lead, such as these sheets, which has a tendency to anneal and recrystallize even during the minute or so of the etching period at 80° C., very curious structures may be obtained. I want to stress the danger of using this hot etch for cold-worked lead, excellent though it is for extruded material which does not tend to alter so easily.

Mr. Jones (*in reply*): I should like further opportunity for thought before dealing with Dr. McKeown's criticism. I may say that in "as-rolled" structures there is very little grain contrast in grain-size. This seems obvious from the photographs, and is confirmed by micro-examination at higher powers. I do not necessarily agree with Jeffries' theory when applied to lead. It is significant that it is possible to confer strains so slight on refined "as-rolled" structures as to cause no apparent structural change whatever; in other words, there can be in juxtaposition both strained and unstrained grains without growth. Apparently a minimum amount of strain is necessary. I agree, of course, that there must be a good deal more intercrystalline movement in straining refined structures than in straining coarse structures.

Mr. Martin's point is a very logical one. If structures of moderate coarseness are very severely worked, as a plumber sometimes works them, the refined "as-rolled" type of structure might easily return, with its consequent

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† Investigator, British Non-Ferrous Metals Research Association, London.

‡ *J. Inst. Metals*, 1933, 52, 73–74.

instability and liability to further grain growth. With regard to recommendations as to how such reintroduced refined structures can be removed in favour of more stabilized ones, that could be done by heating up with a flame for a few seconds at about 100° C. I am very loath, however, to make recommendations unless trouble is consistently encountered. Failure by intercrystalline cracking has been experienced in chemical plant, and this investigation has largely been inspired by such failures. Steps have accordingly been taken to put matters right; but there has been very little of this kind of complaint from the building trades. I believe that not a single case has come to my notice of trouble from grain growth resulting from severe working.

I am surprised that the criticism of hot etching was not made long ago. I agree with Dr. Voce that one has to be, and indeed one is, very cautious in regard to photomicrographs of structures obtained after a hot etch. The abnormal structures were included mainly to show in a new way that lead must be considered rather on its own, as a metal which is liable to sudden changes in structure where other metals are quite static; and, even if these abnormal structures were the result of hot etching, they are still abnormal structures. I may say, however, that in the case of the structures concerned, it was obvious that abnormalities were present before the hot glycerine etch was applied; they were easily visible in the cold stage. Moreover, if such abnormal structures arose solely as a result of the hot etching, one would expect to see them, or indications of them, in almost every specimen etched, which is not the case.

CORRESPONDENCE.

The Author: In further reply to Dr. McKeown, I would say that several experiments were carried out, during the course of the work described in the paper, in the attempt to initiate grain-growth in coarse-grained material, using smaller strains than those reported. These experiments were unsuccessful. It is intended, however, to check this point finally by using very large test-pieces, together with slower rates of straining.

Mr. J. C. Chaston,* B.Sc., A.R.S.M. (Member): In describing this interesting method of securing a fine grain-size in lead and imparting structural stability to it, the author has taken it more or less for granted that large grain-size is undesirable. Can he give any definite experimental evidence that coarse-grained lead is more liable than fine-grained lead to fail by fatigue and intercrystalline cracking? Such lead, of course, deforms in an irregular way and hence often has a lower ductility than fine-grained lead, but it does not appear to follow necessarily that the fatigue strength will be decreased.

A second point which might, I think, be amplified is the reason for choosing 50° C. as the temperature which the lead must withstand without grain growth. As I understand it, the author regards lead as stable if it can be strained by at least 6 per cent. and still show no tendency to recrystallize on heating to 50° C. Why 50° C.? I gather than even this fine-grained "stable" lead will recrystallize if it is heated to 100° C. after straining, while almost any sample of lead remains unaltered in its crystalline form when kept at about 25° C.

Finally, I would suggest an alternative reason to its larger initial grain-size to explain why hot-extruded lead does not recrystallize, like cold-rolled lead, after straining 6 per cent. and heating to 50° C. Might it not be that the hot-extruded lead contains smaller residual stresses than the cold-rolled lead? It would seem that the tendency to recrystallize is a function of the stress stored up in the metal. Thus it might be conceived that the internal stresses

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* Lecturer in Metallurgy, Royal Technical College, Glasgow.

in the hot-extruded lead, when added to those applied by elongating 6 per cent., do not result in total internal stresses high enough to cause recrystallization; whereas in the cold-rolled lead the internal stresses present before straining are sufficiently high to bring the total over the critical value. If this view is correct, hot-extruded lead should recrystallize at 50° C. if it is previously strained by an amount which will not be very much more than 6 per cent. Has the author any data on the minimum degree of straining which must be applied to hot-extruded lead before it will recrystallize at 50° C.?

Mr. W. SINGLETON * (Member): The author and his colleagues are to be congratulated on the interesting and immediately practical paper which they have contributed. Even with our increased metallurgical knowledge, failures in lead used for industrial purposes are by no means infrequent. Of these failures it can safely be said that, in spite of the attention and examination they receive, a very large proportion go unsolved. The history of these cases is full of apparent contradiction, good and bad results being obtained from the same lead when used in the same conditions. In my opinion, this is in large measure due to the fact that lead is frequently put into service without anyone, either manufacturer or user, having any knowledge whether its mechanical and physical condition is satisfactory or not. If and when failure does occur the investigator has frequently no basis to work upon—not even a record of the conditions in which the lead was manufactured.

The figures given on p. 188 for tensile strength of recrystallized and coarse material surprise me, because in the large number of tests we have made on material covering a wide range of grain-size, equally as great as the difference shown between these samples, I do not recollect any variation in strength anything like so great as that which exists between these two samples. The coarse structure material is surprisingly low in tensile strength. Although coarse structure may be undesirable, it is a fact, nevertheless, that many cases exist of lead with a very coarse structure having a long life, in some cases of 30–40 years or longer, in quite normal conditions.

I believe that a paper was published in Germany about 2 years ago dealing with this subject of stabilization of structure in lead, and I believe that an application was made for a patent for the production of stabilized lead. Unfortunately I have not the reference but Mr. Jones might be well advised to look further into the literature.

Mr. E. V. WALKER,† B.Sc., A.R.S.M. (Member): The experiments described in this paper emphasize once again how much care is needed in the interpretation of mechanical tests on lead if a correct forecast is to be obtained of the behaviour of this metal in service.

The author has stated that these grain growth and recrystallization effects could not be produced in a hot-extruded lead. Is this statement applicable to lead containing a small metallic addition of, say, 0·1 per cent. antimony? He also states that lead with a confused and interlocking structure is less liable to fatigue failure in practice than is lead consisting of more regular polygonal grains. Has the author carried out any endurance tests to illustrate this point?

The AUTHOR (*in reply*): In reply to Mr. Chaston I would say that there is no experimental evidence, and it has not been suggested in any part of the paper, that coarse-grained lead is more liable to fail by fatigue than fine-grained lead. It is under conditions of prolonged and slow reversed stresses that trouble is encountered with coarse-grained lead and it is hoped to deal

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with this subject more fully on a future occasion. At stresses up to 500 lb./in.^{2}, coarse-grained lead is extremely rigid and under certain service conditions tends to crack rather than to flow.

With regard to Mr. Chaston's next remarks, one of the fundamental points of the paper is that a stable lead will resist abnormal grain-growth after slight deformations, of the order of ½–2 per cent. A stable lead is most certainly not one which will resist recrystallization after straining 6 per cent. (or more) and heating to 50° C. A strain of 6 per cent. followed by heating to 50° C. would cause recrystallization in commercially pure lead whatever its initial condition, whether cold-rolled or hot-extruded. Further, there is no question of choosing 50° C. as a temperature which lead must withstand without grain-growth. This temperature was chosen as a means of accelerating changes which would proceed more slowly at atmospheric temperatures without introducing other factors.

In reply to Mr. Singleton, it is agreed of course that contradictory results in service are largely due to ignorance of original physical condition, and it is believed that deliberate stabilization of structures at the outset will do much to eliminate uncertainty in the future. Mr. Singleton is mistaken in believing that large numbers of tests have been carried out on material of abnormal grain-size such as that quoted in the paper. It is only latterly that such structures have been reproduced in the laboratory, and these, when tested, have proved to be erratic, as would be expected. In one case a tensile strength of as low as 950 lb./in.^{2} was recorded. It is interesting to know that work has been carried out in Germany on stabilization of structures, and the reference to this is much appreciated.

In reply to Mr. Walker, it was stated that grain-growth could not be produced in hot-extruded lead. It is repeated, however, that recrystallization will occur after severe straining. No direct information is available at the moment regarding extruded lead containing 0·1 per cent. antimony. It is again emphasized that no suggestion has been made that lead with a confused and interlocking structure is more resistant to fatigue failure than material with regular polygonal grains, and Mr. Walker is referred to my reply to Mr. Chaston regarding this point.

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CREEP OF LEAD AND LEAD ALLOYS. PART I.—CREEP OF VIRGIN LEAD.*

By J. McKEOWN,† M.Sc., Ph.D., Member.

Synopsis.

Tensile creep tests have been made on specimens of virgin lead in the form of extruded rod, extruded pipe, and extruded cable-sheath. The tests on rod have been made at room temperature and at 80° C., while the tests on pipe and cable-sheath have been made at room temperature only. The effect on the minimum creep rate of the working produced in flattening cable-sheath and in bending and straightening pipes has been investigated, and this effect has been found to be very marked. It has been shown that results obtained from worked samples may give an erroneous impression of the creep characteristics of the unworked, extruded product.

In the extruded products the effect of initial grain-size on the minimum creep rate has been investigated, and it has been shown that in extruded virgin lead the larger the initial grain-size the higher the resistance to creep at low stresses.

Introduction.

This work has been carried out as part of a research on the properties of lead conducted by the British Non-Ferrous Metals Research Association, and the present paper is a description of the methods used and the results obtained over a period of more than 4 years on virgin leads of high purity. Many tests have also been carried out on several alloys of lead, and it is hoped to present the results of such tests at a later date.

The work was commenced with the intention of obtaining comparative data on the creep of lead and some of the common lead alloys, and a very pure lead was chosen as a basis of comparison. It was assumed at the outset that the only important variable in the raw materials was composition, high-purity leads being assumed to recrystallize at room temperatures after cold-work. Preliminary results showed, however, that the problem was not so simple, but was complicated by a number of unsuspected variables. At present it appears likely that the smallest number of variables exists in the case of the very pure virgin lead, but the investigation is by no means complete.

A considerable amount of work has been done by other investigators on the creep of lead and lead alloys, and data have been published by

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* Manuscript received July 1, 1936. Presented at the Annual General Meeting, London, March 10, 1937.

† Investigator, British Non-Ferrous Metals Research Association.

Archbutt,[1] Townsend and Greenall,[2] Dean and Ryjord,[3] Moore and Alleman,[4] Clark and Upthegrove,[5] Chaston,[6] Moore, Betty, and Dollins,[7] and Betty.[8] In a large proportion of this work the initial conditions of the lead specimens were inadequately studied; the composition not being given exactly, the average grain-size not determined, and the state of age-hardening in those alloys which are susceptible to ageing ignored. Again some of the tests were made on specimens cut from cable-sheathing which had been flattened, and the influence of flattening on the results was not taken fully into consideration.

Moore, Betty, and Dollins have found that "there seemed to be some evidence that lead and lead alloys with large crystalline grains resist creep somewhat better than do lead and lead alloys with small grains." Betty carried out some work on single crystal specimens of commercially pure lead. He found that the strain–time diagrams (creep curves) for the single crystals were quite different from those of poly-crystalline specimens of the same material. In the latter, creep was due to both deformation within the grains and to disturbances at the grain boundaries. According to Betty the mechanism of creep in single-crystal specimens of commercially pure lead was by slip on that octahedral plane on which the resolved shear stress was a maximum.

In the paper by Moore, Betty, and Dollins [7] the question of the effect of the cold-working produced by the flattening of the cable-sheath from which the specimens were machined has been considered, and the authors stated that all the results of tensile tests on specimens cut longitudinally and specimens cut transversely from the sheet showed no difference. They stated that if the effect of flattening was to be noticeable it would have appeared in the tensile tests. On this point the present writer cannot agree with Moore and his colleagues. The amount of cold-work produced in the flattening of the sheaths was very small and the temperature of annealing, being room temperature, was very close to the recrystallization temperature of the materials. Such small amounts of work would not affect the ultimate tensile strength of the materials appreciably, but results given later in this paper show that they do affect the behaviour of the materials in creep at stresses well below the ultimate tensile strength. Some recent work carried out by O. F. Hudson and the present writer has shown that annealed copper worked by overstraining only 0·05 per cent. at room temperature had a definite limit of proportionality induced in it by this treatment. Subsequent annealing of the copper specimen for 2 hrs. at 500° C. failed to remove this range of proportionality of stress to strain and did not, in fact, reduce it.

Again even small amounts of working tend to cause lead and lead alloys to recrystallize at room temperature, and the extent to which this recrystallization and consequent grain-refinement has progressed will depend on both the extent of the cold-work and the time elapsing since the working was applied. H. F. Moore and his colleagues have recognized that grain-size is an important factor in determining the resistance to creep of lead and lead alloy specimens, and yet they have not investigated the effect on grain-size of the flattening process to which their specimens were subjected before testing. It would appear reasonable to conclude that the behaviour of a flattened specimen under creep conditions would be dependent on the time elapsing between flattening and loading the specimen, that is, on the extent to which recrystallization and grain-growth had progressed.

As is shown later in the present paper the effect of flattening on the resistance to creep of lead specimens is not confined to the changes in grain-size alone, and a further factor is present. This factor is apparently that of retention of cold-working, but exactly how it operates is at present unknown although its effect in increasing the resistance to creep is clearly indicated. This factor, the effect of small amounts of cold-working, is obviously of very great importance in the practical consideration of creep of lead and lead alloys, since in practice almost every application of these materials is accompanied by some small amount of cold-working during the installation of the materials in service. A cable during installation is unwound from a drum, thus cold-working the lead sheath, lead pipe is supplied in coils, and sheet lead in rolls.

From the point of view of reproducing service conditions as closely as possible during tests of a material, it would appear that in tests of lead cable-sheathing and water-pipe internal pressure creep tests would be more satisfactory. These tests would subject the material to compound stresses similar in nature to those experienced in service, but unfortunately such tests are by no means easy to carry out successfully. Internal pressure creep tests have been made by Moore and Alleman [4] and also by Chaston.[6] In the former work the rate of creep on the diameter of lead cable-sheaths was measured, while in the latter the length of life to failure was alone investigated. Measurement of diametral creep of lead sheaths present considerable difficulties, and the method of Moore and Alleman was not quite satisfactory as part of the circumference of the sheath was prevented from creeping by the attachment of part of the measuring apparatus. Another difficulty met with in testing of this type is the lack of uniformity of thickness of the wall of the sheath or pipe being tested, this giving rise to uneven distribution of stress and consequent uneven creep.

PRESENT WORK.

Materials.

The materials used in this work are listed below and a spectrographic analysis is also added.

Material.	Initial Average Grain Area, mm.².	Remarks.
1¼ in. diam. rod	0·84	Extruded on pipe press
1¼ ,, ,,	0·01	,, ,, ,,
Cable-sheath, 1 in. outer diam., ¾ in. inner diam.	0·37	,, on cable press
½ in. bore × 6 lb./yd. pipe	0·15	,, on pipe press

Spectrographic Analysis.

Material.	Composition, Per Cent.						
	Sn.	Sb.	Cd.	Cu.	Ag.	Bi.	Zn.
Coarse-grained rod . .	Nil	<0·002	0·00002	<0·0005	<0·0005	0·0005	Nil
Fine-grained rod . .	,,	Nil	0·0001	0·001	0·001	0·001	0·001
Cable-sheath .	,,	<0·002	0·0005	<0·0001	0·0007	0·0006	Nil
Pipe . .	,,	0·002	0·0001	0·0008	0·0008	0·0005	,,

Other elements sought but not detected—As, Te, Tl.

Chemical analysis for iron gave the following results:

Material.	Iron, Per Cent.
Coarse-grained rod	0·0005
Fine-grained rod	0·0005
Cable-sheath	0·0006
Pipe	0·0006

(1) *Long-Time Creep Tests at Room Temperature.*

(a) *Tests on extruded rod specimens.*—The creep tests to be described here were commenced in August, 1932, and some of the specimens are still under test. The work has been carried out mainly in a basement laboratory where the temperature is not subject to wide daily fluctuations. The maximum temperature recorded during the past 4 years was 23·5° C. (summer) and the minimum 12·5° C. (winter). The difference between maximum and minimum temperature during a 24-hr. period rarely exceeded 3° C. For by far the greater part of the time the temperature was between 15°–18° C.

As the tests were to be carried to fracture and as previous experience had shown the difficulties met with in applying extensometers of the clamping type to lead specimens, it was decided to adopt the type of specimen shown in Fig. 1 and to measure the extension between the shoulders by the rods *BB* shown. These rods were cut from the same supply of extruded lead bars, and consideration of the arrangement will show that changes of length due to changes of temperature are eliminated from changes of length due to stress. The separation of fine lines scribed on the strips of platinum foil was measured by means of a measuring microscope reading to 0·01 mm. The parallel length or gauge length of the specimen was 10 cm., and assuming that all the extension occurs on the parallel length the strain may be read to 10^{-4}. The reading to 0·01 mm. is by vernier, and in tests at 400 lb./in.^{2} and over, a greater accuracy of strain reading than $\pm 1 \times 10^{-4}$ is not claimed. For the tests at 200 and 300 lb./in.^{2} this form of measurement was not sufficiently sensitive, and the extensometer shown in Fig. 2 was devised for these tests. In this instrument the lever *E* allows a magnification of 10 : 1. The rod *A* is of aluminium and the bracket *D* of Invar; the length of the aluminium rod being to the gauge length of the test specimen in the inverse ratio of their coefficients of expansion. Measurements of extension of the specimen were made on the end of the lever *E* and the fixed bracket beneath it, scribed lines on platinum foil being used as before, and hence the strain could be read to $\pm 1 \times 10^{-5}$. The range of movement of the end of the lever *E* was not allowed to exceed 3 mm., and when this movement was reached the lever was re-set by means of the nut *B* which had a ball seating on the Invar bracket.

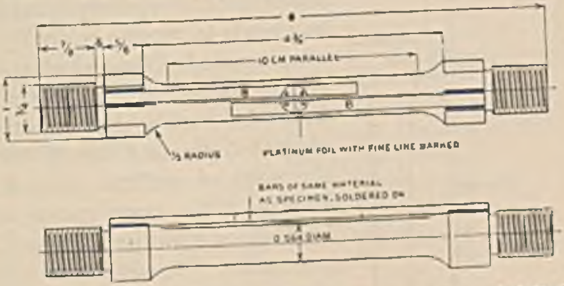

Fig. 1.—Specimen for Long-Time Creep Tests on Extruded Rods. (Dimensions in Inches.)

In the foregoing it has been assumed that all the extension occurs on the parallel length of 10 cm., and that this assumption was substantially valid was shown by the surface of the specimens when they had been strained about 3 per cent. This amount of strain was sufficient to give a roughening of the surface due to displacement of the grains, and this roughening could not be detected beyond the parallel portion of the specimen.

The specimens were machined from the 1¼-in. diam. coarse-grained bar to the dimensions shown in Fig. 1, and the stresses applied ranged from 700 to 200 lb./in.². The results of the tests are given in full in Table I, and the creep curves obtained are shown in Fig. 3. The curves all show that the initial rate of creep is rapid but diminishes and tends to become relatively constant after a period of time which is dependent on the applied stress. It would appear from the curves that an extension of about 4–5 per cent. has to occur before the stage of uniform creep is reached. In Fig. 4 the creep curves are shown for tests on two virgin leads of different grain-sizes. The coarse-grained material, already dealt with in Fig. 3, had an average grain area of 0·84 mm.², while the fine-grained material had an average grain area of 0·01 mm.². The very great difference in creep characteristics of these two materials is clearly shown in Fig. 4, and as shown in Table I a great difference also exists in the values of elongation and reduction of area.

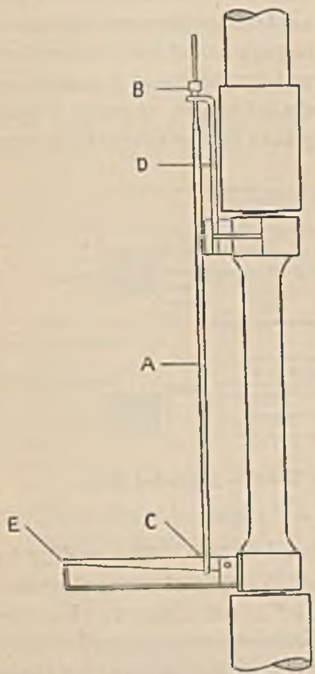

Fig. 2.—Extensometer used in Tests at Low Stresses.

It may be noted that in the coarse-grained material as the applied stress is decreased the elongation at fracture and the reduction in area are decreased. In the fine-grained material, on the other hand, the elongation at the lower stress is greater than that at the higher stress.

In Fig. 5 an attempt has been made to subject the results of the tests to logarithmic plotting. In the case of the coarse-grained material a fairly good straight line passes through the points for 400, 500, 600, and 700 lb./in.², but the points for 300 and 200 lb./in.² are well off the line. This, however, is readily explained by an examination of Fig. 3, where it

TABLE I.—*Long Time Creep Tests on Virgin Lead Specimens at Room Temperature.*

Material.	Average Grain Area at Commencement of Test, mm.².	Stress, lb./in.².	Life, Days.	Extension, Per Cent. on 10 cm. B = Broken, U = Unbroken.	Reduction in Area, Per Cent.	Minimum Creep Rate, Strain/Day × 10⁴.
Coarse-grained extruded rod. Specimens machined from 1¼ in. diam. rod.	0·84	200	660	0·33 *	...	0·04
		300	942	2·0 U	...	0·17
		400	1482	21·0 U	...	0·72
		500	585	19·0 B	50	1·44
		600	210	24·0 B	72	4·17
		700	66	30·5 B	97	13·8
Fine-grained extruded rod. Specimens machined from 1¼ in. diam. rod.	0·01	500	311	87 B	94	10·6
		600	70	60 B	98·5	47·7
Extruded cable-sheath	0·37	500	384	15·3 U	...	2·03
		600	89	20·0 *	...	12·58
Flattened cable-sheath	0·16	500	327	29·0 B	...	1·70
		600	69	25·0 B	...	10·0
Extruded pipe	0·14	500	330	17·6 U	...	3·9
Extruded pipe bent on former of 22 in. diam. and straightened.	0·11–0·15	500	280	11·3 U	...	...

* Test discontinued.

will be seen that at the two low stresses the specimens have not been sufficiently long under test to have reached the stage of minimum creep rate. In fact it seems possible that a period of 10–15 yrs. will have to elapse before the specimen at 300 lb./in.^{2} reaches this stage in the test.

(b) *Tests on virgin lead cable-sheath.*—Virgin lead cable-sheath having an outer diameter of 1 in. and a wall thickness of ⅛ in. was extruded under ordinary conditions but in straight lengths and without any cable core. This material was tested in the two conditions: (1) as sheath and (2) after flattening. The tests were made with two objects in view: (*a*) to determine if the rate of creep of an extruded pipe specimen was of the same order as that of an extruded rod, and (*b*) to determine the effect of flattening the sheath on its creep characteristics. The specimens tested as sheath were fitted with a type of end shown in Fig. 6 (*a*), and some preliminary work showed that the effect of the heating produced during the casting of the ends did not extend to more than 1 in. beyond the inner parts of the ends. To make certain that no such effect would influence the test results the gauge length of 10 cm. on each specimen was taken at a distance of 3 in. from the end holders.

The flattened specimens were produced by slitting a length of the sheath longitudinally, opening it out uniformly by hand and then applying the flattening by squeezing between two planed boards in a vice. The specimen shown in Fig. 6 (*b*) was then machined from the flattened sheath and gripped as shown. Two stresses only were used in these tests, namely, 500 and 600 lb./in.^{2}, and the creep curves obtained are shown in Fig. 7, the results being given in Table I. A third sheath specimen was tested at 500 lb./in.^{2} after it had been annealed for 2 hrs. at 100° C. The original sheath had an average grain area of 0·37 mm.^{2}. Annealing for 2 hrs. at 100° C. produced an average grain area of 0·49 mm.^{2}, while annealing for 2 hrs. at 250° C. produced an average grain area of 1·8 mm.^{2}.

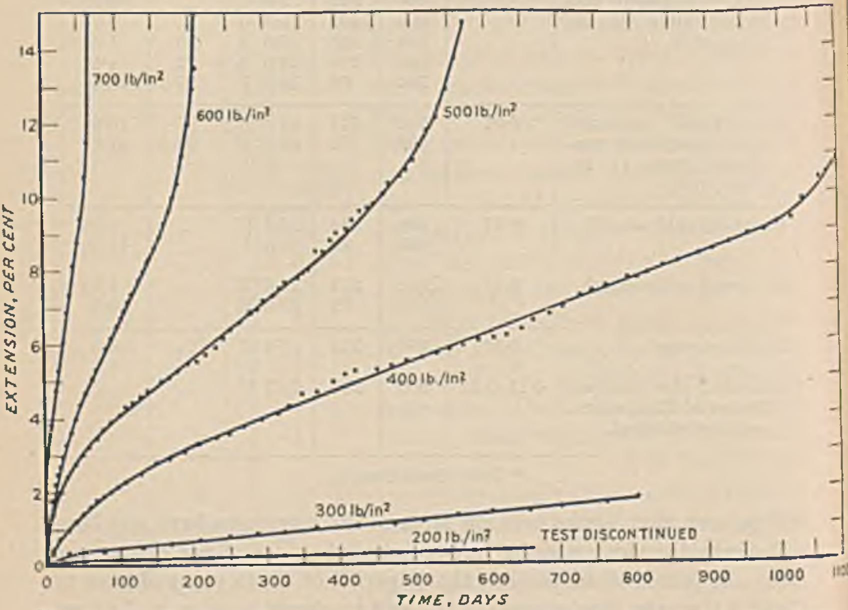

FIG. 3.—Tensile Creep Tests on Specimens of Coarse-Grained Extruded Rod at Room Temperature.

The effect on the creep characteristics of the flattening process is clearly shown in Fig. 7. The creep rate was reduced by the working produced in the flattening and during the two initial stages of the creep test, *i.e.* up to the stage of final rapid and increasing creep rate, the extension of the flattened specimen was less than that of the sheath at the same stress. The refinement in grain-size brought about by flattening the sheath is indicated in Table I.

As shown in Fig. 7, the sheath specimen tested at 500 lb./in.^{2} after annealing for 2 hrs. at 100° C. has given a type of creep curve entirely different from that of the extruded or flattened specimens. The primary stage of rapid but decreasing rate of creep is absent in the annealed specimen, and a very decided change in the rate of creep occurred about 35–40 days after the commencement of the test. The creep rate between 50 and 190 days was fairly constant and was higher than that of the "as extruded" specimen at the same stress.

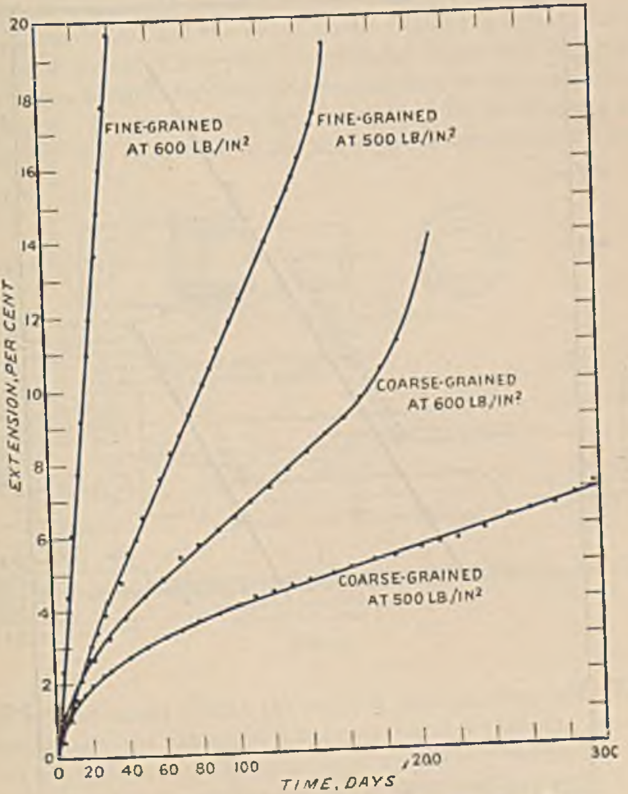

Fig. 4.—Tensile Creep Tests at Room Temperature on Coarse- and Fine-Grained Extruded Rods.

An examination of Table I shows that at stresses of 500 and 600 lb./in.^{2} both sheath and flattened sheath specimens have a higher minimum creep rate than the rod specimens. In the case of the sheath specimens this is probably due to the finer grain-size alone. On the count of grain-size alone one would expect flattened sheath specimens

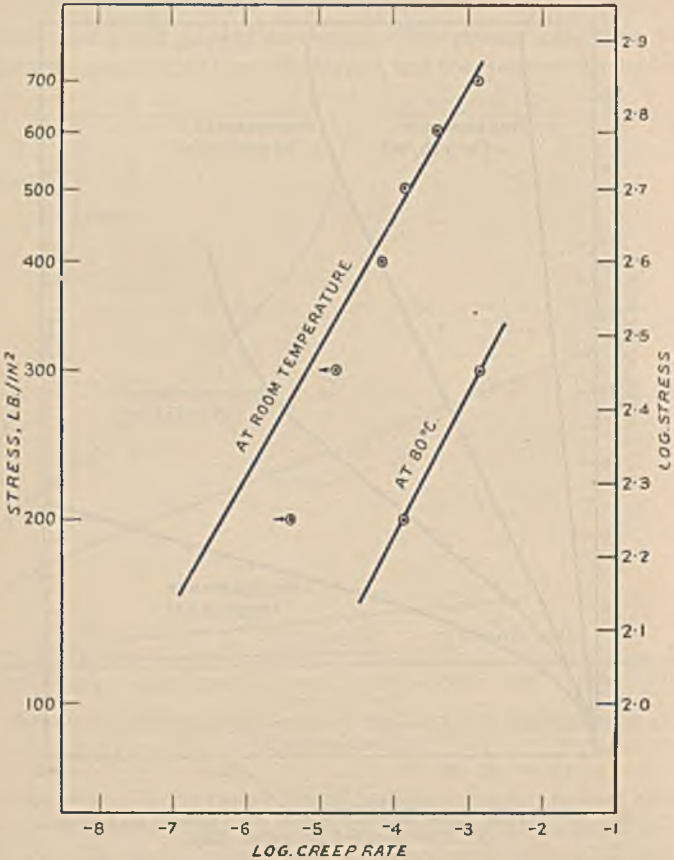

Fig. 5.—Tensile Creep Tests on Coarse-Grained Extruded Rods.

to have a higher minimum creep rate than they have given and certainly a higher creep rate than the sheath specimens. It appears from the results that grain-size is not the only factor influencing minimum creep rate in these materials, and that the effect of working produced in the flattening process is to stiffen the material and increase its resistance to creep.

(c) *Tests on extruded pipes.*—Virgin lead pipe (½ in. bore × 6 lb./yd.) which was specially extruded in straight lengths was obtained for these tests. The specimens were loaded longitudinally, an end grip of the form used for the cable-sheath specimens and shown in Fig. 6 (*a*) being employed.

A test at a stress of 500 lb./in.^{2} was made on the pipe in the "as received" condition, and the creep curve obtained is shown in Fig. 8. The shape of the curve is typical for extruded virgin lead, but the rate of creep is much higher for the pipe material than for the coarse-grained rod material. The creep curve for the latter at the same stress is also given in Fig. 8. In the curve for the pipe specimen another feature which may be noted is that the stage of uniform creep rate does not commence until the extension is between 8 and 9 per cent., whereas in the rod specimen it commences at an extension of 4 per cent.

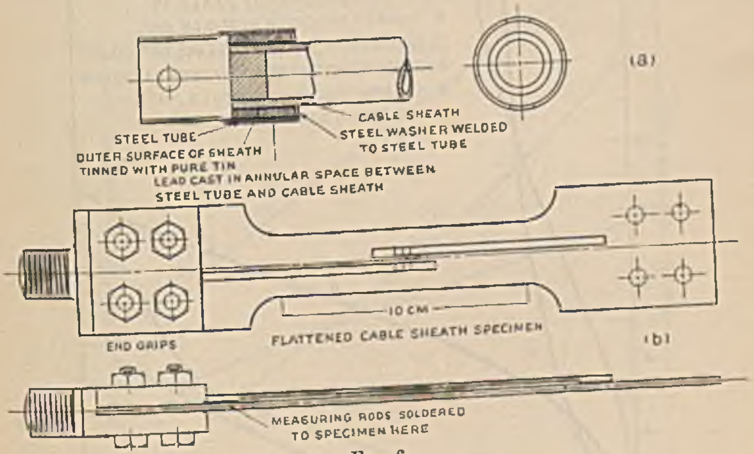

Fig. 6.

As lead pipe is generally supplied in coils, and has to be uncoiled before being used, it was considered that a test on a specimen which had been subjected to somewhat similar treatment would be of interest. Accordingly a length of the straight pipe was bent to the arc of a circle on a former having a diameter of 22 in. (the usual diameter of coils of pipe of this bore and weight) and then straightened uniformly by hand. It is clearly recognized that this procedure does not exactly reproduce the conditions met with in ordinary coiled pipe, where the original coiling is done while the pipe is still hot from the extrusion press and the uncoiling and straightening are done some considerable time later when the pipe has had time to recover at room temperature by slow recrystallization. The method was adopted mainly to enable fairly straight specimens to be obtained, a difficult matter when a length of pipe coiled in the works was used.

A trial length of the pipe was bent and straightened and a section cut out of the middle and prepared for microexamination. When examined 4 hrs. after bending and straightening it was found that in the diametrically opposite zones of maximum bending stress the average grain-size was 0·11 mm.², compared with the original 0·14 mm.², but there was no evidence of recrystallization. In the diametrically opposite zones of zero bending stress no change in grain-size had occurred and there was no evidence of recrystallization or working. The same specimen, when examined 15 days later, showed an irregular grain-size

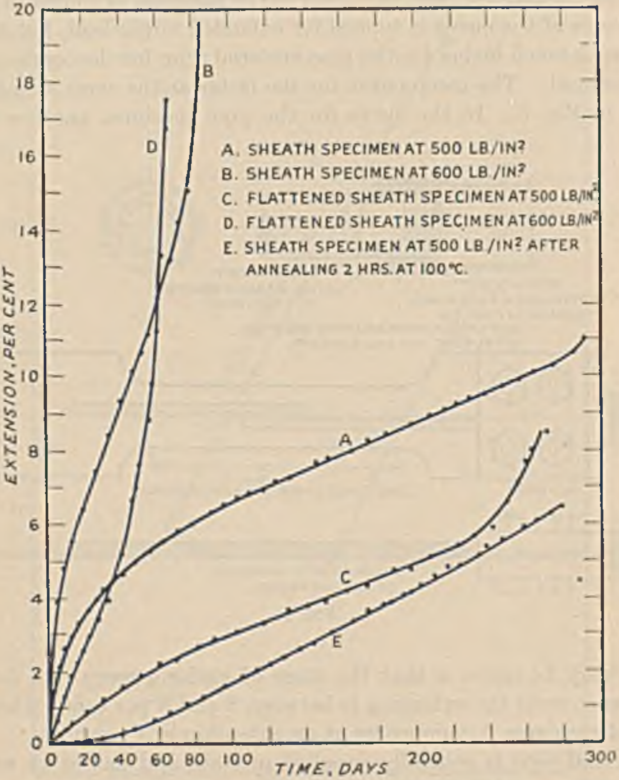

FIG. 7.—Tensile Creep Tests at Room Temperature on Cable-Sheaths.

in the zones of maximum bending stress, and the average grain area was practically unaltered.

The creep specimen was first bent and immediately straightened, then fitted with ends and loaded at 500 lb./in.^{2} about 4 hrs. after bending and straightening. The creep curve obtained from this specimen is shown in Fig. 8, and is remarkable in that the initial stage of rapid but diminishing creep is absent.

The curve so far consists of two stages, an initial stage of uniform rate of creep for the first 30 days, followed by a second stage of uniform but higher creep rate. There is a fairly abrupt change in the direction of the curve about 32 days from the commencement of the test. Very slight change has occurred in the minimum creep rate as a result of the bending and straightening.

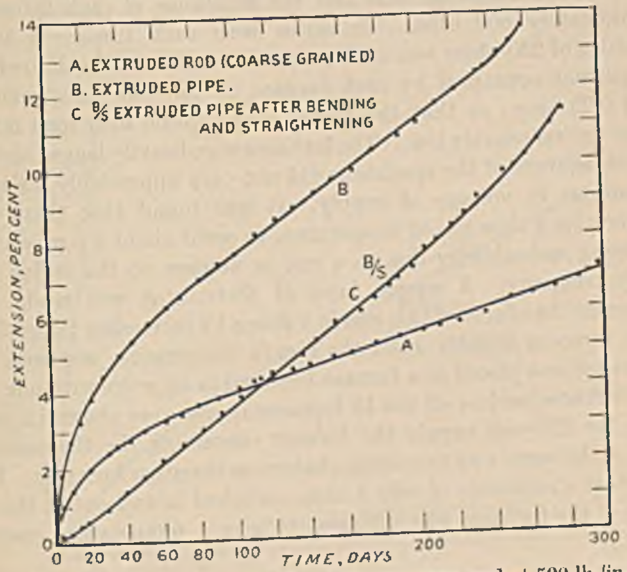

FIG. 8.—Tensile Creep Tests at Room Temperature and at 500 lb./in.^{2}.

(2) *Long Time Creep Tests at* 80° *C.*

Lead pipe may be used to carry water at temperatures up to 100° C.; lead used in sulphuric acid plant is frequently subjected to a temperature in the region of 80° C., and lead cable-sheath may be used at temperatures round about 50° C. In view of this it was decided to carry out some tests at 80° C. to determine the effect of temperature on the rate of creep, the elongation and the life of specimens of virgin lead.

The specimens used in these tests were made from 1¼ in. diam. bar of the coarse-grained material to the same dimensions as the specimens shown in Fig. 1. The measuring bars B.B. were replaced by brass bars extending beyond the end of the furnace, and the extension was measured by the separation of fine lines scribed on platinum foil soldered at the ends of these brass bars.

Tubular wire-wound electric furnaces were used, the winding being of 30 S.W.G. Brightray wire and the resistance of each furnace was approximately 800 ohms. In series with each furnace a variable resistance of 220 ohms was used to set the current at the desired value. The current consumed by each furnace on the 220 volts circuit was about 0·23 amp., so that the power consumption over long intervals of time was reasonably low. The furnaces were heavily lagged and hence the temperature of the specimens did not vary appreciably for average fluctuations in voltage of supply. It was found that there was a tendency for a slow rise of temperature to occur about 5 p.m. each day, this being undoubtedly due to a rise in voltage on the mains of the supply company. A simple form of thermostat was made up to counteract the effects of this rise in voltage by increasing the resistance of the furnaces slightly when the rise in temperature occurred. The thermostat was placed in a furnace identical in all ways with one of the creep furnaces, and as all the 15 furnaces in use were placed in parallel across the 220-volt supply the furnace containing the thermostat reacted in the same way to voltage changes as the other furnaces. It was found that a resistance of only 3 ohms switched in and out of the main circuit of the furnaces was sufficient to give a temperature control of ± 2° C.

Determination of temperatures on different parts of the specimen showed that the extreme ends where the specimen was screwed into the shackles were about 3° C. lower than the centre of the gauge length.

The variable temperature junction of an iron Eureka thermo-couple was enclosed in fine glass tubing and placed so as to touch the centre of the parallel length of the specimen. A special timing switch was used to connect each of the 15 couples at regular intervals to the circuit of a three-thread Cambridge recorder, and a record of temperature of each specimen was obtained every 23 minutes.

The procedure adopted in commencing a test was as follows: the furnace was switched on about 9.30 a.m., and the temperature of the specimen had reached 80° C. about 2 p.m. About 2 hrs. were taken to steady the temperature at this figure and the load was then applied, the readings on the cathetometer of the scribed lines on the platinum foil being taken immediately before and after the application of the load.

Creep curves at 300, 200, and 100 lb./in.^{2} are shown in Fig. 9, and it is seen that the rate of creep diminishes very rapidly with diminishing stress. The curve obtained at 300 lb./in.^{2} is a typical form, *i.e.* a primary stage of rapid but diminishing rate of creep followed by a stage of sensibly constant rate of creep, then a third stage of rapidly increasing rate of creep progressing towards failure of the specimen. At 100 lb./in.^{2} the amount of creep for the first 45 days was only 0·13 per cent., and no further creep took place up to 150 days, when the test was discontinued.

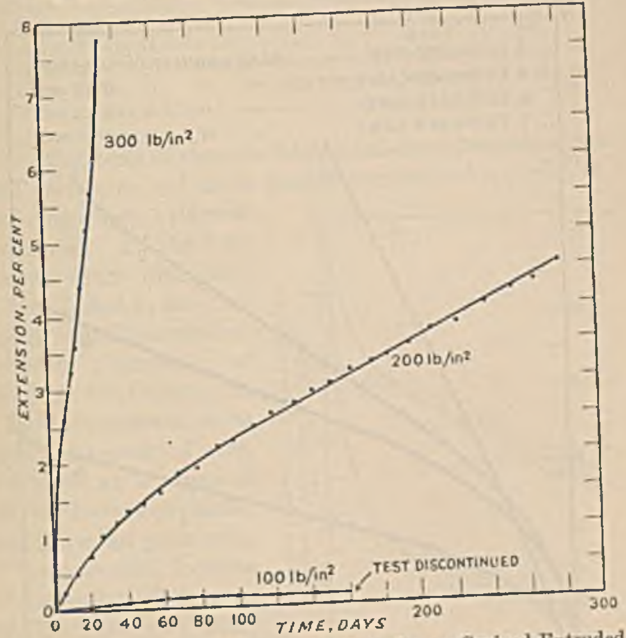

Fig. 9.—Tensile Creep Tests at 80° C. on Coarse-Grained Extruded Rod. Specimens Machined from 1¼-in. diam. Rod.

The creep rates have been plotted on Fig. 5, and so far as one can judge from only two points the tests at 80° C. give a line parallel to that given by the tests at room temperature when logarithm of creep rate is plotted against logarithm of stress.

Only the specimen stressed at 300 lb./in.^{2} at 80° C. has broken up to date, its life was 48 days, the elongation 34 per cent. on 10 cm. (approximately $8\sqrt{A}$) and the reduction in area 100 per cent.

(3) *Effect of Long Time Annealing at* 80° *C. on a Specimen of Virgin Lead.*

A disc was cut from the 1¼ in. diam. coarse-grained rod, and a photomicrograph taken in the "as received" condition. The specimen was then placed inside one of the creep furnaces and held at 80° C. for a total time of 500 hrs., examination of the grain-size being made at 24, 100, 250, and 500 hrs. No change in grain-size occurred, nor was there any other evidence of change in this specimen.

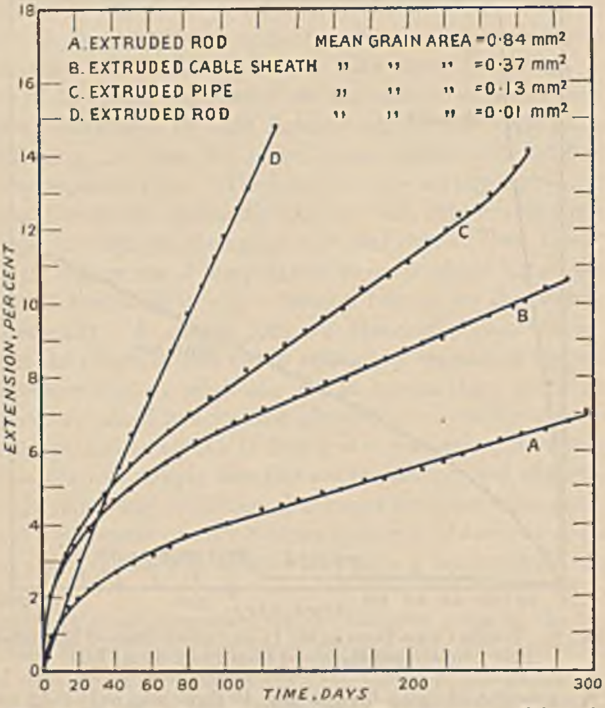

FIG. 10.—Tensile Creep Tests at Room Temperature. Effect of Grain-Size. Stress = 500 lb./in.².

GENERAL DISCUSSION OF THE RESULTS OF THE TESTS.

(a) *Effect of Grain-Size on Creep of Lead in the "As Extruded" Condition.*

In Fig. 10 the creep curves at 500 lb./in.² of four specimens having different grain-sizes are shown, and the grain-sizes and some creep data are given in Table II. An examination of the figure and the table shows that the amount of creep in 100 days and the minimum creep rate are both directly dependent on the grain-size. It may be noted,

TABLE II.—*Grain-Size and Creep of Extruded Lead at a Stress of* 500 *lb./in.*^{2}.

Material.	Average Grain Area, mm.^{2}.	Minimum Creep Rate, Strain/Day × 10^4.	Amount of Creep in 100 Days, Per Cent.
1¼ in. diam. rod	0·01	10·6	11·8
½ in. bore × 6 lb./yd. pipe . . .	0·14	3·9	7·7
1 in. outer diam. × ⅛ in. thick cable-sheath	0·37	2·03	6·65
1¼ in. diam. rod	0·84	1·44	4·05

however, that tests to show the higher resistance to creep of the coarser-grained specimens had to be carried out beyond a period of 40 days before conclusive evidence was obtained. All the four specimens dealt with here have been tested in the "as extruded" condition without subsequent thermal or mechanical treatment. In Fig. 11 the minimum creep rate and the amount of creep in 100 days at a stress of 500 lb./in.^{2} have been plotted against the mean grain area, and these curves indicate that decreasing the mean grain area below 0·1 mm.^{2} decreases very seriously the resistance to creep; this, of course, refers to grain-size produced by extrusion alone. The curves also indicate that the rate of increase of resistance to creep with increase of grain-size becomes less marked as the mean grain area increases above ½ mm.^{2}.

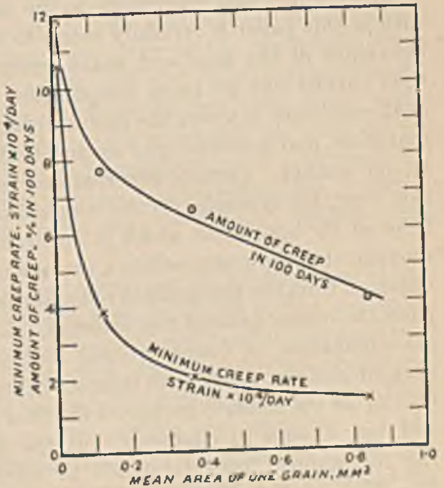

FIG. 11.—Tensile Creep Tests at Room Temperature. Effect of Grain-Size. Stress = 500 lb./in.^{2}.

Clark and White [9] tested hot-rolled brasses of two different grain-sizes in creep at different temperatures, and found that for a given alloy the fine-grain brass was more resistant to creep than the coarse-grain below a certain temperature range, but above this range the coarse-grained material was the more resistant to creep. Since the materials were known to differ only in respect to their grain-size and, therefore, only in respect to the relative amounts of boundary and crystalline material, it was concluded that above this temperature range the boundary material was the weaker and below this temperature range the crystalline material was the weaker. It was then found that this temperature range was the lowest temperature of recrystallization of the material after severe cold-working. It therefore appeared that the "equi-cohesive" temperature was coincident with the lowest temperature of recrystallization.

The observed fact that above a certain temperature the fine-grained material creeps more rapidly than the coarse-grained material is in accord with the early theories of Beilby and Rosenhain, who attributed viscous properties to boundary materials above the equi-cohesive temperature. It therefore appears that above this temperature creep may be considered as a form of viscous flow.

If we apply this conception to the case of the extruded leads dealt with in this paper it certainly seems to explain the differences in creep behaviour of the fine- and coarse-grained materials. The tests have been carried out at room temperature which, for the very pure lead dealt with here, is above the recrystallization temperature of the worked materials, and hence we may assume that the crystal boundary material is the weaker. Certain observations made during the tests confirm this view, for example, (1) the roughening or strain etching of the surfaces of the specimens which is apparently brought about by relative movement of the grains within a viscous matrix, (2) the higher elongation obtained from the fine-grained rod material compared with that obtained from the coarse-grained rod material. Further, the observed fact that the elongation of coarse-grained lead increases, while that of fine-grained lead decreases, with increase of stress, is explained by this view. Clearly as the stress is increased the flow tends to become more plastic and less viscous in character, but the greater end-blocking effect in the fine-grained material tends to minimize the increase in plastic flow, the net effect being that in the fine-grained material the boundary movement decreases more rapidly than the plastic deformation increases, while in the coarse-grained lead the plastic deformation increases more rapidly than the boundary movement decreases, with increase of stress.

It appears certain that throughout any of these creep tests both plastic and viscous flow are occurring, the former predominating in the early stage of the test. In this respect reference may be made to the work of Andrade [10] on lead. He considered that in a creep test at constant stress on a lead wire the flow was made up of two parts:

(1) the plastic, or, to use his own expression, the β flow, and (2) the purely viscous flow.

Andrade suggested a formula to represent the flow of lead under creep conditions:

$$l = l_0 (1 + \beta t^{\frac{1}{3}}) e^{kt}$$

where l is the length at any time t, the initial length being l_0, β and k being constants. An attempt has been made to fit this formula to the curves in Fig. 10, but this has not been very successful, due to two causes. In the first place the curves in Fig. 10 were not obtained at constant stress. Further, Andrade suggested that in his formula $t^{\frac{1}{3}}$ should probably be replaced by a function of t, which approximates closely to $t^{\frac{1}{3}}$ for small values of t but which, as t increases, ultimately becomes constant.

(b) *Effect of Cold-Working on Creep.*

If in an extruded lead a change in grain-size is brought about by a small amount of cold-work in specimens prior to the creep tests being commenced, the relation between grain-size and resistance is no longer a simple one. Thus, flattening cable-sheath produced some slight refinement in grain-size but increased the resistance to creep in the early stages of the test. Bending and straightening of pipe produced in the zones of maximum bending stress, slight refinement of grain-size, but, once more, the resistance to creep in the early stages of the test was increased.

In his work on lead wires already referred to, Andrade has shown that large preliminary strains put the wires in a state to flow viscously, and the present tests on flattened cable-sheath and bent and straightened pipes confirm this statement. The effect of such working is much more pronounced in the early stage of the test than during the stage of uniform creep, *i.e.* the stage where viscous flow always predominates. In this respect it may be noted that the bending and straightening of the pipe has apparently a greater effect in promoting viscous flow than had the flattening of the cable-sheath, for, in the former case, the initial stage of mainly plastic flow is missing, and the creep curve obtained has the characteristic shape associated with purely viscous flow.

The curves given in Fig. 12 show very clearly the effect of preliminary cold-working on the subsequent creep characteristics of a specimen of the coarse-grained rod. The curve *A* is the creep curve at 600 lb./in.^{2} of a specimen tested in the "as extruded" condition. The curve *B* is the creep curve of a specimen which was elongated in tension 5 per cent. on the gauge-length and then tested in creep under a load which would have produced a stress of 600 lb./in.^{2} on the cross-sectional area of the specimen before overstrain. The latter specimen has given a creep curve in which the early stage of the ordinary creep curve, considered to be due mainly to plastic deformation, is absent. It seems probable, therefore, that the curve obtained from the overstrained specimen represents flow largely viscous in character.

A similar specimen elongated 5 per cent. in tension, sectioned and aged at room temperature, was found 15 minutes later to have a grain-size approximately ½ that before working. Later very slight recrystallization was detected, but the further grain refinement was small. It is of interest to note that while the minimum creep rate of the original material was $4{\cdot}17 \times 10^{-4}$ strain per day the creep rate of the overstrained material was $2{\cdot}0 \times 10^{-4}$ strain per day and the relative mean grain areas 0·84 and 0·46 mm.², respectively. It would appear, therefore, that in this test as also in the tests on the flattened cable-sheath and the bent and straightened pipe specimens, the effect of the cold-working in increasing resistance to creep is much more pronounced than the decrease in creep resistance which would be expected as a result of the reduction in grain-size.

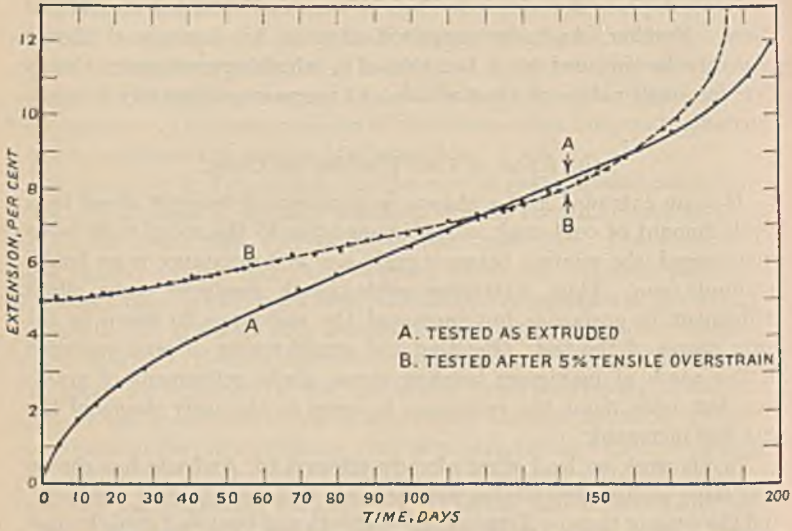

FIG. 12.—Tensile Creep Tests at Room Temperature on Coarse-Grained Extruded Rod. Stress = 600 lb./in.².

The overstrained specimen had a life of 186 days and a total extension (including the original 5 per cent. overstrain) of 30 per cent. A cross-section was taken on the parallel length away from the fracture within a few hours of failure, and a grain count gave the mean grain area as 0·42 mm.^{2}. From this it appears probable that the grain-size had not altered appreciably during the creep test, and if this be so it tends to confirm the statement that the flow occurring during the test was mainly at the grain boundaries. Specimens of this lead which had been rapidly overstrained 12½ per cent. in tension were found to have completely recrystallized within 1 hr. The creep specimen on the other hand had at the commencement of the creep test an average grain-size of 0·46 mm.^{2}, during the test was stretched much more than 12·5 per cent. in tension, but had not recrystallized. This suggests that during the creep test the plastic deformation within the grains was insufficient to bring about recrystallization, and that the movement which did occur took place at the grain boundaries.

Intercrystalline Cracking of Lead.

In several of the specimens tested in creep at low stresses intercrystalline cracking has been clearly observed. It has been mentioned previously that during a test the grain boundaries show on the surface of the specimen after an extension of approximately 3 per cent. At a later stage in the test some of the grain boundaries have been observed to open in the form of deep cracks, with a separation of adjacent grains. This has been observed most clearly in the coarse-grained specimens at stresses of 400 and 500 lb./in.^{2} and also in the specimen overstrained 5 per cent. before testing. Intercrystalline cracking of lead may thus occur under steady stress conditions (creep) as well as under the influence of alternating stresses.

In a recent paper by J. N. Greenwood,[11] intercrystalline cracking under creep conditions of a specimen of lead sheet at a stress of 500 lb./in.^{2} has been referred to and illustrated.

It is clearly recognized that the work recorded here is by no means exhaustive, and further investigation of the creep of lead is proceeding. The work done has shown the very great importance of a complete knowledge of the history of the materials tested, and in this connection it may be noted that a very extensive research is being carried out in the University of Melbourne under the direction of Professor J. N. Greenwood.[12] This work, details of which have very recently come to hand, aims at a complete investigation of the effect of small amounts of impurities on the mechanical properties of lead with particular reference to recrystallization, grain-size, and creep characteristics. This work and the work of the present author have shown the problem to be a very complex one, but it is felt that a thorough investigation of the effect of previous thermal and mechanical history on the creep characteristics of lead at room temperature will materially assist in the elucidation of the many problems presented by the study of creep in other materials at elevated temperatures.

ACKNOWLEDGMENTS.

The author desires to express his thanks to the Council of the British Non-Ferrous Metals Research Association for permission to publish this paper.

Thanks are also due to the author's colleagues, Dr. E. Voce and Mr. W. A. Baker, for their valuable assistance in the micrographic work.

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[12] (*a*) R. S. Russell, "The Influence of Impurities on the Properties of Lead," *Proc. Australasian Inst. Min. Met.*, 1932, [N.S.], (87), 135–166. (This has since been treated as Part I of a series of papers, the rest of which are given below.)
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DISCUSSION.

Mr. J. C. Chaston,* B.Sc., A.R.S.M. (Member): The experiments on flattened samples of cable-sheath show, I think, beyond question that lead which has recrystallized can still retain a certain amount of internal stress. This is a somewhat remarkable conclusion. One thinks of recrystallization as a process in which all internal stress is removed and the metal transformed to an aggregate of new, stress-free crystals; this view evidently requires qualification. The author has shown that samples of cable-sheath which have been flattened (and then, presumably, recrystallized) at room temperatures have very different characteristics from extruded samples which have not been cold-worked but which have a similar crystal size. The magnitude of the residual internal stresses is obviously not large. They do not affect the tensile properties, and there is no appreciable difference in hardness between flattened and unflattened sheaths. In creep experiments conducted at the University of Illinois it was concluded that there was no harm in flattening the cable-sheath because there was no difference in the hardness before and after flattening. I think that the author has shown conclusively that that was quite an erroneous assumption, and therefore it leads, I am afraid, to the conclusion that the results of this American work are practically worthless.

Was there any difference between the fatigue characteristics of a material which had been annealed and those of one which had been cold-worked?

It is interesting to inquire if there is any method for testing quickly whether a sample of lead contains internal stresses. One possible method would be to try the effect of annealing at a higher temperature. If no further grain growth occurred, the material might be regarded as reasonably free from stress.

The samples of hot extruded cable-sheath which the author used were 2 years old, and I believe that when those samples were annealed at 100° C. for 1 hr. no further grain growth occurred. These samples thus seem to have been practically free from internal stress. If, however, a sample of freshly extruded lead is annealed it shows pronounced grain growth. That seems to indicate that internal stress is present in freshly extruded lead. The conclusion I draw from these observations—which I believe the author can confirm—is that there is a possibility that the residual stresses present in freshly-extruded lead, shown by crystal growth on annealing, can disappear in the course of 2 years.

I have not so far been able to obtain more precise information as to the time required for stresses to be relieved, and I mention these observations mainly to support the author's conclusion that it is essential in creep tests on lead to control the previous history of the specimen. Even hot-extruded specimens cannot always be relied on to be strain-free.

There seems one further way of testing the assumption that this cold-worked and recrystallized material may contain stress. The author has given results on creep tests at 80° C.; can he tell us whether there is any difference at 80° C. in the creep characteristics of flattened and unflattened cable-sheath?

Mr. H. C. Lancaster † (Member): I regret the author's title "Creep of Virgin Lead." The word virgin has little significance, when dealing with such a highly technical subject. Thousands of tons produced yearly in the U.S.A. containing in one brand 0·06 per cent. copper, and in another 0·050 per cent. bismuth, can claim to be virgin lead. Refining processes are such that from the most impure material a product can be produced with a purity far

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† Technical Adviser, Locke Lancaster and W. W. and R. Johnson and Sons, Ltd., London.

exceeding that of any material that the author has used in his experiments and which he terms "a very pure lead."

The author quotes Greenwood, who rightly stresses the importance of knowing the complete history of the materials tested, and the effect of small amounts of impurities on the mechanical properties, recrystallization, grain-size, and creep characteristics. Rosenhain emphasized the necessity, when carrying out such investigations, of starting with absolutely pure metal; the author, however, has in effect used far from pure lead for his experiments, and, moreover, has compared the physical properties of an extruded rod of 1¼ in. diameter which he has reduced to ⅛ in., having put in cold-work, and in addition destroyed the skin effect, which naturally remains in the case of the extruded cable and pipe.

To prove the vital importance of carrying out this highly technical work, lead of extreme purity was prepared by producing 1 ton from 3 tons of material. Professor Judd Lewis could find no antimony, arsenic, tin, copper, or silver, which are the common impurities, but was not quite positive about a mere trace of bismuth, and asked whether one millionth part, *viz.* 15 grains in 1 ton, could be added for confirmation. Two 12-lb. ingots were cast, one with the addition of 0·001 per cent. nickel (analysis gave 0·0006 per cent.). An examination immediately showed that this small addition altered the usual characteristics (1) when cast, and (2) when rolled down to 5 lb. substance and etched, the difference being most striking. Even this small addition improved the fatigue limit.

Mr. W. Singleton * (Member): Much of the published work on the creep of lead and lead alloys has suffered in value because little or no attention has been given to such factors as composition, work-hardening, precipitation-hardening, &c. Dr. McKeown is correcting this state of affairs, and in this paper he has gone a long way to clarify our knowledge on creep. His observations on the importance of factors other than just grain-size, are well supported by his experimental results.

The effect on the creep rate of flattening a test-piece cut from a cable sheath is important in that it may help to explain some of the discrepancies in the results obtained by different workers. This effect of flattening will probably become more important when applied to lead alloys which are capable of work-hardening. This method of obtaining test-pieces from pipes or cable-sheathing appears to be extensively used in America and in all probability accounts for the difference occasionally observed between the results of mechanical tests obtained in America and those in this country, where the tests are usually carried out on the material in the form in which it is manufactured.

Dr. McKeown has not mentioned the effect of alternations in temperature which occur widely in practice, *e.g.* in chemical plant when subjected to repeated heating and cooling. In this case there is frequently a type of creep in the linings of vessels which results in laps and folds, and finally cracks, and which, for a lack of a better expression, is described as thermal creep. It may be argued that this is not creep as usually understood, but is the result of rapidly applied stress in the form of repeated expansion and contraction. This may be so in some cases, but it is certainly not so in all. In these practical conditions of thermal creep the reverse effect of that obtained on constant temperature tests appears to be the case—fine-grain material giving better resistance than coarse-grain material.

We are often asked why a lead alloy which work-hardens, and therefore does not elongate to the same extent as ordinary lead at a given load in a

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tensile strength test, should elongate more and fail more quickly when submitted to a creep test or prolonged tensile test at a similar load. The two appear contradictory. The usual explanation is that the tensile strength is determined by the strength of the grains themselves, whilst the creep strength is determined by the strength of the grain boundaries. This raises other questions. At what stage between a tensile test and a creep test does movement in the grain boundaries become the main factor?. What determines the position of that change and how is it affected by grain-size?

Dr. McKeown (*in reply*): I think that Mr. Chaston is under some misapprehension with regard to the flattened cable-sheath. I have observed it for a fairly long period and have been unable to find any recrystallization occurring in it. I have not attempted to carry out fatigue tests on lead which has been cold-worked or annealed and therefore cannot answer his question. I agree that newly extruded sheath is apparently in a state of internal stress and can recrystallize and be subject to grain growth when annealed. The extruded sheath used in the present investigation was about 2 years old when the tests were started and annealing at 100° C. produced a very slight increase in grain-size, as mentioned in the paper.

No attempt has been made to carry out tests at 80° C. on flattened or unflattened cable-sheath, but it is hoped to do so in the future.

Mr. Lancaster's question as to the advisability of comparing machined specimens with extruded pipe and sheath specimens is one that has been raised very frequently. In this work a method has been developed for preparing tensile creep specimens in lead and lead alloys which we are sure does not give rise to any working of the materials. Micro-specimens have been examined both before and after annealing and our method of machining has not produced any recrystallization or grain growth in leads.

With regard to Mr. Singleton's remarks, I regard thermal creep as an entirely different thing from what is examined here. Thermal creep is due to expansion followed by contraction, and the resulting change in dimensions is due to the fact that lead has practically no elastic limit and the greater part of any deformation which occurs is inelastic and not recoverable.

CORRESPONDENCE.

Professor H. F. Moore, B.S., M.E., M.M.E., D.Sc. (Member),* Mr. B. B. Betty,† and Mr. C. W. Dollins ‡: Reference is made in this paper to work on the creep of lead and lead alloys in sheathing used for protecting underground cables and certain criticisms are made of that work. In considering these criticisms the somewhat different objectives of Dr. McKeown's study and that at Illinois may well be considered. The work at the University of Illinois was carried out from the point of view of the user of lead sheathing. The problem was the study of the amount of creep in commercial lead sheathing of various chemical compositions, and produced in various ways. Such an investigation is a useful study of a product available on the market. It is not an investigation of the effect of varying conditions of manufacture at any

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one plant producing lead sheathing. Variations in different processes of extruding of lead sheathing as well as differences in chemical composition produced wide variations—so wide that the effect due to flattening transverse specimens seemed to be covered up by the variations in product of different manufacturers, variations which the experimenters could not control.

We believe that an investigation of available commercial material is a legitimate engineering investigation, and, in this case, the investigation has been of service as a guide to users of lead sheathing in forming judgments as to the justification for using the more expensive alloys of lead sheaths of underground cables.

The statement * that " if the effect of flattening specimens was noticeable it would have appeared in the tensile tests " is criticized by Dr. McKeown. It still seems to us, in view of the fact that the flattening of longitudinal specimens was in a direction perpendicular to the test load, while the flattening of transverse specimens was in a direction parallel to the test load, that if this flattening produced much effect there should have been systematic variations in the creep test results of longitudinal and transverse specimens. No systematic well-marked difference was observed. Dr. McKeown quotes the work by himself and Mr. Hudson on annealed copper very slightly overstrained in which it was found that " a definite proportional limit " has been induced by this treatment. We fail to see that an effect produced on annealed copper carries much weight in considering the behaviour of lead, and, furthermore, in common with several other investigators have not been able to find either any definite limit of proportionality of lead, or any correlation between an arbitrarily determined limit of proportionality and the creep properties of lead. In passing, we may say that we are very doubtful whether there exists any absolute limit of proportionality for any material.

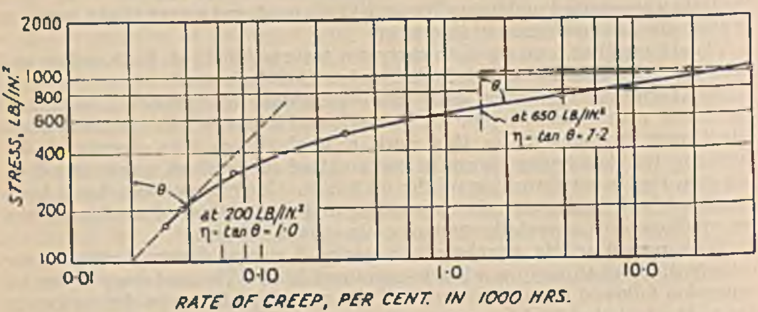

FIG. A.—Rate of Creep of Tensile Specimen from Extruded Sheath of Commercial Lead at Various Stresses.

It may well be the case that a careful study of the effect of flattening on lead sheet produced under laboratory conditions would show some effect on creep properties. In studying available lead sheathing as produced, this effect seems to be quite obscured by various other conditions.

The imperfections in the study of the creep of sheathing under hydraulic pressure due to effect of attached pieces of metal on which to take micrometer measurements is of course a fair criticism. In later tests attachments to the lead sheath have been made much smaller. Nevertheless, such measurements have been of value (1) in demonstrating that such creep would actually occur in lead sheathing under pressure and, (2) in giving some basis for a study of the

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* *Univ. Illinois Eng. Exper. Sta. Bull.* No. 272.

effect on creep of a stress at right angles to the maximum stress. This matter has been taken up very fully by R. W. Bailey.* In passing, we may observe that we are unable to agree with Bailey's fundamental formula for variation of creep rate C_x with uni-axial stress X, which is $C_x = AX^n$, in which A and n are constants. A study of several lead alloys under varying stresses showed a variation of creep rate † which indicated that n was not a constant as shown by the creep-rate–stress diagram which was found to be a curved line on log–log plotting paper. Fig. A is a typical diagram.

In Fig. 5, Dr. McKeown shows a relation between the logarithmic creep rate of extruded rod and the logarithm of the tensile stress. He does not show a straight-line relation between these quantities. After several years of experience in testing lead at the University of Illinois, it has been found most convenient to plot stress against logarithm of creep rate. If Dr. McKeown's data in Fig. 5 are plotted on a semi-log diagram it will be found that his room temperature test results do show a linear relation, as is shown in Fig. B.

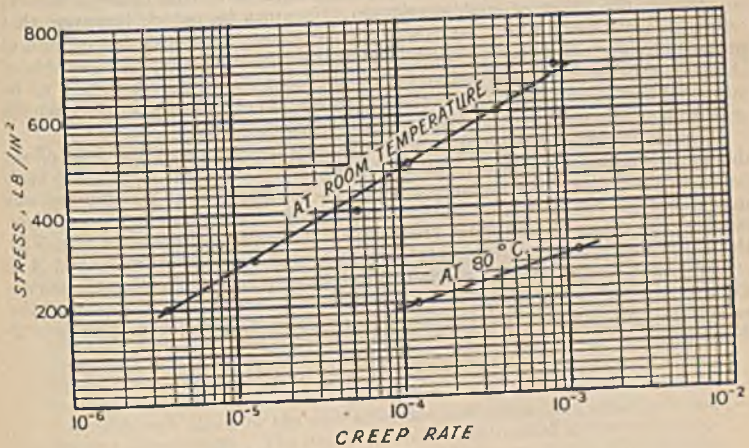

Fig. B.

The Author (*in reply*): The investigation of the effect of flattening on the creep characteristics of lead cable-sheathing was put in hand by the British Non-Ferrous Metals Research Association because member firms had directed our attention to the differences between the results of their creep tests and our own. It was discovered that the laboratories of the member firms had been carrying out their creep tests on flattened samples of cable-sheath whereas our tests, up to that date, had only been carried out on unflattened sheaths. At the outset the objectives in our work were the same as those in the work of Professor Moore and his colleagues, namely, a study of the effect of chemical composition on the creep properties of commercial lead sheathing.

The curves A and C of Fig. 7 show clearly the profound effect on the creep behaviour of flattening cable-sheath. The sheath, as was explained, was flattened so that the resulting specimens were loaded in the direction of the

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* *Proc. Inst. Mech. Eng.*, 1935, **131**, 131–349.

† The creep rate was determined during the second stage of creep when it is very nearly constant for lead alloys.

longitudinal axis of the sheath. It was not possible, from the small diameter sheath used, to prepare transverse specimens, but it seems reasonable to conclude, from the evidence given by the other tests on the effect of working, that such transverse specimens would also have shown the considerable effect of flattening on the creep properties. Whether any difference would be observed between the creep properties of transverse and longitudinal specimens we cannot say; this can perhaps be tried most conveniently by testing the effect of uni-directional rolling on lead sheet. The evidence of the tests carried out indicates that a small amount of cold-working can be retained by pure lead at ordinary temperatures and the retention of this work is shown most clearly in the behaviour of the lead under creep conditions.

The effect of flattening we know to be even more important in lead alloys which work-harden and retain this work-hardening for longer periods than pure leads.

The reference to annealed copper was made to indicate that even drastic annealing after small amounts of overstrain did not in this material remove completely the effect of such overstrain. It must be noted, however, that only a delicate form of test, in this particular case a determination of limit of proportionality using very sensitive measuring instruments, was capable of showing the presence and retention of the cold-working. It is not to be supposed that such a crude test as the determination of ultimate tensile strength would show the presence of such small amounts of work.

I have carried out a large number of creep tests on lead and lead alloys during the past 5 or 6 years, and all the evidence obtained from these tests tends to verify the formula suggested by R. W. Bailey. It was pointed out in the text (p. 207) that the two specimens at the lowest stresses had not yet reached the stage of minimum creep rate. This was indicated in Fig. 5 by the arrows attached to the points corresponding to these stresses, and it is certainly not correct to draw a line through these points. Plotting the curves for the two stresses of 200 and 300 lb./in.^{2} to a larger scale shows that the minimum creep-rate stage has not been reached, the creep rate is still diminishing.

THE EFFECT OF CAST STRUCTURE ON THE ROLLING PROPERTIES OF ZINC.*

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By L. NORTHCOTT,† Ph.D., M.Sc., MEMBER.

SYNOPSIS.

Preliminary work on zinc of 99·99 per cent. purity showed that the casting temperature of ingots cast by the Durville method has little effect on the structure, density, tensile strength, notched-bar impact value, or rolling properties.

The examination of ingots made by utilizing directional solidification showed that the directional properties of the zinc crystals are such that in columnar form the strength measured in the direction of growth is about four times that at right angles to it. Less pronounced differences were observed in the notched-bar impact values. The selective weakness of the metal along one set of crystal planes was also demonstrated by the tearing action of the cutting tool when machining in certain directions, and resulted in the development of a number of surface cracks. The weak plane was shown by X-ray examination to be the basal (0001) plane of the hexagon.

The connection between cold-working and the absence of columnar crystals was investigated by determining the degree of hot-working necessary to permit subsequent cold-working and correlating the results with the accompanying changes in structure. Provided that the initial hot reduction was not less than about 40 per cent., rolling could be completed satisfactorily in the cold. Hot-rolling was found to be associated with recrystallization and consequent release of internal stress; recrystallization was almost complete after about 40 per cent. hot reduction, although much of the cast structure was obliterated after half this amount of reduction. The importance of the equi-axial structure in cold-working was confirmed by tests on specially prepared ingots of equi-axial structure.

Columnar crystal aggregates may be completely cold-rolled if the direction of rolling between light passes is changed according to a crystallographic plan provided that the plane of growth of the crystals is in the rolling plane. No indication has been found that any of the peculiarities of zinc in working are due to boundary effects. Failure in zinc at atmospheric or moderate temperatures takes place by characteristic transcrystalline cracking in which the cracks tend to occur along the basal plane in any one crystal. This form of failure would appear to be limited to a small range of metals and alloys, possibly mainly of the hexagonal crystal type. The effect is greatly intensified by the powerful tendency of zinc to form large columnar crystals, since in an ingot of rectangular section the columnar crystals developed from one mould face have their directions of weakness in the same planes.

The addition of 0·75 per cent. cadmium to the zinc produced a small crystal structure but increased the recrystallization temperature so that complete cold-rolling was no longer possible. The total reduction before

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* Manuscript received November 24, 1936. Presented at the Annual General Meeting, London, March 10, 1937.

† Research Department, Woolwich.

cracking started was, however, greater when the rolling direction was changed than when rolling was carried out in one direction only.

An account is also given of the conditions under which zinc ingots can be initially rolled during cooling after casting; satisfactory strip was obtainable provided the temperature of the ingot at the commencement of rolling was within the range 350°–100° C., which, when 16 lb. ingots were used, entailed an interval of from 2½ minutes to 1 hr. after the completion of solidification.

INTRODUCTION.

THE research described in this paper was initiated to investigate the difficulties encountered in the first stages of breaking down chill-cast ingots. Some metals and alloys are liable to fracture when rolled or forged in ingot form, and require careful manipulation in the initial stages of working, although subsequently the metal may be worked without special precautions. In many instances difficulty in breaking down has been found to coincide with a coarse columnar type of crystal structure.

This paper deals with one section of a research carried out for the British Non-Ferrous Metals Research Association on the effect of cast structure on the rolling properties of metals and alloys. In the first instance pure zinc was selected for study as a metal commercially obtainable in a high state of purity, known to form a wholly columnar structure under all practical casting conditions, and of which ingots cannot be worked cold.

MATERIAL USED.

The zinc used was of Evans Wallower 99·99 + per cent. quality; the maker's batch analysis and confirmatory tests at the Research Department, Woolwich, are given in Table I.

TABLE I.—*Chemical Analysis of Zinc.*

	Zinc.	Iron.	Lead.	Cadmium.	Copper.
Maker's batch analysis, per cent. . .	99·9939	0·0004	0·0047	0·0008	0·0002
Confirmatory tests, per cent. . . .	...	<0·002	0·0041	<0·001	

EFFECT OF CASTING TEMPERATURE.

(a) *Method of Casting.*

Three triple ingots (9 × 4½ × 1 in.) were cast by the Durville method at 440°, 500°, and 600° C., respectively. A coal-gas flame was employed to prevent oxidation of the metal, and no mould dressing was used.

(b) *Density.*

The density of each ingot was determined after removing the head. The results are given in Table II, from which it will be seen that the casting temperature had a negligible effect on the density of the ingot.

TABLE II.—*Ingot Density.*

Marks.	Casting Temperature, ° C.	A, Grm./c.c.	B, Grm./c.c.	C, Grm./c.c.
NNL 1 . . .	440	7·136	7·136	7·136
NNL 2 . . .	500	7·137	7·139	7·139
NNL 3 . . .	600	7·138	7·138	7·138
Rolled zinc . .		7·149 grm./c.c.		

(c) *Effect of Casting Temperature on Structure.*

The ingots were sectioned as shown diagrammatically in Fig. 1. The cut faces of the longitudinal slices, approximately 1 in. wide and of the full thickness of the ingot, obtained from each side of the ingots B and C of each group, were machined, polished, and etched. The sections showed a completely columnar crystal structure and a large number of small fissures (Fig. 2, Plate XXXVIII), which were later

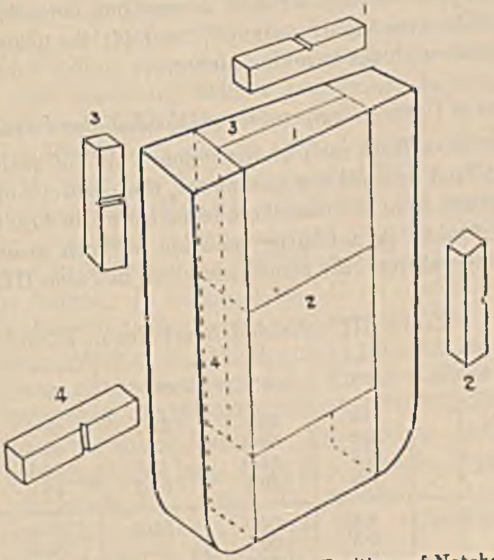

FIG. 1.—Method of Sectioning Ingot and Positions of Notched Bars.

found to be due to the tearing action of the cutting tool and not evidence of pre-existing unsoundness. Increasing the casting temperature had little effect on the macrostructure, but slightly increased the occurrence of fissures in the prepared surfaces.

(d) *Effect of Casting Temperature on Tensile Properties.*

The longitudinal slices cut from the " A " ingots were each machined to a tensile test-piece, 0·564 in. in diameter, but one piece from each ingot broke while being machined. The second piece from the ingot cast at 440° C. was found to be slightly cracked before loading in the testing machine. The maximum load of the remaining test-pieces was 1·4 tons/in.^{2}, and the elongation 3 per cent. on 2 in. Cracking was first observed in NNL 2 at a load of 1 ton/in.^{2} and in NNL 3 at 0·8 ton/in.^{2}. Cracks developed continuously in both test-pieces until the maximum load was reached, when the specimens were withdrawn before fracture was completed. Microexamination of the fractured test-pieces showed that (*a*) the cracks were trans-crystalline; (*b*) the cracks were approximately straight in any one crystal; (*c*) the unbroken crystals were highly twinned; and (*d*) the plane of fracture did not coincide with the twinning planes.

(e) *Effect of Casting Temperature on Notched-Bar Impact Value.*

The four slices from each of the ingots " A " of each group were machined to Izod notched-bar test-pieces, the positions of the notches in the test-pieces from the four slices being shown in Fig. 1. The test-pieces were broken in a Charpy machine at both atmospheric and increased temperatures; the results are given in Table III.

TABLE III.—*Notched-Bar Value in Ft.-lb.*

Mark.	Position.	20° C.	100° C.	125° C.	150° C.	200° C.
NNL 1	1	5·6	35·2	63·7	56·3	44·2
	2	5·3	50·2	...	60·9	46·7
	3	5·6	51·0	...	54·1	38·0
	4	5·3	40·1	51·5	45·9	45·9
NNL 2	1	5·8	60·9	53·3	60·0	55·0
	2	5·3	50·2	...	58·5	52·8
	3	5·6	37·6	...	56·8	55·5
	4	6·3	44·2	48·0	56·8	54·6
NNL 3	1	5·6	57·3	38·0	56·3	45·0
	2	6·1	36·0	...	41·7	53·7
	3	5·3	26·2	...	33·3	45·0
	4	5·1	26·9	44·2	44·2	51·9

These results show that the maximum resistance to fracture occurs in the neighbourhood of 150° C. and that the ingot cast at the highest temperature (600° C.) has the lowest impact value.

(f) *Effect of Casting Temperature on Rolling Properties.*

The four slices from the body of the "B" and "C" ingots of the three casts were selected for rolling. The crystal structure was wholly columnar, the direction of growth of the crystals lying across the thickness of each slice, and therefore at right angles to the rolling plane. The slices were polished and examined for cracks before being rolled; a number of small machining fissures were observed in all the slices. Sections were rolled at atmospheric temperature in the condition as cast, and after annealing for 5 hrs. at 150° and 300° C., and others were hot-rolled at temperatures of 150° and 300° C. For hot-rolling, the pieces were heated in an oil-bath to 150° C. or in a salt-bath to 300° C. The rolls were not heated.

All the pieces cracked at less than 10 per cent. reduction when rolling was attempted in the cold, and no improvement was given by a previous annealing at 150° or 300° C. The cracks, which increased progressively with rolling, appeared to be of the type already discussed in connection with machining fissures and tensile failures, and are shown in Fig. 3 (Plate XXXVIII).

On rolling at 150° C., all sections showed slight surface cracking on one side by the time they had been reduced 20 per cent. in thickness and also on the other side after a further 10 per cent. reduction. After reheating, continued rolling flattened out the cracks and all strips were rolled to 0·005 in., the finished strips being then free from cracks or other defects. In rolling at 300° C. no cracks occurred and no difficulty was found in taking the material down to 0·005 in. Samples were cut for examination at 15, 30, 50, and 75 per cent. reduction, and the microstructures of the transverse faces, Figs. 6–8 (Plate XL), show stages in the conversion of the coarse columnar casting structure into small equi-axial recrystallized material. The specimen reduced 15 per cent. showed twinning inside large twins in a columnar crystal and the initiation of recrystallization along the boundaries; traces of the original crystals still remained at 30 per cent. reduction, but were absent at 50 per cent. (Fig. 8, Plate XL).

During these preliminary rolling trials, in no instance did there appear to be any improvement in rolling properties as a result of the previous annealing at 150° or 300° C., nor could any difference be detected between the sections from the ingots cast at different temperatures. Further to test whether any advantage could be obtained by high temperature annealing which might have the effect of coalescing an insoluble and embrittling impurity, an ingot was annealed at 375°-400° C. for 100 hrs. and then rolled. Cracking occurred at the same stage and in the same manner as before, which suggested that rolling difficulties were not due to a weak grain boundary constituent. This is confirmed by the fact that the fracture of cast zinc commences by transcrystalline cracking, and not by fracture along the grain boundaries.

EFFECT OF CRYSTAL ORIENTATION ON PROPERTIES.

In view of the earlier indications that the zinc crystal was exceptionally weak along certain planes, tensile and notched-bar tests were carried out on specimens cut parallel and transversely to the direction of growth of columnar crystals. In order to obtain crystals of sufficient size for this purpose, a circular mould was constructed in which the sides consisted of a Salamander crucible lagged on the outside, and the base was a 3-in. diameter water-cooled copper rod let into the base of the crucible. Three ingots were obtained by the Durville method, the same casting temperatures being used as before, namely 440°, 500°, and 600° C. The three ingots were sectioned along the axial face, and the two cut faces of each ingot machined. To determine the tearing effect of the cutting tool on the crystals in different directions, one face (*A*) was machined in a direction parallel to the direction of growth of the columnar crystals and the second face (*B*) was machined transversely. It was found that only when the tool cut across the crystals were portions of the crystals torn out. The effect is well illustrated in the photographs of the polished faces of one of the ingots (Fig. 10, Plate XLI); the crystal structure as developed by etching is shown in Fig. 11. The fissures were of the type described earlier (p. 232) in connection with the tensile test-pieces and rolled slices.

(a) *X-Ray Examination.*

Slices parallel to the axial face and not more than one crystal thick were obtained, and an X-ray examination carried out to determine the orientation of the space lattice of the columnar crystals. In every instance the basal (0001) plane of the hexagonal lattice (Fig. 17), was found to coincide with the direction of growth of the crystals, with the hexagonal axis transverse to the columnar crystal.

(b) *Notched-Bar Impact Value.*

The effect of crystal orientation on the notched-bar impact value of the material was determined by taking test-pieces longitudinally and at right angles to the direction of growth of the crystal, that is, the notch was, respectively, (*A*) perpendicular and (*B*) parallel to the direction of crystal growth. The results of tests carried out at atmospheric and increased temperatures are given in Table IV.

The test showed that resistance to fracture was appreciably greater when the notch was at right angles to the direction of growth of the columnar crystals. The effect was small at room temperature and generally most marked within the usual working range of temperature.

TABLE IV.—*Effect of Crystal Orientation on Notched-Bar Value in Ft.-lb.*

Ingot.	Position.	20° C.	100° C.	150° C.	200° C.	250° C.
NNL 4	(*A*)	5·8	75·5	69·9	...	49·9
	(*B*)	5·0	46·5	49·0	51·2	36·6
Increase of *A* over *B*, per cent. . .		16	62	43	...	36
NNL 5	(*A*)	6·1	73·6	64·7	59·7	50·4
	(*B*)	5·8	52·0	56·1	32·0	39·0
Increase of *A* over *B*, per cent. . .		5	42	15	86	19
NNL 0	(*A*)	6·3	70·3	70·8	60·6	57·5
	(*B*)	5·8	53·8	51·7	44·0	29·7
Increase of *A* over *B*, per cent. . .		9	31	37	38	93

The average difference due to orientation over all the tests was 42 per cent.

(c) *Tensile Properties.*

Two ingots were cast at a temperature of 500° C., the columnar structure confirmed by examination of the axial faces, and flat tensile test-pieces, 1½ × ¼ × ⅛ in. along the parallel portion, made from both ingots, with the axis parallel and transverse to the columnar crystals. The test-pieces were polished and etched, and examined with a low-power microscope during the tests. The tensile results are given in Table V.

The direction of fracture of all test-pieces was approximately perpendicular to the direction of the applied stress, and the actual failure occurred by cleavage parallel to the basal plane in the case of the transverse crystal test-pieces, and to the hexagonal plane in the longitudinal crystal test-pieces.

From the results of the tensile tests it would thus appear that the tensile strength of the columnar crystals is in one instance roughly three times, and in the other, four and a half times as great in the direction of growth as it is at right angles to it. In other words, the crystal in the direction of the (1010) plane resists fracture much more than that along the (0001) plane.

Microexamination of the test-pieces during loading showed twinning to occur spontaneously and not gradually; a twin once formed did not appear to grow in length; a slight clicking noise occurred with the formation of twins. Particularly in the longitudinal crystal test-pieces, twinning occurred usually along at least two planes in each crystal (Fig. 14, Plate XLII), and there was little evidence of slipping. Twinning was less prominent and slip-lines more prominent in the transverse crystal test-pieces, in which fracture occurred along the weak basal plane parallel to the slip-planes, with the characteristic cleavage typical of zinc, and resulting in minimum deformation (Fig. 13, Plate XLII).

TABLE V.—*Effect of Crystal Orientation on Tensile Strength.*

Mark.	Number of Crystals.	Longitudinal or Transverse.	Ultimate Stress, Tons/in.^{2}.	Average Tensile Strength, Tons/in.^{2}.
15A1	6	longitudinal	3·46	3·43
15A2	5	,,	3·12	
15A3	6	,,	3·71	
15A4	18	transverse	1·12	1·11
15B1	18	,,	1·64	
15B2	21	,,	0·81	
15B3	24	,,	1·07	
15B4	23	,,	0·99	
16A1	3	longitudinal	3·93	3·40
16A2	12	,, *	3·84	
16A3	6	,,	2·97	
16A4	4	,,	2·86	
16B1	24	transverse	0·68	0·77
16B2	38	,,	1·12 †	
16B3	18	,,	0·81	
16B4	17	,,	0·45	

* Crystals inclined about 20° from longitudinal.
† Coarse crack across the width at 0·67 ton/in.^{2}.

THE DEPENDENCE OF COLD-WORKABILITY ON THE PREVIOUS HOT BREAKING DOWN OF THE CAST STRUCTURE.

To determine the degree of hot-rolling required to permit subsequent cold-working, a series of slab ingots was cast and given preliminary reductions varying from 5 to 80 per cent. soon after the completion of solidification, whilst the ingots were still hot. The slabs were then cooled to atmospheric temperature and rolling continued in the cold. The results of these tests are summarized in Table VI.

The first ingot, which had been given a preliminary reduction whilst hot of 5 per cent., cracked in the first cold pass of 0·1 in. reduction; those reduced 15 and 25 per cent., cracked in the second cold pass. As the cracking of these three ingots became worse at the next stage, rolling was discontinued. Of the two ingots which were given a 40 per cent. reduction whilst hot, one appeared to have rolled satisfactorily, but showed transverse cracks when cold, and these extended at the next stage. The second was hot-rolled to the same preliminary reduction, after allowing a longer period of cooling after casting, and this rolled satisfactorily in the cold. Two ingots were similarly given a 50 per cent. reduction whilst hot, one ingot being allowed to cool to a lower temperature before commencing rolling. Both hot-rolled well; the cooled ingot rolled cold without difficulty. The hotter ingot showed edge cracking in the first cold pass, but this did not extend later, and the strip was successfully reduced to 0·03 in. thick. Ingots given preliminary hot reductions of 60, 70, or 80 per cent. rolled to thin strip satisfactorily. The fractures of ingots reduced 5, 15, and 25 per cent. whilst hot and given one or two passes in the cold are illustrated in Fig. 5 (Plate XXXIX) together with the fracture of an unrolled ingot. Evidence of recrystallization is shown by the section reduced 5 per cent., but traces of columnar fracture are present at 15 per cent. reduction. Although the fracture of the 25 per cent. sample appears to show complete recrystallization, it may be inferred from the microexamination of the hot-rolled pieces described in an earlier section that the cast structure is not completely obliterated at this stage. The ability to cold-roll ingots after a preliminary hot reduction is apparently associated with the complete conversion of the original cast columnar crystals into very small equiaxial crystals.

Table VI.—*Effect of Varying Degree of Hot-Rolling Previous to Cold-Rolling.*

Original Thickness, Inches.	Thickness after Hot-Rolling, Inches.	Hot Reduction, Per Cent.	Thickness at which Cracks Appeared, Inches.	Thickness at which Rolling was Discontinued, Inches.
2	1·9	5	1·8	1·7
2	1·7	15	1·5	1·4
2	1·5	25	1·3	1·2
2	1·2	40	(1·2) 1·0	1·0
2	1·2	40	...	0·03
2	1·0	50	0·8	0·03
2	1·0	50	...	0·03
2	0·8	60	...	0·03
2	0·6	70	...	0·03
2	0·4	80	...	0·03

Comparison Between Columnar and Equi-Axial Crystal Ingots.

(a) *Development of Equi-Axial Structure.*

In view of the ability to roll zinc in the cold once it has been given sufficient hot-rolling to cause complete recrystallization and to convert the coarse columnar type of structure into small equi-axial crystals, attempts were made to obtain the equi-axial structure in the cast ingot. Earlier experiments on the effect of casting temperature had shown that wide variations had little effect in modifying the columnar structure which is so pronounced a feature of all zinc castings. Reducing the casting temperature to a minimum whilst still retaining the flowing characteristics of liquid metal in no instances resulted in an equi-axial structure, although different mould conditions were employed; other expedients were therefore necessary. "Seeding" with zinc dust, either in the Durville process or when pouring direct from the crucible at as low a temperature as possible, failed to promote the required structure, and no advantage was gained by pouring slowly into a water-cooled mould. Slow pouring and stirring the liquid in the mould with a carbon rod resulted in some improvement, and wholly equi-axial crystal structure was finally obtained by transferring pasty metal from a large crucible, seeding with a little zinc dust, and stirring whilst pouring. In order to compare the mechanical and working properties of the columnar and equi-axial crystal types of ingots, a 50 lb. ingot of each type was cast from the same crucible. The columnar crystal ingot was Durville cast at 600° C., the sides of the mould consisting of a warmed carborundum ring and the base of a copper plate, the underside of which was sprayed with water immediately after casting. The equi-axial crystal ingot was obtained by the method described above, the mould consisting of a carborundum ring and baseplate both heated to about 200° C.; the ingots were of the same dimensions. The etched axial faces of the two ingots are illustrated in Figs. 15 and 16 (Plate XLIII) from which it will be seen that the crystal structures are wholly columnar and wholly equi-axial, respectively.

(b) *Comparison of Rolling Properties of Columnar and Equi-Axial Structures.*

Slices about $\frac{7}{16}$ in. thick were obtained from three planes to permit rolling to be carried out, in the case of the columnar crystal sections, with the direction of growth of the crystals (*a*) parallel to the direction of rolling, (*b*) parallel to the axis of the rolls, and (*c*) at right angles to the rolling plane. Dealing with the columnar crystal sections first, it was observed that after about 5 per cent. reduction cracks developed parallel to the axis of the rolls irrespective of the orientation of the crystals and increased on further rolling, and that cracking occurred most easily along the direction of growth of the crystals. Sections of the equi-axial crystal ingot when rolled in one direction only also cracked, although at a slightly later stage and on continued rolling the degree of cracking was less than with the columnar crystal pieces.

(c) *Cold-Rolling of Cast Zinc.*

According to Mathewson and Phillips * twinning can occur along the pyramid face with a maximum deformation of 6·75 per cent., measured as a reduction in thickness perpendicular to a basal plane. Although twinning does not in itself result in much deformation, it has the important effect of producing a re-oriented space lattice, in the twinned layers, in which the basal plane is 94° 5′ removed from the pre-existing basal plane, but lies approximately in some one of the six prism face positions according to the pyramid face on which twinning has occurred. Additional deformation in the direction of the applied stress may then occur by slip on the new basal plane; the direction of the stress with respect to the orientation of the crystal will determine whether basal slip or twinning occurs first.

Although Mathewson and Phillips incline to the view that less stress is required to produce slip than to cause twinning, from the micro-examination of test-pieces in the present work it appeared that although some slip occurred at an early stage and developed on further loading, twinning was much more general. In no instance have crystals of cast zinc been found free from twinning. An attempt was made to prepare such crystals by very slow cooling from the melt, but a fine acicular type of twinning was observed, apparently resulting from cooling stresses; some uncertainty exists as to how far the ingot was strained in the cutting operation, although continual polishing and deep etching did not appear to reduce the proportion of twins.

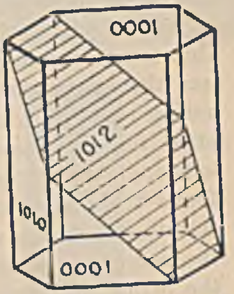

Fig. 17.—Zinc; Crystal Structure.

From a consideration of the above conclusions of Mathewson and Phillips, and the observations of the mode of deformation and recrystallization made in the present work, it was thought that cold-rolling of the cast material should be possible provided that the preliminary reduction is made in a direction normal to a twinning (1012) plane, to initiate slip on the basal plane and the formation of the first order of twins on one of the pyramidal planes, and that before fracture can occur the direction of rolling is changed to the normal of another twinning plane. This would arrest the application of much further stress on the original planes now highly stressed and divert it to planes which had been stressed only slightly. The purpose of changing the

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* *Amer. Inst. Min. Met. Eng., Inst. Met. Div.*, 1927, p. 143.

direction of rolling repeatedly would be to obtain advantage of the full capacity of the material to distort by twinning and slip; any tendency towards recrystallization would be to permit unlimited distortion. The success of the method in the case of small reductions would depend on changing the direction of rolling before the commencement of cracking, and for large reductions additionally, on the initiation of recrystallization at a suitable stage.

This method was adopted in the further rolling of sections from the two 50 lb. ingots described above, and proved successful when the correct conditions were followed. The method finally adopted for the columnar crystal sections was to roll first in the direction of growth, then diagonally, with the direction of crystal growth at about 45° to the rolling direction, turn through 90° to initiate twinning on another pyramidal plane, then in a direction at right angles to the original direction to permit distortion from slip on the basal plane of the twins, and then repeat as before. After a reduction of about 50 per cent., rolling could be continued satisfactorily in one direction only. Thin strip, free from cracking, was obtained by this method in both the columnar crystal and equi-axial crystal section. The process was found to be comparatively simple to carry out with the equi-axial structure, but care was needed with the columnar crystals to obtain the maximum deformation in any one direction without exceeding the permissible limit and so cause cracking. The advantage of the equi-axial structure is that the orientation of the crystals is different over three planes instead of two in the case of columnar crystals, so that with any given reduction there is less fear of exceeding the safe limit. That thin strip was obtainable suggested that recrystallization occurred even at atmospheric temperatures when sufficient reduction was given; this was confirmed by micro-examination of a section reduced about 50 per cent. Fig. 9 (Plate XL) shows evidence of the cast structure and an area of apparently strain-free recrystallized material. That recrystallization has taken place in these samples at atmospheric temperature to a degree comparable with that observed in the hot-rolled pieces after, say 30 per cent. reduction, is probably due to the higher stress which it has been possible to apply to the metal without fracture by the method described above; it is a general feature of the stress recrystallization of all metals that the greater the stress the lower is the temperature of recrystallization. Changing the direction of rolling of slices in which the columnar crystals were disposed at right angles to the rolling plane was not effective in preventing cracking, nor was it expected to be since with such an orientation the rolling stresses reach their maximum along the weak basal plane of the crystals.

PLATE XXXVIII.

2

Unetched. Etched.

3

FIG. 2.—Longitudinal Ingot Section. × ½.

FIG. 3.—Cracks developed in Cast Zinc by Cold-Rolling; Section Polished and Etched; Rolling Direction. × 4.

FIG. 4.—Section of Slab Ingot for Rolling; Columnar Crystals from Base. × ½.

[*To face p.* 240.

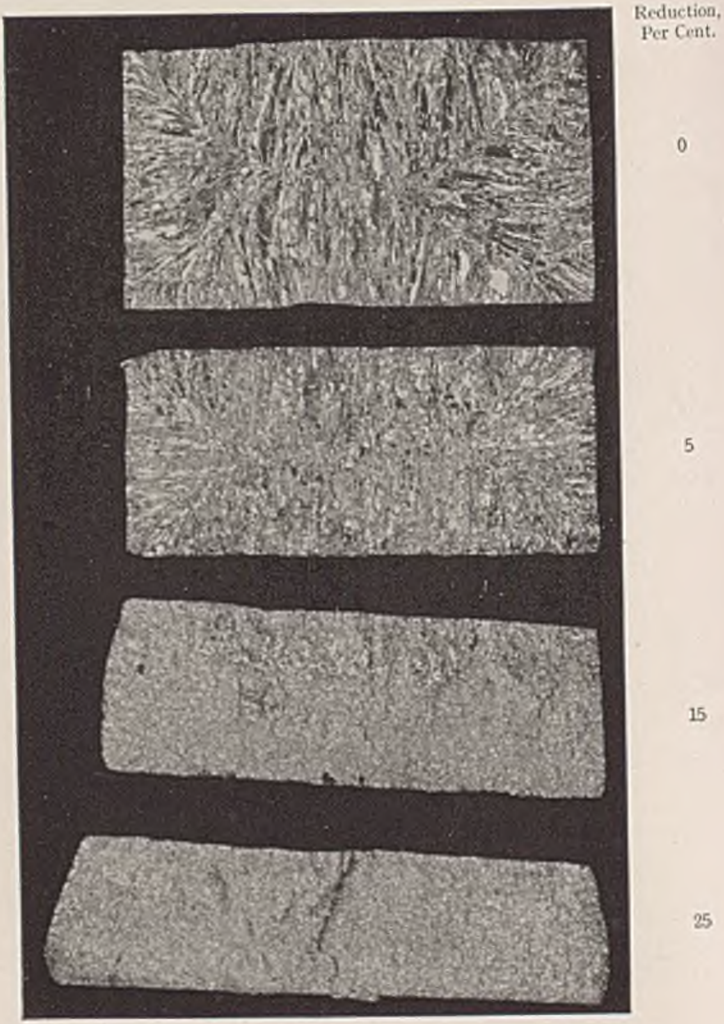
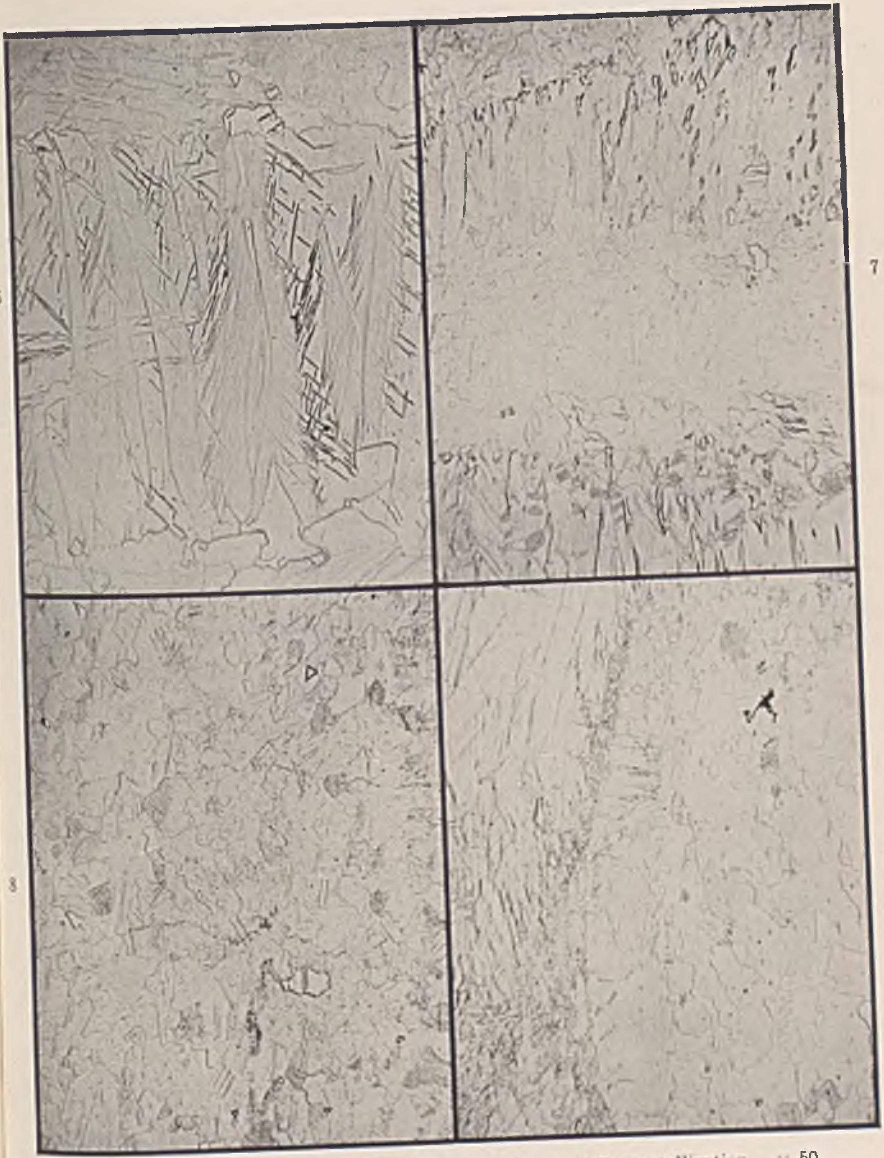


FIG. 5.—Fractures of Ingots As Cast and After Hot-Rolling. × $\frac{2}{3}$.

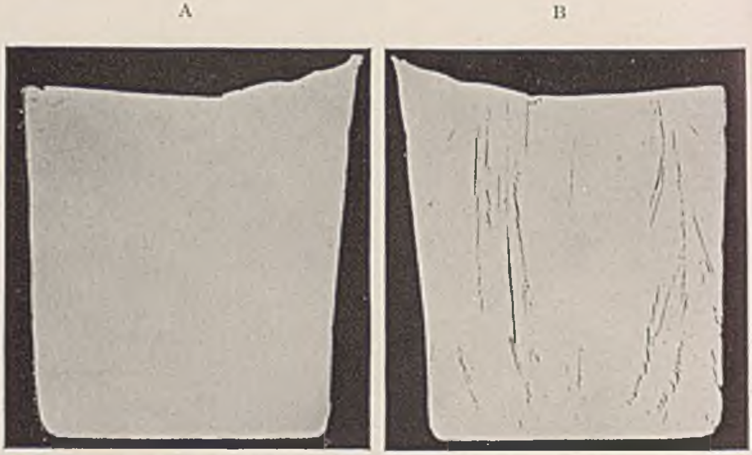
PLATE XL.



Microstructure of Zinc After Rolling, Showing Stages of Recrystallization. × 50.
FIG. 6.—15% Reduction at 300° C.
FIG. 7.—30% Reduction at 300° C.
FIG. 8.—50% Reduction at 300° C.
FIG. 9.—Cold-Rolled 50% in Different Directions.

PLATE XLI.

10



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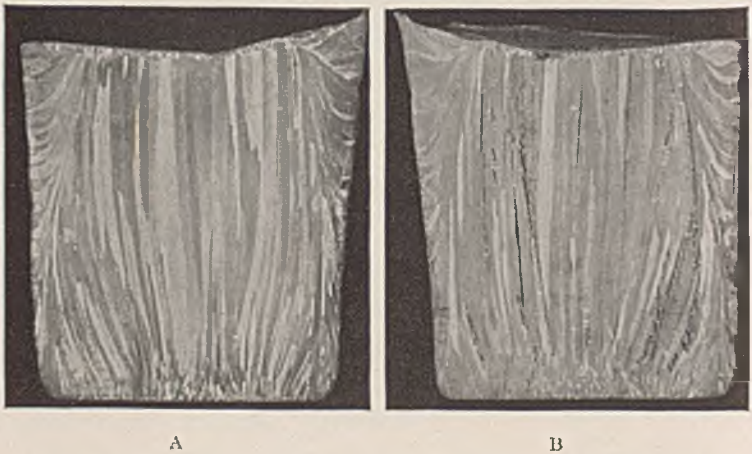

FIG. 10.—Two Halves of Ingot Machined; A, Vertically; B, Horizontally. × ½.
FIG. 11.—Etched Axial Faces of Ingot Shown Above. × ½.

PLATE XLII.

12

13

14

FIG. 12.—Loaded Zinc Test-Piece under Oblique Illumination; Surface Rippling Due to Twinning; Crystals Longitudinal. × 3.

FIG. 13.—Fracture of Transverse Crystal Test-Piece, Showing Slip Lines. × 40.

FIG. 14.—Fracture and Structure of Longitudinal Crystal Test-Piece. × 4.

15

16

Etched Axial Faces of Zinc Ingots. × ⅗.

Fig. 15.—Columnar Crystals.

Fig. 16.—Equi-Axial Crystals.

The method has been applied satisfactorily to an ingot, 4 × 4 × ½ in., in which the crystals were disposed vertically for the full height of 4 in. (Fig. 4, Plate XXXVIII), by using a chilled copper base and hot iron sides. Although this method of rolling zinc is not recommended as an alternative to hot-rolling, it is interesting as showing how crystal deformation may be controlled.

There remains to be explained the difference in rolling properties between the recrystallized rolled material and the cast equi-axial crystals. It is suggested that the responsible factor may be found in the large size of the cast crystals, the average diameter of which was about ⅓–½ of the thickness of the section at the commencement of rolling. No success has yet been obtained in producing cast material having equi-axial crystals of a size comparable with that developed by recrystallization.

TABLE VII.—*Tensile Strength of Columnar and Equi-Axial Crystals.*

	Columnar Crystals.				Equi-Axial Crystals.			
	Longitudinal.		Transverse.		Longitudinal.		Transverse.	
	1.	2.	1.	2.	1.	2.	1.	2.
Maximum stress, tons/in.^{2}	3·3	3·3	0·89	0·78	1·6	1·9	2·7	2·08
Elongation on 2 in., per cent.	3·5	5·5	4·0*	1·5	6·0	5·0	1·5	4·0
Reduction of area, per cent.	4·4	6·4	2·6	1·6	0·8	3·2	2·2	0·4

* High value due to cracking and slight separation in crystals near the fracture.

(d) *Tensile Tests.*

Test-pieces, 2 × ½ × ½ in. parallel portion, were obtained from both ingots in the longitudinal and transverse directions and the results of the tensile tests are given in Table VII. It is thought that too much reliance need not be placed on the figures for elongation and reduction of area, which are included only to give a relative idea of the general lack of ductility. The maximum stress results for the columnar crystal aggregates confirm those obtained on smaller test-pieces given in Table V, and show that the tensile strength of the columnar crystals taken in the direction of crystal growth is about four times as great as it is across that direction. The maximum stress figures for the equi-axial crystal pieces are, as would be expected, roughly midway between those obtained in the longitudinal and transverse directions for the columnar crystals.

To obtain small equi-axial crystals, an alloy of zinc containing 0·75 per cent. cadmium was cast at low temperature. The small equi-axial structure was confirmed and pieces cut for rolling. The cadmium addition had, however, appreciably increased the temperature of recrystallization. Sections of the alloy were rolled in different directions and in one direction only, and cracking was first observed after total reductions of 24 and 14 per cent., respectively. When similarly rolled at 100° C., cracking was observed at 45 and 25 per cent., respectively, and although further rolling was possible, particularly of that piece in which the direction of rolling was changed, it appeared that the temperature would have to be still further increased to ensure complete freedom from cracking.

ROLLING OF INGOTS IMMEDIATELY AFTER CASTING.

In view of the ease with which zinc could be rolled whilst hot, experiments were made to determine whether practical advantage could be taken of the heat in the ingot immediately after casting. The general procedure adopted was to cast the pure zinc into a chill mould 9 × 4 × 2 in. thick, strip the mould as soon as solidification was considered to be complete, and commence rolling as quickly as possible. In the first instance three ingots were cast and were rolled successfully to thin strip without reheating; particulars are given in Table VIII.

TABLE VIII.

Casting.	Casting Temperature, ° C.	Ingot Thickness, Inches.	Number of Passes.	Final Thickness, Inch.
1	600	2	13	0·075
2	500	2	11	0·08
3	450	2·2	11	0·06

The first ingot was actually stripped a little too soon, thus allowing some liquid metal to escape, and the strip showed a little edge cracking. A greater time interval (5–10 minutes) was allowed before rolling the other two ingots, and these rolled satisfactorily. The third ingot was broken down from the original thickness of 2·2–1 in. in only three passes without difficulty.

Determination of Most Suitable Initial Rolling Temperatures.

It appeared desirable to determine (*a*) the most suitable temperature for commencing rolling and (*b*) the permissible time interval between casting and rolling. The general procedure was to cast from the crucible into the 9 × 4 × 2 in. mould, strip the mould as soon as possible, and measure the temperature of the ingot and the time interval between the end of solidification and the commencement of rolling. A surface type of pyrometer was used to measure ingot temperatures, the bare couple being pressed against the middle of one face of the ingot; the lag in temperature indication was quite small. Rolling was not continued beyond the 0·1 in. stage. The results are summarized in Table IX.

Thus, rolling was satisfactory when carried out in the temperature range 300°–100° C., and even the rolling commenced at 350° yielded strip which was sound except for some edge roughness.

TABLE IX.—*Variation in Rolling Temperatures.*

Temperature at Commencement of Rolling, ° C.	Time Interval between Solidification and Rolling.	Remarks.
380	10 seconds	Little edge cracking at 0·8 in.; 0·1 in. strip showed cracks up to 0·25 in. in from edge.
350	2¼ minutes	Slight edge cracking at 0·5 in.; 0·1 in. strip only rough at edges.
300	6 "	Strip satisfactory.
250	11 "	" "
200	21 "	" "
150	33 "	" "
100	59 "	" "
75	64 "	Cracking started at 1·6 in. stage extended at 1·4 in. stage and rolling discontinued.
50	84 "	Cracking started at first pass but became increasingly confined to edges; 0·1 in. strip appeared satisfactory.

During the rolling commenced at 50° C., temperature measurements and visual examination were made at each stage. The original thickness was 2 in. and the temperature 50° C. The first pass to 1·8 in. resulted in general surface cracking; at the second pass to 1·6 in. the cracks widened but were mainly confined to the surface and the temperature had increased to 62° C.; at the 1·4 in. stage the surface quality was improved and the temperature was now 71° C.; the surface quality continued to improve at the 1·2, 1·0, and 0·8 in. stages, the temperature having now increased to 101° C. and cracking was mainly confined to about ⅛ of the width along each side; the 0·65 and 0·50 in. stages increased the temperature to 109° C. and the middle width of the strip appeared quite free from cracking; further reduction to 0·4 and 0·3 in. caused the strip to reach its maximum temperature, 113° C., after which the material was becoming sufficiently thin to lose its heat to the rolls; at 0·22–0·15 in. the temperature had decreased to 106° C. and at the last stage of 0·10 in., the temperature was 97° C. There was a continual improvement in the surface quality of the strip as rolling was continued such that the finished strip appeared free from cracks.

The results of the experiments show that even with relatively small ingots (16 lb.), the material is readily workable if rolling is commenced within 1 hr. after completion of solidification, and that, provided that the hot reduction is not less than about 50 per cent., rolling may be completed in the cold.

CONCLUSIONS.

The investigations described in this paper have shown that the crystals of zinc, which belongs to the hexagonal system, are weaker along certain planes—the basal (0001) plane of the hexagon—than along others. In columnar form zinc crystals are for this reason weak at right angles to the direction of growth. The cracking of ingots of pure zinc when cold-rolled under ordinary conditions is thus due to the properties of the crystals themselves and not to grain boundary effects. The effect is greatly intensified by the powerful tendency of zinc to form large columnar crystals, since in an ingot of rectangular section the columnar crystals developed from one mould face have their direction of weakness in the same planes. The cold-rolling of pure cast zinc is possible under certain controlled conditions, but the method is not likely to be applicable to commercial work.

ACKNOWLEDGMENT.

The investigation described forms part of a programme of research carried out for the British Non-Ferrous Metals Research Association to whom the author is indebted for permission to publish these results.

DISCUSSION.

MR. G. L. BAILEY,* M.Sc. (Member): As Dr. Northcott has said, this work is part of a larger investigation on the effect of cast structure on the working properties of metals and alloys, with particular reference to cold-rolling. It is known that there are materials which are liable to crack in the breaking-down stages of cold-rolling, particularly when in a condition of coarse grain in the cast ingot. Zinc is not normally cold-rolled, and is so easily rolled hot that there is no particular point industrially in developing a technique of cold-rolling zinc from the cast ingot; at the same time, zinc forms a very interesting case, the study of which was expected to throw some general light on the whole question of the cracking of certain materials in cold breaking-down. Zinc has the added advantage that it can be easily obtained of an extremely high degree of purity, and it is with that high purity zinc that the author has worked.

It has become apparent as a result of this investigation that there are various causes for the cracking of materials in cold breaking-down, and the

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* Development Officer, British Non-Ferrous Metals Research Association, London.

remedies are correspondingly diverse. Some materials are particularly sensitive to small changes in composition; ingots of some alloys are cold-rollable over a fairly wide range of composition if of a fine-grained structure, but will crack if of coarse grain as cast. In the case of zinc, however, the difficulty has been shown clearly to be due to the inability of the individual crystal to withstand severe deformation in the cold.

Dr. Northcott's study of the behaviour and the properties of crystal aggregates, both columnar and equiaxial, of pure zinc has led to the clear conclusion that it is not possible industrially to cold-roll zinc even of high purity unless possibly—and this point has not finally been settled—some method of casting can be devised which will give an even finer equi-axial grain than Dr. Northcott has yet succeeded in obtaining. I confess that I am very interested to know whether it is possible to produce such a fine-grained zinc ingot and, if so, whether such an ingot, having a grain-size approximately the same as that of rolled and annealed strip, could be cold-rolled direct from the cast state. That interest, however, is theoretical and not practical so far as zinc is concerned, and the hot-rolling of zinc is likely always to be the easiest method of dealing with this particular metal.

There is one point on which the paper is open to criticism. Many of the points brought out by the author are not new. A very great deal of work has been carried out on zinc, its macrostructure, working properties, and the effect of composition (particularly in Germany), but the author has not referred to this published work. It is difficult to quote particular instances, because the literature is so voluminous, but Seidl and Bauer and Zunker have worked on zinc on somewhat similar lines to those which Dr. Northcott has followed, and some of their conclusions are closely parallel to those which he has reached. This paper would have been improved very considerably, in bringing out the new methods of approach which the author has adopted and the new results obtained, if it had included a careful and detailed comparison between the author's work and that of other investigators.

Mr. H. M. Ridge * (Member): Zinc of 99·99 per cent. purity has been on the market for a comparatively short time. It is used in die-casting and should be important, amongst other things, because of its anti-corrosive properties.

I hope that in due course the author will be able to publish similar data and information for the kind of metal which is normally used for rolling zinc sheets, and to extend the investigation to cover electrolytic zinc. The changes and improvements in the production of zinc in recent years have been so rapid that much research is still required.

I would emphasize that figures such as are given, for instance, in Table IX cannot be applied to metal of slightly different composition. I know of no instance where the effect of even very small amounts of impurities is so great as in the case of zinc.

Of almost as much importance as the actual casting temperature, and possibly of even greater importance, is the rapidity of solidification and of cooling, particularly round the solidification temperature. It is obvious, of course, that that will affect the crystal growth, but it also affects a good many other things, as is found in rolling zinc sheets.

Another point to which I would particularly direct attention, is the effect of gas in the metal. This 99·99 per cent. pure metal, so far as I know, has a reasonably low gas content, but in most of the zinc now used in this and other countries the effect of gas is very important.

Mr. R. Chadwick,† M.A. (Member): I am surprised that the author was

* London.

† Research Metallurgist, I.C.I. Metals, Ltd., Birmingham.

troubled with the cracking of pure zinc ingots rolled at 150° C. In spite of the fact that ingots were etched and examined before preheating, it appears likely that fine cracks were in fact present; these may have been produced during the cutting and machining operations, but it is quite likely that stresses during the cooling of the ingots, or even in the early stages of preheating, gave rise to some cracking. In commercial rolling practice it is considered undesirable to allow ingots to cool below 100° C. between casting and rolling because of this danger of cracking.

Prolonged annealing of pure zinc ingots was carried out in an attempt to improve rolling properties, but unfortunately on the one alloy for which such a treatment would have been useful, *i.e.* the 0·75 per cent. cadmium alloy, this was not apparently done. Alloys containing cadmium in excess of 0·1 per cent. are always heavily cored, but this can be largely removed by soaking at 200° C. for about 24 hours, without in any way affecting grain-size. If this had been done it would undoubtedly have improved the ductility, and it should have then been possible to obtain a greater amount of cold-rolling without cracking.

Regarding the recrystallization of partially rolled cast material, the author observed recrystallization at room temperature after 50 per cent. rolling reduction. I would direct attention to diagrams which I published * showing the extent of such recrystallization from cast zinc carefully cold-rolled so as to avoid any increase in temperature, and showing that work-hardening and recrystallization occurred to the same extent as in the cold-rolling of annealed strip. Dealing with rather less pure material, I obtained complete recrystallization after 30 per cent. reduction in a period of about 3 months, whilst after 50 per cent. reduction only about 1 week, and after 60 per cent. reduction only 24 hours was required. The author does not state what period elapsed between rolling and examination, but it does not appear that the purer material employed has very greatly affected the rate of recrystallization after varied amounts of cold-rolling.

Mr. C. Wainwright †: During an investigation of the properties of certain magnesium alloys,‡ X-ray examination showed that above rolling temperatures of about 200° C. little or no strain was left in the material by rolling, as determined by an absence of broadening of the high-angle reflection lines. At lower rolling temperatures, however, where there was a considerable deterioration in mechanical properties, broad lines were invariably obtained. This strain could be removed by an extremely short anneal at 200° C., and it was therefore remarked that " the ' rate of annealing ' factor is of considerable importance, and that for successful hot-rolling the rate of removal of distortion by annealing should exceed the rate at which distortion of the lattice by deformation would occur." In the present work, were any observations of residual strain made by the X-ray method, and, if so, was there evidence, under any conditions, of a similar fairly critical region ?

Dr. Northcott (*in reply*): I am very doubtful about the possibility of developing a method of casting to give a very fine crystal structure in the case of very pure zinc. The purer the zinc, or the purer any metal, the greater will be the difficulty in preparing a fine equi-axial structure. As indicated in the paper, the less pure the zinc, or alternatively the greater the quantity or number of additions made, the greater is the ease in obtaining a fine equi-axial structure. That, however, has another disadvantage, which arises in connection with Mr. Chadwick's remarks.

* *J. Inst. Metals*, 1933, 51, 102, 120.

† Scientific Officer, Metallurgy Department, National Physical Laboratory, Teddington.

‡ Prytherch *J. Inst. Metals*, 1935, 56, 133.

With regard to the omission from the paper of references to previous work, and particularly to that of German workers, I would say that this would probably have involved a general survey as long as the present paper. Moreover, most of the German work deals with impure zinc, or else on single crystals of zinc, and there is no doubt that the method of deformation of single crystals in the case of an hexagonal material like zinc is very largely different from the mode of deformation of crystal aggregates as found in ordinary ingots.

As to the extension of the work to other qualities of zinc and the type of material used commercially, that is a matter for the British Non-Ferrous Metals Research Association. No determinations were made of the rate of cooling around the solidification temperature. It might be said that the purer the material the less important is the rate of solidification through the solidification temperature, because a perfectly pure metal will solidify at one temperature only, and, provided that the rate is such that there is a decrease in temperature, it does not matter what the rate is. No determination was made of the effect of gas on the solidification of zinc, but it is probable that with good quality zinc no great trouble need be feared from the presence of gas (I assume that Mr. Ridge referred to gas absorbed from furnace atmosphere) unless the metal is taken to a very high temperature, and even then the high vapour pressure of the zinc would prevent much gas absorption and its release during solidification.

I agree with Mr. Chadwick's suggestion as to the cracking of the zinc at 150° C. that it was probably due to incipient cracks developed in the machining of the original slices. As to the rolling of the zinc containing cadmium, this bears on the point raised by Mr. Ridge; the cadmium was added for one purpose only, namely to reduce the crystal size, and in no sense was any attempt made to compare the cadmium content with that found in industrial qualities of zinc. With pure zinc it is found that very small additions of a large number of elements, if not of most, will decrease the crystal size in a pronounced manner, but such elements have the disadvantage of raising the recrystallization temperature.

CORRESPONDENCE.

THE AUTHOR (*in further reply*): The purpose of the prolonged annealing was not to improve the rolling properties of zinc alloys but to determine whether there was any embrittling constituent present in the commercially pure zinc. Mr. Chadwick's experiments, to which he refers, were of course carried out upon previously hot-rolled and recrystallized material. In reply to Mr. Wainwright, X-ray examination has shown that there was evidence of residual strain in zinc cold-rolled throughout though not in the hot-rolled and annealed strip, but no work was carried out to determine the critical region.

THE THEORY OF AGE-HARDENING.*

By MARIE L. V. GAYLER,† D.Sc. (Mrs. Haughton), Member.

Synopsis.

A general theory of age-hardening is put forward, based on data relating mainly to the age-hardening of alloys of the Duralumin type and of beryllium–copper and silver–copper alloys.

Age-hardening takes place by two processes: (i) diffusion, and (ii) precipitation, the second overlapping the first. Both processes take place within wide temperature limits which are peculiar to every alloy system, *i.e.* the "temperature range." The rate at which each process takes place depends, apart from other factors, on the temperature of ageing. The limits of the temperature range are indeterminate, but approximations can be obtained for all practical purposes. If the temperature of ageing be close to the lower limit, both stages of the ageing will take place excessively slowly; if the temperature of ageing be close to the upper limit, the first stage will proceed so rapidly that its effect will not be detected. Each of the two processes is characterized by changes in physical properties which will present maxima, or minima, depending on the ageing temperature, the characteristics of the first being gradually replaced by those of the second. The softening which occurs when an alloy is aged at a higher temperature, after being previously aged at a lower temperature, is now explained in the light of the new theory.

Curves are given representing the relationships between (i) hardness and duration of ageing, (ii) maximum hardness and temperature of ageing, and (iii) time of attaining maximum hardness and temperature of ageing.

This paper forms part of a research carried out for the Metallurgy Research Board of the Department of Scientific and Industrial Research, who have granted permission for publication.

Introduction.

From the published researches [1] on copper–aluminium alloys, the view has been put forward that two kinds of hardening take place during ageing, one of which has been termed "incipient" precipitation [2] and relates to the changes taking place prior to the rejection of copper from solution, while the other is connected with precipitation proper. The suggestion [3] has also arisen that, owing to diffusion, a concentration of copper atoms takes place at certain definite positions on the aluminium lattice. Intensity measurements [4] of the lines of the X-ray spectra during age-hardening have given experimental support to this

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* Manuscript received November 9, 1936. Presented at the Annual General Meeting, London, March 10, 1937.

† Scientific Officer, Department of Metallurgy, National Physical Laboratory, Teddington.

view, while the discovery of a structure intermediate [5] between that of $CuAl_2$ and the aluminium solid solution is still further confirmation of it. On the other hand, X-ray evidence has also shown that considerable ageing takes place without (as yet) any measurable change in lattice parameter.

These facts are not easy to explain on the basis of the precipitation theory alone, as it stands, while the two different kinds of ageing taking place during age-hardening have not yet been united in a common theory.

A. NEW THEORY OF AGE-HARDENING.

The author and Preston [1] put forward the theory that precipitation from solid solution entailed two processes: (i) the rejection of atoms of the dissolved metal from the lattice of the solid solution, accompanied by the possible formation of molecules; (ii) a "coagulation" of these rejected atoms or molecules, resulting in the formation of minute crystallites. The second of these two processes was considered to follow the first closely and largely to overlap it. The present author now considers that as it stands this theory does not explain the cause of the hardening which she and Preston called "incipient" hardening,[2] *i.e.* the state of the alloy prior to actual precipitation, but the theory accounts for the changes in hardness due to the actual precipitation of discrete particles. There is need, therefore, for a theory which will account for these two kinds of hardening and, in the opinion of the present author, an examination of published data and that now submitted reveals the fact that they are really dependent on each other and must co-exist to a greater or less extent according to the temperature and duration of the ageing process. Briefly, age-hardening takes place in two stages, the second overlapping the first. The theory put forward by the present author and Preston embraced the second stage only.

I. *First Stage.*

In this stage, ageing is considered to be due to the diffusion of solute atoms to planes about which precipitation proper will ultimately take place, as already suggested by Desch.[6] This diffusion will cause increasing concentration of solute atoms about planes of precipitation of the lattice of the solid solution, and consequently will cause an increase in resistance to deformation and an increase in electrical resistivity. No change in the lattice parameter of the solid solution has, as yet, been detected during this stage of the ageing process.

II. *Second Stage.*

This stage directly follows the first and takes place nearly simultaneously. Some of the diffusing atoms will form molecules with neighbouring atoms of the solvent metal (or other diffusing solute atoms, depending on the constitution of the alloy in question), and these will gradually form groups of molecules which will tend to produce, when a sufficient number is present, a gradual decrease in electrical resistivity and a lessening of the rate of hardening. As the molecular groups increase in size local stresses will be set up in the lattice of the solid solution, as shown by diffuseness of the lines of the X-ray spectra.

When a group of molecules thus formed grows to such an extent that the solid solution can no longer withstand the stresses set up, release of these stresses is caused by the rejection of this group from the solid solution lattice and precipitation proper has taken place.

It follows, however, that where large groups of molecules are adjacent to each other, precipitation of molecular grouping intermediate between that of the solute and solvent metal may conceivably take place owing to the fact that the parent lattice cannot stand the stress set up. One or more of the molecular groups may, therefore, be rejected from solution before a group which constitutes the phase to be precipitated is formed.

These stages of age-hardening form part of one process, *i.e.* the formation of molecules and crystallites of a phase which is ultimately precipitated from solid solution. In other words, age-hardening may be considered not so much as due to *precipitation* but rather as the process by which crystals of a phase are formed on passing through a metastable to a stable state. An analogy may be found in the recrystallization of a cold-worked material. The first effect of cold-work is the breaking down of crystal grains, and consequent hardening; on annealing at different temperatures, recrystallization and growth of crystal grains will occur and will proceed at rates depending on the temperatures of treatment. This results in a decrease of hardness until ultimately a minimum hardness value is reached which is dependent on the grain-size developed.

An examination of data already published, and those now submitted, reveals the fact that the two hardening processes mentioned above are really dependent on each other and must co-exist to a greater or less degree according to the temperature and duration of ageing.

The following generalizations hold for the age-hardening of alloys of any system of alloys which show that phenomenon :

(1) Age-hardening is due to two processes : (i) diffusion ; and (ii) precipitation, the latter taking place concurrently with the former.

(2) Both processes take place within wide temperature limits which are peculiar to every alloy system, and which will be termed the " temperature range." It would appear that the upper limit of the

range is determined by the slope of the solid solubility curve, while the lower limit, whilst depending on the above, also is affected by the character of the solid solution itself.

(3) The rate at which each of the processes can take place depends, apart from other factors, on the temperature of ageing. Each rate is excessively slow at the lower limit of the temperature range and exceedingly rapid at the upper limit.

(4) The limits of the temperature range within which the age-hardening can take place are indeterminate, but approximations can be obtained for all practical purposes.

(5) If the temperature of ageing be close to the lower limit of the temperature range, the first stage of the ageing process, *i.e.* diffusion of solute atoms, will take place so slowly that the second stage will only enter after an exceedingly long time, and then excessively slowly. Ageing at temperatures close to the upper limit will cause the first stage to proceed so rapidly that its effect will not be detected. At intermediate temperatures of ageing both processes will take place, but the degree to which they do so will depend on the temperature and duration of ageing.

(6) Each of the two ageing processes will be characterized by changes in physical properties which will present maxima or minima depending on the ageing temperature, the characteristics of the first gradually being replaced by those due to the second.

B. DIAGRAMMATIC REPRESENTATIONS OF AGE-HARDENING.

In accordance with the theory now put forward, a curve representing change of hardness in an alloy during ageing must embrace both stages of the ageing process. Since the rates at which these stages proceed depend on the temperature at which the alloy is aged, it follows that the changes in hardness cannot be represented by one curve alone, as suggested by Jenkins and Bucknall,[7] but that they must be represented by curves characteristic of the ageing temperature. In Fig. 1 are given the general types of hardness–time curves which are likely to be observed, the temperature being highest in curve *A* and decreasingly lower in curves *B*, *C*, *D*, *E*, and *F*.

It has just been stated that the first and the second stage of the ageing process both take place at excessive speed when the temperature of ageing is near to that of the upper limit of the range of temperature in which age-hardening takes place. In Fig. 1, curve *A* represents the hardness–time curve of an alloy aged at such a temperature. The first stage of the ageing process takes place at excessive speed and its effect cannot be determined, since the second stage sets in almost instantaneously and is immediately followed by precipitation proper.

Since softening at this temperature will occur almost simultaneously with the hardening, it follows that at such a temperature the maximum hardening obtained must ever be appreciably lower than that which it may be possible to attain at some lower temperature.

If the ageing temperature corresponds with that of the lower limit of the temperature range, the first stage will take place at an exceedingly slow rate and, consequently, the second stage also can only proceed at an excessively slow rate. Curve *F* (Fig. 1) represents the hardness-time curve of an alloy aged at such a temperature. Theoretically, the curve F should be extremely close to the time axis, as similarly the first part of curve *A* is exceedingly close to the hardness axis.

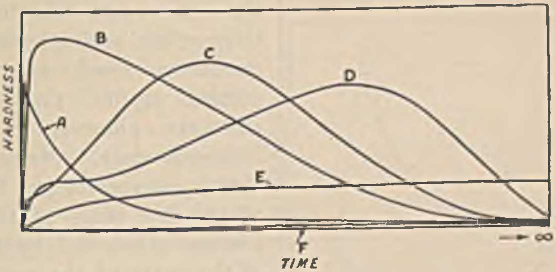

Fig. 1.—Curves Representing Time–Hardness Changes at Different Ageing Temperatures.

Curve A.—Upper Temperature Limit of Ageing: Both Stages of Ageing Take Place Excessively Quickly. *Curve B*.—Second Stage of Ageing, Perhaps Slight Indication of First Stage. *Curves C and D*.—First and Second Stage of Ageing Both Apparent. *Curve E*.—First Stage of Ageing and Perhaps Entry of Second Stage at an Excessively Slow Rate. *Curve F*.—Lower Temperature Limit of Ageing: Both Stages of Ageing May Take Place Excessively Slowly.

Curves representing changes during ageing at temperatures within these two temperature limits, must be represented by general types such as *B*, *C*, *D*, and *E*. Curve *E* represents the changes taking place when the first stage of the ageing process predominates, but the entry of the second stage may take place after prolonged ageing and may be detected by electrical resistivity measurements.

When both stages of the ageing process are definitely detectable, *i.e.* at higher ageing temperatures, the time–hardness curves take forms similar to those given in curves *C* and *D*. The maximum hardness attained during the first stage of the ageing process increases and then decreases with increase of ageing temperature, while simultaneously the maximum hardness attained during the second process increases and decreases, but at a different rate.

Illustrations of these types of curves may be seen in Fig. 4, which will be referred to later. These represent the ageing of an alloy of Duralumin composition aged immediately after quenching at room temperature, 100°, 150°, 200°, and 250° C.

The straight line relationship between log-time of attainment of maximum hardness, or of maximum electrical resistivity, and the reciprocal of the ageing temperature, must be reconsidered, therefore, in the light of the theory of age-hardening now put forward. The maximum hardness thus plotted represents that obtained during the latter part of the second stage of the ageing process, while maximum resistivity which is plotted against time indicates that the alloy is in quite a different state. Maximum resistivity occurs when the effect of the first stage of the ageing process is *balanced* by the effect of the entry of the second stage of the process. Maximum hardness and maximum resistivity, therefore, cannot be compared, since they are indicative of different conditions in the alloy.

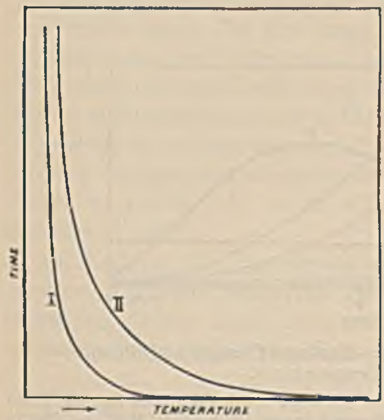

Fig. 2.—Relation Between Ageing Temperature and Time of Attainment of Maximum Hardness of the First Stage of the Ageing Process (Curve I) and of the Second Stage (Curve II).

If the time of attaining maximum hardness of both stages of the ageing process be plotted against temperature, curves of the type shown in Fig. 2 will be obtained. The maximum of both stages of ageing takes place after an exceedingly long time at low temperatures (that of the first, however, being attained before that of the second), while at high temperatures both maxima are reached in an extremely short time. Here again there is a difference in the time taken to reach the maximum of both stages, that corresponding to the first being reached in appreciably less time. Hence, in Fig. 2, curves I and II (which represent the times of attaining maximum hardness of each stage of the ageing process in relation to temperature) are displaced relatively to the time axis.

There remains, finally, the relationship between maximum hardness and temperature. Since a maximum is obtained in the physical properties during both processes, and since at no temperature can the second stage take place independently of the first, it follows that the maxima relating to the first stage of the ageing process must precede that of the latter, but will probably take place at a lower temperature (cf. Figs. 1 and 4). Electrical resistivity measurements as well as measurements of mechanical properties confirm this conclusion, as shown later. It follows, therefore, that the straight line relationship between maximum hardness and temperatures does not completely express the full facts since (*a*) two maxima play their part, (*b*) there is a maximum on each maximum hardness–temperature curve. Fig. 3 represents diagrammatically the relation between the maximum hardness and temperature of both stages of the ageing process. The point *C*, where both curves meet, corresponds to the "balance" between the first and the second stage of the ageing process. At such a point, electrical resistivity will immediately decrease and the hardening due to the first stage of the ageing process will not be apparent.

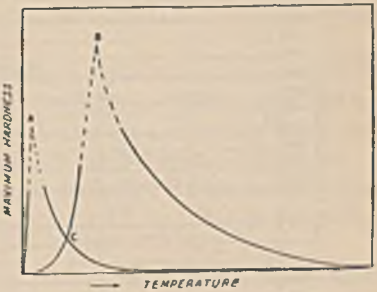

Fig. 3.—Relation Between Maximum Hardness and Temperature.

The maximum *A* may or may not be greater than that of *B*, but the experimental evidence at hand suggests that it is most probably a great deal lower.

In cases where more than one phase is being precipitated from the supersaturated solid solution, the changes taking place during ageing will be complicated by the interaction of the various constituent atoms on each other, and the total effect of the precipitating phases will depend on the mutual effect on (*a*) their solid solubility, (*b*) rate at which the first and second stage of ageing proceed for each phase to be precipitated, and (*c*) the combined effects of (*b*) which may be represented by the resultant of several superimposed effects of the type shown in Fig. 3.

C. EXPERIMENTAL EVIDENCE OF THE NEW THEORY OF AGE-HARDENING.

If an alloy be quenched and aged, it follows that there must be a temperature near the lower limit of the critical temperature range at which diffusion of the solute atoms will proceed too slowly to be detected by physical methods; but if the temperature of ageing be slightly increased diffusion may occur at such a slow rate that it can only be detected after a lapse of time. Ageing temperatures which are well within the temperature range will result in more rapid diffusion and the

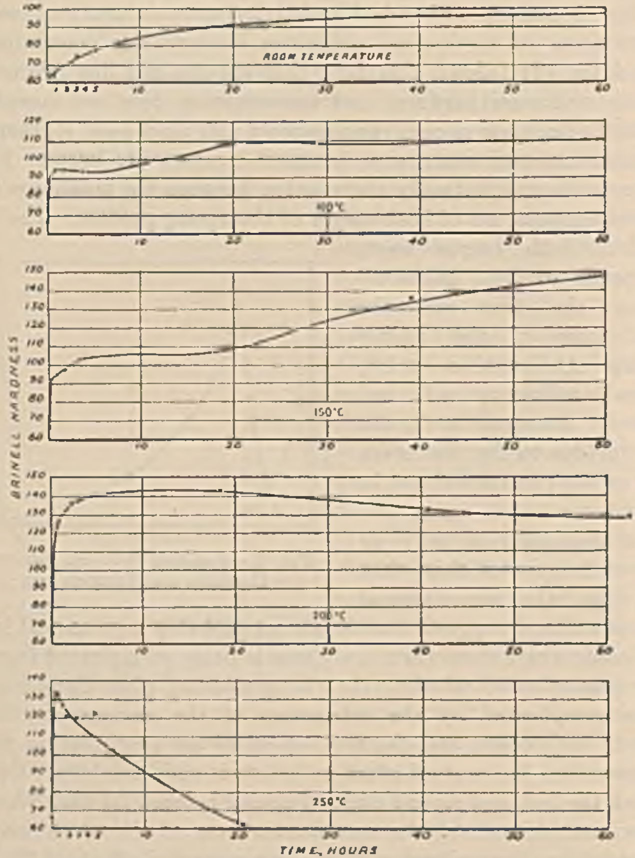

FIG. 4.—Alloys Heat-Treated at Temperature Indicated, Immediately After Quenching from 500° C.

Alloy H_2 4·0 Per Cent. Cu
0·51 „ Mg
0·3 „ Si
0·11 „ Fe

consequent possible detection of the first stage of the ageing process by various physical means. The subsequent entry of the second stage may take place only gradually, and will also be demonstrated by another change in the physical properties of the alloys. Such a type of ageing is that which occurs, for example, in alloys of the Duralumin type when ageing at room temperature (cf. Fig. 4).

Further, the ageing temperature in the extreme case may be so high that the diffusion of the solute atoms and their subsequent re-arrangement into molecules, &c., will take place so rapidly that the first stage of the ageing process cannot be detected and the second only will be apparent; this occurs when Duralumin is aged at 250° C. immediately after quenching from 500° C. (Fig. 4).

In Fig. 4 also are plotted, on a more open scale than originally published, the results of a previous investigation by the present author and Preston [1] on the ageing of an alloy (H_2) containing copper 4, Mg_2Si 0·8, and iron 0·1 per cent. The alloy was quenched after prolonged annealing at 500° C. and immediately heat-treated at the temperatures indicated.

Ageing at room temperature results in a gradual increase in hardness, while ageing at 100° and 150° C. produces an initial rapid increase within the first half-hour, after which there is a definite slowing of the hardening, which is followed by a more rapid increase in hardness. If the temperature of heat-treatment be 200°–250° C., the initial increase in hardness to a definite maximum is rapid, but this is followed by marked permanent softening.

Ageing Duralumin at a temperature below room temperature, *viz.* 0° C., decreases the rate of hardening as compared with that at room temperature, as shown by Meissner's results.[8] Aitchison [9] points out, also, that the ageing of quenched Duralumin is delayed for a period of many days if maintained at a temperature of — 80° C., while at the temperature of liquid air the alloy appears to remain permanently soft. These results, together with those shown in Fig. 4, indicate that the first stage of the ageing process of Duralumin is characterized by an increase in hardness which increases to a maximum at or about some temperature near room temperature, and that the rate of hardening increases with ageing temperature. Additional support for this first hardness maximum is shown in diagrams submitted by Teed [10] in his discussion on Jenkins and Bucknall's paper. In these figures are plotted changes in mechanical properties taking place in Duralumin heat-treated at 0° C., room temperature, 65°, and 100° C. These observations show that the temperature giving maximum properties due to the first stage of the ageing process lies possibly between room temperature and 65° C., the subsequent increase in mechanical strength, &c., being due to the gradual entry of the second stage of the ageing process.

With further increase in the ageing temperature, the rate at which the first stage proceeds becomes so rapid that it is quickly masked by the definite entry of the second stage of ageing (cf. Fig. 4, ageing at 200° and 250° C.). Ageing at temperatures below that at which the maximum hardness of the first stage of ageing is obtained, *i.e.* — 0° and — 80° C., causes the rate of ageing to be reduced and consequently the second stage only appears after prolonged ageing (cf. Fig. 1). From the above remarks it is clear, however, that the first stage of the ageing process is mainly responsible for the ageing of Duralumin at room temperature. Whether the second stage enters during room temperature ageing can only be determined by use of more sensitive physical properties than hardness, such as electrical resistivity. Such measurements, however, have been carried out by the author and Preston [1] during their original investigation on the ageing of aluminium alloys, and they found, during ageing over a period of 6 days, that in the case of

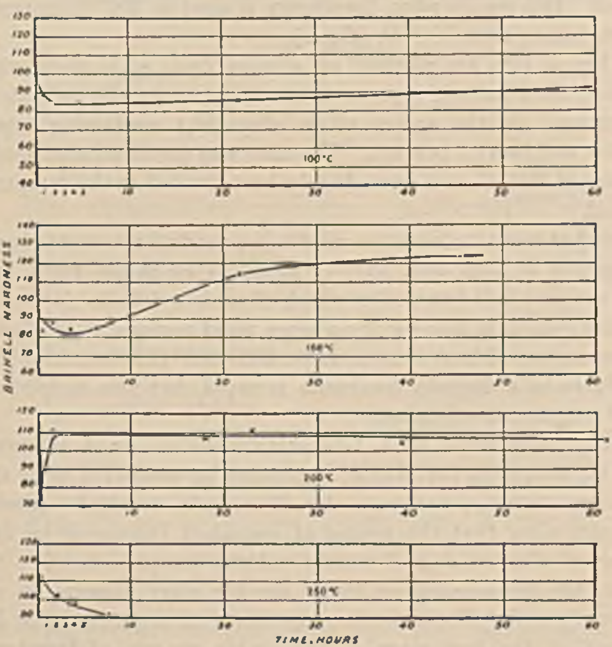

FIG. 5.—Alloys Age-Hardened at Room Temperature and Then Heat-Treated.

Alloy H_2 4·0 Per Cent. Cu
0·51 " Mg
0·3 " Si
0·11 " Fe

alloy H_2 (copper 4, magnesium 0·5, silicon 0·3, iron 0·11 per cent.) the electrical resistivity increased, remaining practically constant after two days. Eucken and Warrentrup,[11] however, have since shown that in the case of an alloy containing copper 4 and magnesium 0·5 per cent. only, the electrical resistivity remained approximately constant over the period 3–8 days, after which it gradually decreased. Both these results suggest that the second stage of the ageing process is beginning to overlap the first stage.

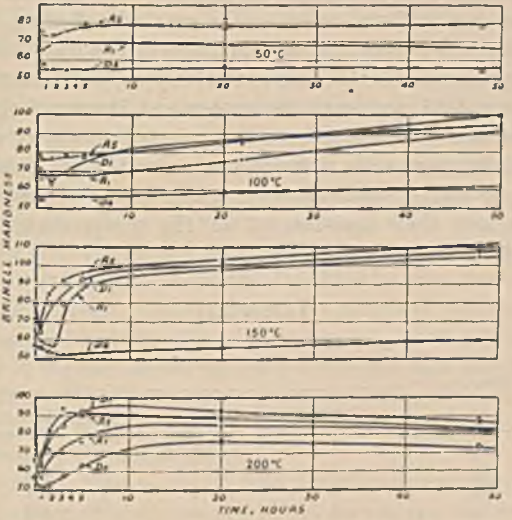

FIG. 6.—Forged Sand-Cast Bars Heat-Treated for 20 Hrs. at 500° C., Quenched in Water at Room Temperature and Then Aged at the Temperatures Given.

	Per Cent.		
	Cu	Fe	Si
A_1	4	0·1	...
A_5	4	0·1	1·0
D_1	4	...	0·1
D_4	4	0·6	0·1

Additional evidence is found in results of the same investigation by the author and Preston,[1] in the case of the alloy H_3, containing copper 4·5, silicon 0·17, and iron 0·13 per cent., which shows only a small increase in hardness on ageing at room temperature, while the electrical resistivity increases over a period of 2 days, after which it appears to decrease slightly. Stenzel and Weerts,[12] using an alloy containing only 4·3 per cent. copper (which shows a marked increase in hardness on ageing at room temperature), have found that the electrical resistivity increases rapidly up to 1 day, after which it decreases more gradually.

Again, further support of the existence of the first stage of the ageing process is to be found in the data obtained by the author and Preston during ageing, at different temperatures, of other aluminium alloys, and also from measurements obtained on the alloy of the Duralumin type already mentioned (H_2) when heat-treated after previous ageing at room temperature.

Ageing at higher temperatures alloys previously aged at room temperature causes a profound effect, *viz.* a marked softening. This was originally observed by the author[13] in alloys of the Duralumin type of various compositions. In the case of alloy H_2 (copper 4, magnesium 0·5, silicon 0·3, iron 0·11 per cent.) the author and Preston[1] obtained the results shown in Fig. 5, which have been plotted on a very open scale; in Fig. 6 are also given some new results obtained by the present author in the case of forged sand-cast bars which have been aged at room temperature and then heat-treated at the temperatures indicated. The compositions are given in Table I.

TABLE I.

Alloy.	Per Cent.		
	Copper.	Silicon.	Iron.
A_1	4	nil	0·1
A_5	4	1·0	0·1
D_3	4	0·1	nil
D_4	4	0·1	0·6

It is interesting to note that in all cases: (*a*) an initial softening occurs which is followed by an increase in hardness; (*b*) the higher the ageing temperature, the greater is the softening; (*c*) the higher the ageing temperature, the more rapidly the subsequent increase in hardness sets in; or, conversely, the lower the ageing temperature the greater the time interval over which softening persists.

This is a most important experimental fact, which, however, can be fully explained by the new theory.

Masing and Koch[14] have found that the same phenomenon of softening followed by hardening takes place in the case of a beryllium–copper alloy containing 2·52 per cent. beryllium which was partially aged at 150°–200° C. and then at 200°–300° C. The electrical resistivity increases in the range 150°–200° C., but decreases in the range 200°–300° C. These authors note that this change in electrical resistivity suggests that some distinction might be made between two types of ageing, but they consider that the initial hardness decrease, which depends only on an increase in the ageing temperature, is against this view, and that the effect can be explained on the basis of Volmer and Weber's [15] hypothesis of a minimum size for crystallization nuclei, decreasing with decreasing temperature.

Masing and Koch also studied this "anomaly" in more detail by investigating the changes in hardness and in electrical resistivity during ageing of a Duralumin containing copper 4·40, zinc 0·09, iron 0·40, manganese 0·35, magnesium 0·66 per cent., and the rest aluminium. They found that the initial decrease in hardness was associated with a more or less pronounced decrease in electrical resistivity. An explanation of the phenomenon of the softening followed by hardening on heat-treating alloys aged at some lower temperature may now be given as a result of the new theory of age-hardening. The initial softening is due to the fact that the second stage of the ageing process has started and is overlapping the effects of the first, causing (*a*) the softening which is the first sign that the second process is proceeding (cf. Fig. 4), and (*b*) also causing the increase in electrical resistivity, due to the first stage of the ageing process, to be replaced by a decrease. Further, the fact that the degree of and the rate of softening depend on the temperature of ageing is in support of the theory put forward that the second stage of ageing takes place more rapidly as the temperature is increased; consequently, the effect of the first stage is overlapped at a rate and to a degree dependent on temperature.

This so-called "anomalous" behaviour is shown, therefore, to be the natural effect of the sequence of the second on the first stage of age-hardening.

It is interesting to note that this decrease in hardness is not accompanied by a decrease in tensile strength.

The present author and Preston [2] examined the X-ray spectra of an alloy containing 4 per cent. copper only (1) immediately after quenching from 500° C.; (2) after ageing for 7 days at room temperature; (3) after heat-treating the aged alloy for 20 minutes at 200° C., *i.e.* when the minimum of the softening would be attained; and (4) after 24 hrs. at 200° C. To quote from the original:

"The first three photographs are indistinguishable although marked hardness differences are found for the alloys in the three conditions. In the first and third, the Brinell numbers are in the neighbourhood of 60, whilst in the second condition the figure is of the order of 80 or thereabouts, as shown in the graph (Fig. 1, Plate XVIII). In the fourth condition the hardness has a value of about 100, and the displacement of the lines in the X-ray photograph shows that the copper has been to a very large extent precipitated. . . ." The entry of the second stage, therefore, is accompanied by no measurable (as yet) change in lattice dimensions. Further confirmation of this statement will be found in v. Göler and Sachs's[3] results on ageing 5 per cent. copper–aluminium alloy. These investigators also show that the first effect of heat-treating the alloy aged at room temperature produces no change in lattice parameter but a definite change in mechanical strength.

Fink and Smith[16] have recently shown that the age-hardening of a 5 per cent. copper–aluminium alloy is accompanied by visible precipitation on crystallographic planes, but that no lattice parameter change could be detected until the specimen was aged for a much longer time than was necessary to produce visible precipitation. Fink and Smith consider, in view of their results, that it is unnecessary to complicate or modify the original theory of age-hardening, as put forward by Merica, Waltenburg, and Scott,[1] that age-hardening is caused by the precipitation of particles from super-saturated solid solution. They do not explain satisfactorily, however, the anomalous behaviour of electrical conductivity and density, &c., which takes place prior to the visible precipitation on the crystallographic planes.

The fact that age-hardening at room temperature proceeds for 3 months before it can be detected visibly is additional confirmation of the view put forward by the present author. Fink and Smith have shown visible evidence of precipitation taking place during the ageing of their alloy, but their results do not show what change has been going on in the alloy *before* this precipitation has occurred. The marked increase in hardness at room temperature, the increase in electrical resistivity followed by a marked decrease during the ageing period of three months according to Stenzel and Weerts,[12] the changes in density, &c., all take place prior to the visible precipitation demonstrated by these authors and need explanation. In the light of the present theory, the second stage of the ageing process is taking place in these authors' alloy when precipitation is observed, but the first stage of the ageing process is the cause of the change in physical properties which occur *before* visible precipitation can be detected.

Hengstenberg and Wassermann[4] have shown that while no appreciable diminution of the sharpness of the X-ray lines of the X-ray spectra occurred during ageing of Duralumin at room temperature, ionization measurements of intensity showed a decided increase during ageing. Their results suggested that the precipitation process is most likely an agglomeration of copper atoms at numerous points within the aluminium solid solution. These authors also considered that this aggregation of copper atoms on the slip planes would account for an increase in strength.

Mehl, Barrett, and Rhines[17] suggest two possible mechanisms by means of which copper atoms lying on the 100 plane of the aluminium lattice could move for the transformation into $CuAl_2$, and suggest that the easier one may be the manifestation of the room-temperature ageing process in a 4 per cent. copper–aluminium alloy, and the more complicated precipitation that of the other. This supposition, however, does not explain the fact that ageing at room temperature is accompanied by changes in physical properties quite distinct from those occurring when precipitation can be detected.

Stenzel and Weerts[12] in the case of a copper–aluminium alloy containing 4·3 per cent. copper found that during ageing at 20° and 75° C. the lattice constants remained unchanged within the limits of error, but that, nevertheless, variations occurred in the solid solution. They showed that the electrical resistivity increased and decreased, whilst the tensile strength increased and then remained approximately constant after 4 days on ageing at 20° C. and after 1 day at 75° C. Further, heat-treating the quenched alloy containing 5 per cent. copper at 100° C. for 1 week produced no sign of precipitation but considerable change in mechanical properties.

To sum up: there is much evidence that the first stage of the ageing process is accompanied by no—as yet—measurable change of lattice parameter, but that changes in other physical and mechanical properties indicate that this first stage is gradually being replaced by a second, which results ultimately in the visible precipitation of discrete particles. The maximum hardness obtained during the second stage of the ageing process is attributed to the formation of groups of molecules, of such dimensions that maximum distortion of the parent lattice occurs. The actual precipitation of a crystallite is the result of subsequent growth and consequent increase of lattice strain and internal stresses. More crystallites are formed with time, and then coagulation sets in and produces marked softening.

Whether the precipitated crystals themselves are perfect crystals is a matter on which the researches of Wassermann and Weerts[5] throw doubt. From the X-ray analyses of an alloy containing copper 5, iron 0·3, and silicon 0·3 per cent., quenched and aged for 30 hrs. at 200° C., these authors observed interferences belonging neither to those of the aluminium solid solution nor to $CuAl_2$. Wassermann and Weerts designate this as an intermediate structure and assume that it has a form corresponding with that of $CuAl_2$, but that it is structurally still closely related to that of the solid solution.

The present author and Preston,[1, 2] v. Göler and Sachs,[3] Schmid and Wassermann,[18] and Stenzel and Weerts [12] have shown that a diffuseness and broadening of the X-ray spectra takes place during the ageing of alloys of the Duralumin type at certain temperatures, which corresponds with a marked increase in mechanical strength and decrease in ductility. The maximum hardness was attained at the same time as the maximum amount of broadening and diffuseness of the lines of the X-ray spectra.

At the same time as the above, other physical changes occur in the alloys. A very rapid decrease in density was first observed by the present author and Preston and confirmed by Kokubo and Honda.[1] Accompanying this change in density is a marked decrease in electrical resistivity (cf. Fraenkel, Gayler and Preston, Stenzel and Weerts).

It is seen, therefore, that during the age-hardening of an alloy two stages are passed through which are characterized by definite physical properties. The first of these stages is gradually overlapped by the second and the physical properties of the alloy will vary, therefore, according to the rate at which the second stage overlaps the first.

In the case of silver–copper alloys, Wiest [19] concluded that during ageing the super-saturated solid solution passes through three stages;

(*a*) a stage in which no change in lattice parameter could be detected;

(*b*) a second stage indicated by a slight broadening of the interferences;

(*c*) an increase in hardness accompanied by a large change in lattice parameter due to the precipitation of the solute atoms.

The increase in hardness accompanying (*a*) and (*b*) is attributed to changes within the lattice caused by atomic movements preparatory to precipitation.

As compared with the theory now presented, fundamentally they are very similar, but in the present theory Wiest's three stages of ageing are considered inter-dependent; his second stage is not given a separate existence, since it is merely the beginning of the present author's second stage, overlapping the first.

After this paper was written and before it was submitted for publication an advance copy of an invaluable contribution on "Ageing Phenomena in a Silver-Rich Copper Alloy" by Cohen [20] reached the present author. Cohen finds that "The fundamental mechanism of ageing of the silver–copper alloys, therefore, appears to be quite similar to that of the aluminium–copper alloys, in that both will age-harden by knot formation and by precipitation. The detection of these pre-precipitation effects in the silver–copper alloys, which have generally been considered to harden by precipitation only, is sufficient to indicate that perhaps we are no longer justified in classifying age-hardenable systems as either knot-hardening or precipitation-hardening. Such a classification seems both arbitrary and unnecessary. . . ." "Thus, it is believed that the mechanism of ageing (not of hardening) in these alloys is actually the same at all temperatures. It is only the increased overlapping of the knot and precipitation stages as the ageing temperature is raised that gives rise to the different hardening effects above and below 169° C."

Cohen has found experimentally that two hardness peaks occur on ageing his 8 per cent. copper–silver alloy at temperatures below 169° C. and attributes the first to "knot formation." The softening that occurs between the two peaks he considers is caused by relief of strain when precipitation takes place.

The theory put forward by the present author, based mainly on the ageing of alloys of the Duralumin type as well as on that of beryllium–copper and silver–copper alloys, is in general agreement with that of Cohen. There are differences, however, in interpretation of the first stage of the ageing process and of the "intermediate" softening; also the existence of a maximum has been shown to exist on the maximum hardness–temperature curves of the first stage of the ageing process as well as on that of the second; the theory has also been developed on more general lines.

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NOTE.

Discussions on this paper have shown that it would be helpful if the suggestion of the presence of "molecules," "groups of molecules," and of "crystallites" in the lattice were discussed more fully.

The term "molecule" is used in its chemical meaning, *i.e.* in the case of copper–aluminium alloys, one atom of copper associated with two atoms of aluminium represents a molecule of $CuAl_2$. X-ray analysis shows, however, that the unit cell is made up of four molecules of $CuAl_2$, *viz.* four atoms of copper and eight atoms of aluminium.

In the first stage of the age-hardening process of such an alloy, concentration of copper atoms takes place in definite positions on the lattice. It cannot be assumed that this results at once in an ordered arrangement of these atoms, but it is likely that this concentration of atoms is likely to cause localized stresses to be set up. X-ray evidence indicates that localized regions of high concentration of solute atoms exist; the fact that no change in the X-ray line spectra has as yet been detected during the initial stages of ageing, suggests that localized strain-hardening is responsible for the increase in hardness on ageing the alloy. The increase in electrical resistivity of such alloys supports the view that no disorder–order transformation is occurring.

A re-arrangement of these solute atoms, taking place more or less at once, results in the formation of "molecules" by some of the copper atoms attaching themselves each to two neighbouring aluminium atoms. A certain amount of local distortion of the lattice will also be caused by these attachments.

This "molecule" formation constitutes the beginning of the second stage of the age-hardening process, which proceeds concurrently with the first. These "molecules" will increase in size, owing to diffusion, causing distortion which, in its early stage, may be localized, but which as growth proceeds rapidly affects the whole matrix. When four atoms of copper have attached themselves to eight atoms of aluminium, the unit cell of $CuAl_2$ is formed. This has been termed a "crystallite." It is not known how many unit cells associated together form the critical size of crystal which sets up such high distortion in the lattice of the matrix that it can no longer be held in solid solution, but is rejected. It is known that phases of intermediate structure are precipitated, and it is now suggested that there is a critical number of atoms of copper and aluminium grouped together in an arrangement approaching that of the unit cell, above which precipitation of the phase occurs, and up to which the grouping can be held in solid solution, causing great distortion of the matrix.

This building-up process of crystals of the phase to be precipitated must bear relation to certain definite planes, as the researches of Mehl and his colleagues * on Widmanstätten structures show. No attempt is made here to analyze this actual process; it is desired, however, to emphasize the idea that association of groups of atoms and molecules is necessary for the precipitation of a crystal, since it is unlikely that such a complex structure can be formed directly from the solid solution without being the result of some "building-up" process.

The localized distortion due to concentration of solute atoms and the formation of comparatively few "molecules" or small "groups of molecules" of $CuAl_2$ will result in high tensile strength and high ductility. Heat-treating at higher temperatures will first remove these localized stresses, by diffusion rather than by precipitation. On extending the time of heat-treatment an increase in the number and size of "groups of molecules" will occur, until precipitation proper takes place. As suggested by Merica, a critical dispersion of discrete particles is probably responsible for the high tensile strength and low ductility of alloys heat-treated at high ageing temperatures.

DISCUSSION.

Professor N. F. Mott,† M.A., F.R.S. (University of Bristol): I am interested in what the author has said about the resistance of age-hardening systems. According to the ideas of wave mechanics, the resistance of an alloy is explained in the following way. The electron wave which accompanies a beam of electrons is pictured as being scattered by the dissolved atoms, for instance by the copper atoms dissolved in a supersaturated solution of copper in aluminium. If one wants to understand the change of resistance during precipitation, one has to ask whether isolated copper atoms in the aluminium lattice will have more scattering power than little groups of, say, 3 or 4 or 10 copper atoms which have segregated together in the lattice. From the point of view of wave mechanics, therefore, it seems that one would expect the resistance first to increase and then to decrease, because the maximum scattering power of the groups of copper atoms will arise when the size of the groups is comparable with the wave-length to be associated with the electrons. This wave-length is about four or five inter-atomic distances.

The problem is analogous to the scattering of light when it passes through an atmosphere saturated with water-vapour. When the atmosphere contains water-vapour molecules, small compared to the wave-length of light, there is very little scattering and the atmosphere is transparent. If the water-vapour molecules condense into little particles of a size comparable with the wave-length of light, we get the all too familiar fog, the light being scattered as it goes through the atmosphere. If the little droplets which form the fog condense still further and form rain-drops, the atmosphere becomes transparent again.

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* R. F. Mehl, C. S. Barrett, and F. N. Rhines, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 203.

† Melville Wills Professor of Theoretical Physics, University of Bristol.

I suggest that the author's curves, giving the change of resistance with time, are to be explained in a similar way. There are first the small copper atoms, which do not scatter much, and then the little aggregates of copper—Dr. Gayler's first stage in the precipitation—which scatter more strongly, and finally, big aggregates of the copper–aluminium compound, which again scatter less, so that the resistance decreases.

It may be true, of course, that the initial increase in the resistance is due to strain, as has been suggested elsewhere. These remarks are only meant to suggest a *possible* alternative explanation.

Dr. Gayler has given curves plotting hardness against time for various temperatures. If these are plotted logarithmically against the reciprocal of the temperature will a straight line be obtained, and is the variation of the rate of hardening with temperature at all the same as the rate of diffusion of copper in aluminium?

Dr. W. O. **Alexander**, B.Sc. (Member) took part in the discussion but later amplified his remarks in writing, for which see p. 269.

Dr. L. H. **Callendar**,* B.Sc., A.R.C.S. (Member): In an early stage of the process of ageing, an examination of the lines of the X-ray spectra shows a diffuseness and broadening. Is this visible evidence for the first stage of the process according to the author's theory, that is the diffusion of the solute atoms, or would this stage not show up at all in the X-ray spectra? In the latter case, is this broadening, &c., attributed by the author to the beginning of the formation of molecular groups, or is it evidence of a later stage, the formation of crystallites?

The formation of molecular groups is stated to be accompanied by a decrease in electrical resistivity. It seems that there is here only indirect evidence that any precipitation has actually started, for the particles do not become visible under the microscope for a very long time after the process has started.

Using a direct chemical method for investigating the precipitation of silicon from aluminium, I found † that starting with the silicon in solid solution and then annealing at 200° C., the beginning of the precipitation of graphitic or molecular silicon coincided in a remarkable manner with the beginning of a decrease in electrical resistance. As the direct chemical method used was of the same order of accuracy as the resistance measurements, and it indicated precipitation after annealing for only 3 hrs. at 200° C., whereas the particles only became visible under the microscope after annealing for some 500 hrs. at 200° C., it was evident that I was observing a much earlier stage of the process than that indicated by microscopic methods or lattice parameter measurements.

Connecting my results with Dr. Gayler's theory, it is possible to get considerably nearer to direct evidence for the beginning of precipitation, using as links the indirect evidence of falling electrical resistance, broadening of the lines of the X-ray spectra, &c.

Rosenhain,‡ in discussing my results said there was some doubt whether we were dealing with molecules or crystallites, and also that my results did not show an initial increase of resistance with the beginning of precipitation, as might have been expected under the older precipitation theory. Dr. Gayler's new theory clears up this apparent anomaly, for the first stage, the diffusion of solute atoms, accompanied by an increase of electrical resistance would take place too rapidly at 200° C. to be detected.

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† *J. Inst. Metals*, 1933, 51, 199. ‡ *J. Inst. Metals*, 1933, 51, 213.

The AUTHOR (*in reply*): I am glad that Professor Mott is studying this problem of age-hardening on a mathematical–physical basis, because it is a problem which is now really in the realms of physics. As regards plotting the logarithm of the time of attaining maximum hardness against the reciprocal of absolute temperature, I think that the straight line relationship holds over a definite range of temperature at which age-hardening takes place, but that at high and low temperatures there is a slight curving away at either end of the line, as shown by the dotted line in Fig. A. Cohen, in a recent paper on copper–silver alloys, which embraces the theory which I have put forward, has plotted the beginning of hardening as well as maximum hardness, &c.; he states that they take place according to this straight line relationship. If his results are extrapolated, which I think is justified, the beginning of hardening in the copper–silver alloys should take place in 5½ days at room temperature, and in 24 hrs. at 50° C. Cohen examined the age-hardening of these alloys over a period of "several days" at room temperature, and could not detect any ageing. If that "several days" was more than 5½ days, I suggest that there is evidence that this straight line relationship does not hold over the whole temperature range, and that the curve should be of the form given in Fig. A. If, however, the "several days" was only 3 or 4 days, there is a possibility that the straight line relationship holds. At any rate, this fact is now capable of experimental proof in a reasonable time, since at 50° C. the beginning of hardening should take place in the copper–silver alloy in about 1 day.

FIG. A.

I do not know whether the variation of the rate of hardness is similar to the rate of diffusion. I would refer Professor Mott to a paper by Brick and Phillips * on the diffusion of copper and magnesium into aluminium.

CORRESPONDENCE.

DR. W. O. ALEXANDER,† B.Sc. (Member): I have made observations of age-hardening phenomena and the attainment of equilibrium of supersaturated solid solutions of aluminium-, copper- and nickel-base alloys. The chief physical properties measured were electrical resistivity and hardness.

Dr. Gayler's explanation has much to commend it; I advanced it as a working hypothesis in a D.S.I.R. report and thesis in 1933. It is obvious and logical that such a first stage as diffusion of the atoms towards planes where they

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* *Metals Technology*, 1937, 4, (2).

† Research Fellow, Metallurgy Department, Birmingham University.

eventually precipitate does exist, but the supreme difficulty is to determine the influence of the diffusing atoms on the physical properties. This theory involving as it does a knowledge of diffusion, is given without any reference by the author to the mechanism of diffusion, a certain knowledge of which I consider to be essential before there can be a further discussion of a general theory of age-hardening. In " mechanism of diffusion " I include such problems as the nature of the driving force causing the atoms to diffuse and embracing uphill diffusion; whether aggregation is to be solely attributed to chance encounters, and if so why this first stage should be self stopping; and whether the author suggests that one $CuAl_2$ molecule exists as a separate entity and whether, having been once formed, aggregation to $CuAl_2$ particles occurs by movement of the molecule or by resolution and diffusion as a copper atom. I submit that much of the author's experimental evidence in this paper is, in the present state of knowledge, unconvincing.

The interpretation of the significance of the variations in electrical resistance measurements are unsound because, short of phase equilibrium conditions, the manner of change of resistance during the attainment of equilibrium has never been adequately studied. The increase in resistance which is ascribed only to the first stage might just as easily be due to a stress effect accompanying the known density changes; further, all the work done on disorder–order arrangements in metallic alloys shows a decrease in resistance, and stage (1) is certainly a departure from disorder, even if complete order of the copper atoms is never really approached. A decrease of resistance would, therefore, be expected on these grounds.

Fig. B.

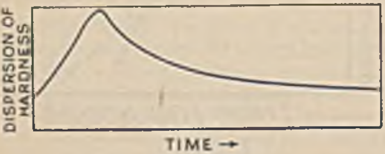

Fig. C.

It has been pointed out previously * that the use of hardness curves taken on Duralumin specimens is not satisfactory, since the double maxima might just as readily be attributed to the incipient separation of, say, two phases independently from the supersaturated solid solution.

I have made observations on the age-hardening of straight copper-aluminium alloys, using materials of high purity. Each hardness figure was the arithmetic mean of the diameters of 20 impressions. The values of the dispersion in hardness were obtained by taking the quartile + *ve* and − *ve* deviation values and plotting against time, as for the hardness curves. Of all the curves, some three dozen of which were drawn, only three showed this inflection and double maxima, as in Fig. B. This arrest in the hardening rate coincided with a large dispersion in hardness values as shown in Fig. C, which suggests that the deviation from a smooth curve has little experimental significance.

Mr. E. H. Bucknall,† M.Sc. (Member): No one will question the implicit assumption of this theory that precipitation-hardening alloys must pass through

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* *J. Inst. Metals*, 1935, 57, 175.

† Scientific Officer, Metallurgical Department, National Physical Laboratory, Teddington.

early stages of ageing closely parallel to those in which a knot-formation hardening alloy reaches maximum hardness. This view arises on any of a variety of assumptions with regard to the mechanism of precipitation, as, for example, that non-inoculated crystallization proceeds at an appreciable velocity only at the centre of highly supersaturated zones. In age-hardening alloys the formation of such a zone may not demand long-distance migration of solute atoms, since in a face-centred cubic alloy of the quite ordinary solute content of 3·1 atomic per cent. the dissolved atoms are separated only by the small distance $2a$, where a is the lattice parameter, so that 6 solute atoms have only to be exchanged with solvent atoms at a distance a to establish a group of 7 solute atoms (as these atoms are not nearest neighbours 12 diffusional steps are involved); 5 interchanges amongst nearest neighbours may produce a group of 4 solute atoms. That segregation of solute on a broad scale does not occur is indicated by the absence of shift in the lattice parameter, such as would accompany the impoverishment of wide ranges of the solid solution at a stage before precipitation occurs. The formation of groups even of 4 or 7 solute atoms involves, on a probability basis, considerable local atom movement; this explains the observation that the time of attainment of maximum hardness in a knot-formation hardening alloy is related to temperature according to the diffusion law.

The existence of the knot structure does not seem necessarily to imply high hardness, and before accepting Dr. Gayler's theory that two successive maxima of hardness must appear, in almost all age-hardening curves, one looks for solid evidence that what were previously regarded as precipitation-hardening alloys show an additional, early hardness maximum and the knot-formation hardening alloys an additional, late hardness maximum, corresponding to the stage of true precipitation. It is only on the first of these that any evidence is as yet presented and that is not entirely convincing. In Fig. 4 the inflected curves can only be justified if the accuracy of hardness measurement is better than about 5 Brinell numbers, since uninflected curves can be drawn to this accuracy; yet one point, at 250° C., is regarded as in error to the extent of about 12 Brinell numbers. The curves of Fig. 4 are presumably only a minor part of the body of data supporting the statements regarding the effect of temperature on the position and magnitude of the arrests and Figs. 2 and 3; alone these curves supply only two points in each of the figures and do nothing to contradict the view that the maximum attainable hardness really increases steadily with decrease in ageing temperature but that at low ageing temperatures the maximum is not reached in experiments of the ordinary duration.

According to the theory, the early stages of ageing are accompanied by the segregation of part of the solute content into areas of increased concentration, this process can only produce an expansion in an alloy which later contracts if the divergence between the actual and theoretical atomic volumes increases more than proportionately to increase of concentration. This mode of divergence from Vegard's law occurs in the alloys of silver and copper, at least on the copper side, so that in these alloys segregation to form knots would produce an anomalous change of volume, and the question arises: Is it such volume changes and the resulting lattice strain which are the causes of hardening by knot-formation? If this view be taken, then this type of age-hardening is virtually an example of work-hardening and would be expected to disappear on increasing temperature, as Dr. Gayler's theory also suggests.

Dr. Morris Cohen * (Associate Member): I am gratified to note the close similarity between Dr. Gayler's theory and the ideas which I expressed in a

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recent paper on the age-hardening of a silver-rich copper alloy.* About 3 years ago, I studied the ageing mechanism of a commercial Duralumin at four ageing temperatures, and found that at room temperature and at 100° C. the hardening took place without any change in the lattice parameter of the aluminium-rich supersaturated solid solution. At 300° C., however, the age-hardening occurred simultaneously with a change in lattice parameter, while at 200° C. the hardness curve showed two peaks, the lattice parameter remaining constant until just after the initial hardness peak. These results indicated that below 100° C., the hardening took place without the precipitation of $CuAl_2$ particles, whereas above 300° C. it was accompanied by actual precipitation. The data at the intermediate temperature of 200° C. were interpreted as direct evidence of a two-stage ageing process in which pre-precipitation-hardening was followed by precipitation-hardening. The mechanism of this two-stage process was visualized in the following manner: The matrix lattice, being supersaturated with respect to copper, strives to throw the copper out of solid solution. This can only be accomplished, however, by the formation (precipitation) of $CuAl_2$ crystallites, hence the copper atoms diffuse from their scattered random positions on points of the aluminium lattice into localized regions in preparation for the subsequent precipitation of discrete particles of $CuAl_2$. It was assumed that the lattice distortion produced by these segregations or "knots" † of copper atoms in the aluminium lattice just prior to precipitation was sufficient to account for the age-hardening below 100° C. and also for the initial hardening at 200° C. The secondary hardening at 200° C. was attributed to the actual formation of $CuAl_2$ crystallites, this precipitation stage following the "knot" formation stage. At 300° C., the ageing took place so rapidly that the pre-precipitation stage was not detected.

It was felt that this two-stage picture of the age-hardening process might be applied to other age-hardenable alloys, but in view of the fact that the Duralumin used contained appreciable amounts of magnesium, silicon, and iron, as well as the usual 4 per cent. of copper, no generalization was made at the time. With this thought in mind, however, the ageing characteristics of a silver–copper alloy ‡ of high purity were studied at several ageing temperatures. As Dr. Gayler states in her paper, these results again gave direct evidence of a two-stage ageing process, which in my opinion lent considerable weight to the concept that "knot" formation (or diffusion and molecule formation, as Dr. Gayler prefers to call it) must precede precipitation, and that they form two consecutive steps in the general mechanism of age-hardening. It was also shown that as the ageing temperature was increased there was more and more overlapping of the "knot" formation and precipitation stages until at 169° C. and above, no pre-precipitation-hardening could be detected.

Thus it is seen that Dr. Gayler and I are in very strong agreement as to the basic mechanism of the ageing process. I differ from Dr. Gayler, however, on one point: I do not believe that actual molecules of $CuAl_2$ must form in the solid solution before precipitation. There is little evidence to indicate that $CuAl_2$ can exist as molecules; $CuAl_2$ owes its identity to its characteristic crystal lattice in which the number of aluminium atoms to copper atoms are present in the ratio of 2 to 1. I prefer, therefore, to use the less definite term "knot," in which the type of atomic bonding is the same in the supersaturated solid solution, and does not change until the actual precipitation of the $CuAl_2$ lattice takes place. Naturally, this is only a fine point and cannot be proved one way or the other.

I should like to have Dr. Gayler's explanation of the intermediate flattening out of the hardness curves which occurs when the second stage sets in. In my

* M. Cohen, *Metals Technology*, 1936, 3, (7); *A.I.M.M.E. Tech. Publ.* No. 751.

† See P. D. Merica, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, 99, 13.

‡ M. Cohen, *loc. cit.*

alloys, an actual intermediate softening was detected at this point in the ageing process. This was explained as follows: "When precipitation sets in, the intermediate softening occurs, presumably because the initial particles were too small to be very effective in hardening, and so they do not counterbalance the softening caused by the relief of distortion as the knots leave the matrix lattice to form discrete particles. However, as the particles grow in size, the hardness begins to increase again; and if the ageing is prolonged sufficiently, the particles pass through the critical size for maximum hardening. . . ." I wonder how Dr. Gayler differs from this interpretation.

It is hoped that further work on other age-hardenable systems will throw more light on the possible universality of this two-stage ageing process.

Dr. W. L. Fink,* M.S. (Member) and Mr. D. W. Smith:* In much of the experimental work and discussion on the age-hardening of aluminium–copper alloys there is indiscriminate consideration of the results on binary aluminium–copper alloys and on very complex alloys containing copper, manganese, magnesium, iron, silicon, zinc, &c. The mechanism of age-hardening in the binary alloys is rather complex, so that it seems undesirable to complicate the situation further by the presence of several additional alloying elements. Certainly, if a polynary alloy is used, that should be borne in mind constantly, and the results should not be considered as pertaining to the binary aluminium–copper alloys.

Dr. Gayler adversely criticizes a paper which we published † on the age-hardening of a binary aluminium–copper alloy at 100°, 160°, and 200° C. The entire criticism, however, is based on a statement concerning the time at which visible precipitation had been observed at room temperature. The statement was not intended to imply that no precipitation occurred at room temperature in less than 3 months, which is Dr. Gayler's interpretation; in fact, subsequent examination of this same alloy aged at room temperature revealed precipitation in as short a time as 1 hr. after quenching. This point will be considered further in a paper which is now being prepared.

Dr. Gayler's new theory of age-hardening offers some difficulties. For example, the first stage of ageing is supposed to consist of diffusion of solute atoms to certain positions within the lattice. It is assumed that this ordered arrangement would result in an increase in electrical resistivity; most of the available experimental evidence indicates that it would result in a decrease. Another difficulty is presented by the new concept of precipitation (the second stage). The concept that molecules and *crystallites* of a new phase form prior to precipitation from solid solution is unique and seems to require a new definition of solid solution and precipitation.

Dr. R. H. Harrington ‡ (Member): I wish first to point out a marked agreement between the general principles established by Dr. Gayler and those which I described in a previous paper,§ and then to discuss several of the details derived from these principles by Dr. Gayler.

In my paper I classified the types of age-hardening as: (*A*) simple precipitation-hardening, *e.g.* the Fe–W system; (*B*) simple lattice-strain hardening; *e.g.* the room-temperature ageing of Duralumin; (*C*) complications due to allotropy, *e.g.* the Fe–C system; (*D*) other causes of age-hardening effects.

Of present interest is an illustration to my paper, here reproduced as Fig. D,

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‡ Research Laboratory, General Electric Company, Schenectady, N.Y., U.S.A.

§ "The Present Status of Age-Hardening," *Trans. Amer. Soc. Metals*, 1934, 22, 505–531.

and some attendant observations from the paper. The two stages of age-hardening in Duralumin, (1) the "diffusion" stage and (2) the "precipitation" stage, are clearly marked and described in Fig. D. It is seen, then, that simple lattice-strain may result from "atomic precipitation," or aggregation, of solute atoms within the solid solution lattice: this is the diffusion stage. The second stage is, of course, the true precipitation and formation of discrete particles of compound with maximum hardness attendant on achievement of a critical dispersion. It has been noted during the study of about 100 age-hardening alloys that many, after quenching from solution temperatures, show an increase in hardness at low drawing temperatures followed by a minimum hardness, and finally a maximum precipitation-hardness at a higher temperature. In many alloys the precipitation of a true compound begins to take place immediately on heating and masks any tendency to produce simple lattice-strain hardening.

Now to discuss the present paper: Because of the broad meaning of "age-hardening," it seems preferable to think of this paper as describing "The Theory of Precipitation-Hardening," since this reaction probably takes place always in the two stages, either consecutively or concurrently. It is probable that the two stages have their dual existence only when a metastable solid solution breaks down within the "ageing range"; that is, when a solid solution breaks down during very slow cooling from the solution temperature, it is improbable that the "diffusion stage" will have any similar distinct existence.

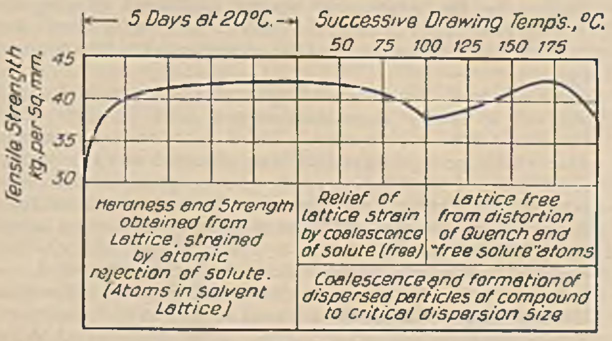

FIG. D.

The author states that: "When a group of molecules thus formed grows to such an extent that the solid solution can no longer withstand the stresses set up, release of these stresses is caused by the rejection of this group from the solid solution lattice and precipitation proper has taken place." This statement inevitably leads one to picture groups of molecules in an isolated locality and yet within the solvent lattice just before precipitation. This idea of molecules of like atoms, as well as unlike, existing within the solvent lattice might seem untenable if taken literally. It may be that, instead of molecular bonding, the aggregated solute atoms may exert a metastable superlattice structure or secondary lattice effect immediately prior to formation of the true precipitated phase. Undoubtedly the time is rapidly coming when, in dealing with strained lattices, we must consider the effects of localized pressures as well as the two variables temperature and concentration (equilibrium diagrams being based on the assumption that pressure is constantly 1 atm.). It also seems possible that this solute aggregation into "groups" might equally well mark the maximum of the first stage.

Would not the phase "ageing range" convey a more specified (and equally adequate) meaning than does "temperature range" (bottom of p. 251)?

In discussing the lower limit of the "temperature range" (ageing range), it seems probable that there is always a tendency for these quenched solid solutions to start precipitation at any temperature from the lowest temperature for retention of the solid solution up to the solution temperature. Some alloys immediately begin to "age-harden" with the metastable solid solution at room temperature. Thus the "lower limit" has a measurable meaning only in the practical sense of test data.

Regarding the relationship of hardness and resistivity, there are two different relationships possible whenever two hardness maxima appear in the age-hardening: (1) It seems probable that the maximum hardness resulting from the "diffusion stage" will be closely associated with the maximum resistivity possible for the alloy; while (2) the maximum hardness for the precipitation stage will usually occur before the minimum resistivity is developed (as in beryllium–copper alloys).

It must be remembered, of course, that Fig. 2 will not apply to all alloys for in many of them the second stage seems entirely to mask the first, with which it is practically coincident.

Regarding Fig. E, for some alloys in which the second stage appears to mask the first, the hardness–temperature curve appears to indicate that point *C* is coincident with point *A* and its relationship to resistivity is not so clearly defined under these conditions.

In conclusion, I cannot, at the present time, agree to some of the details of general application of the author's theory but I believe that the author's main principles of the two-stage mechanism are well founded. It is always necessary for time and future data to give accurate meaning to such a fundamental theory.

Dr. C. H. M. Jenkins * (Member): It is interesting to consider those alloy systems which do *not* exhibit age-hardening although the systems possess certain necessary solubility conditions. These systems do not appear to possess any abnormal differences in the rate of diffusion, nor has it been found that the constituents separating by decrease of solubility shun the cleavage planes or the grain boundaries of the crystals. All that can be deduced from the facts is that age-hardening has not occurred because a metastable or transitory lattice does not form. This in effect hampers the free separation of atoms held in excess of the solubility limit. It is this process of entanglement which should be carefully studied in the future.

I do not agree with the suggestion (p. 252) that the changes in hardness cannot be represented by one curve, as was put forward in an earlier paper with Mr. Bucknall. The initial kinks in the various property curves and the characteristically diffuse lines in the X-ray spectra are, I suggest, due to "positional" hardening in the crystals. No doubt, hardening does not occur at the same speed in various crystals or in all parts of the same crystal. The structure of martensite shows that the cleavage planes and the grain boundaries have an influence. The curve which we proposed represents a "mass" property and is not an expression of the crystalline mechanism.

In addition to the absence of evidence that small particles are necessarily hard, I would emphasize a point which has not been made by the author. Briefly it is this: hardening is not so much the result of the formation of a new phase, *i.e.* a second constituent, as the result of the *alteration of the parent lattice* in its attempt to generate the new second phase. From this main idea.

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it is deduced that there should be a relationship between the proportion of material which enters into a change and the degree of hardening produced. We have evidence of this effect. In a high-carbon steel, which is capable of undergoing very considerable hardening, the forces are derived from the attempt of about 99 per cent. of the material to change from γ- into α-iron (as well as smaller forces bound up with the solution of the carbides), whereas in aluminium alloys only 1–3 per cent. of the material is tending to change its condition from a form in which it is in solution into one in which it is out of solution.

The author's view that diffused crystallites are the cause of age-hardening does not explain the well-known effect produced in an aluminium alloy if it is cold-worked after solution treatment. Age-hardening is immediately produced. This fact is not in accordance with the idea of *diffusion*, but can readily be accounted for by the suggestion that a transitory phase exists. Such a phase is set up by conditions unfavourable to the ready separation of a second constituent from solid solution. Age-hardening is thus the disturbance of the normal mode of separation.

In all previous considerations of age-hardening no reference has been made to the possibility of a pseudo-ordered arrangement, but there is evidence of a remarkable degree of age-hardening in an alloy reheated for a short time to a *temperature close to the solubility limit*. This fact is closely parallel to changes from disorder to order in regard to the velocity of transformation. I would suggest that the transitory lattice is not unlike an ordered arrangement in that it calls for little positional shift in the atoms. A further consistent feature is that a higher temperature of ageing produces a higher value of the maximum hardness attained, but experimental conditions for rapid heating and cooling of specimens at high temperatures form an artificial limit at present to the attainable maximum hardness.

The author states that " ageing is considered to be due to the diffusion of solute atoms to planes about which precipitation proper will ultimately take place as already suggested by Desch." Since the introduction of atomic physics, the term " diffusion " has never been re-defined, but in its original meaning the word implied that a movement among the atoms had taken place with the result that some atoms had moved to distant positions. The degree of movement in the diffusion process is atomically speaking large. The general conception of diffusion implies that the term is related to a " mass " property and is affected by well-recognized laws in relation to time and temperature.* If the term were to be applied to the rapid translation of atoms such as might be set up during plastic deformation or slip movement there is considerable probability of misconception, but the author does not suggest such an occurrence although such translations of atoms are possible ; I would hesitate, however, to apply the term " diffusion."

Dr. D. STOCKDALE † (Member of Council) : There are certain difficulties raised by this theory which may prevent its general acceptance. In the first place, I would support Dr. Alexander's contention that an increasing concentration of solute atoms about planes of precipitation would probably lead to a decrease in electrical resistance. This process is analogous to super-lattice formation where there is generally a spectacular decrease in resistance. Increasing concentration of solute on certain planes necessarily means increasing concentration of solvent on other planes, and it is to be expected that the nett effect on the electrical resistance would be a decrease.

I submit that the theory does not explain preliminary softening and that

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* R. M. Brick and A. Phillips, *Metals Technology*, 1937, 4, (2), show the rate of diffusion of copper and magnesium into aluminium.

† Fellow of King's College, Cambridge.

nowhere in the paper is there a real explanation of this phenomenon. There is a statement of the experimental fact that there is such softening, but there is nothing more than that. The first stage of hardening is caused by diffusion; the second by "molecule" formation. The second stage "follows the first and takes place nearly simultaneously." If these two processes both cause hardening and follow each other without intermission, how can there be any softening?

The free use which the author makes of the word "molecule" is open to criticism. Is a small clump of atoms meant, or is some definite bonding, electrovalent or covalent, implied? It would perhaps avoid confusion if the word "molecule" were reserved to describe the smallest particle of an element or compound which can have an independent existence in the vapour phase or in solution and another word such, possibly, as "microcrystallite" used in connections such as these. If there is in this case something in the nature of a chemical molecule in the lattice will not the disturbance be such that there will be a marked increase in the electrical resistance?

The following have been put forward by various workers as experimental facts in connection with the aluminium–copper alloys:

(*a*) Maximum hardness is reached before there is any change in lattice parameter.

(*b*) Maximum hardness is reached before there is any substantial change in volume.

(*c*) There is definite precipitation before there is any substantial hardening.

(*d*) The density of the precipitate is greater than that of the parent solid solution.

If these really are facts, it follows that during the early stage of age-hardening the aluminium lattice will be very imperfect, though perhaps these imperfections may be much localized. Taylor's theory suggests that such a lattice would have a high yield-point and it would, I think, possess a high electrical resistance. The critical dispersion theory, although I accept it with reluctance, accounts for the second stage of hardening and the decrease in resistance. There are, in effect, two reactions—lattice change and aggregation of precipitate—both leading first to hardening and then to softening. At certain temperatures the lattice might heal faster than the precipitate aggregates. Initial softening and certain other anomalies can be explained along these lines.

Dr. H. **Sutton** * (Member) and Mr. J. W. **Willstrop**,† B.Sc. (Member): As regards the first stage of the age-hardening process, is it not possible that movement of copper atoms may occur at dislocations? Proximity to a grain boundary or a dislocation would seem likely to be the important factors affecting the probability of a copper atom leaving the lattice. During this age-hardening at normal temperature, no change in lattice parameter has yet been observed, and it would appear, therefore, that only a small number of copper atoms, if any, leave the lattice.

G. I. Taylor ‡ showed that if an imperfect crystal be subjected to shear stress it will yield through the successive "jumping" of single atoms in a row near the dislocation to the next position of stability. The weakness of the crystal at the dislocation is due to the spacing of the atoms in this locality being different from the ideal. The spacing of the atoms in the row

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† Scientific Officer, Royal Aircraft Establishment, South Farnborough.

‡ *Proc. Roy. Soc.*, 1934, [A], 145, 362–404.

immediately below the dislocation is less than normal while that of those in the row above is greater. In the case of a solid solution of copper in aluminium the movement of a copper atom to the position *A* in Fig. E, owing to its smaller size, will allow the neighbouring aluminium atoms to adopt a more normal spacing. In consequence, the resistance of the crystal to shear would be expected to be greater when the position *A* is occupied by a copper atom than when an aluminium atom is in that position. Hence, in an imperfect crystal of a solid solution of copper in aluminium we may expect an increase in hardness by the movement of copper atoms to regions of abnormally close packing.

As regards the first stage, the author refers briefly in para. 4, p. 250, to increase in electrical resistivity being caused by the diffusion. She does not suggest the manner in which the increase in electrical resistivity is caused, but the effect of cold-working has been considered in that connection by Rosenhain and others. That conception would agree with the data of O'Neill, Farnham, and Jackson.*

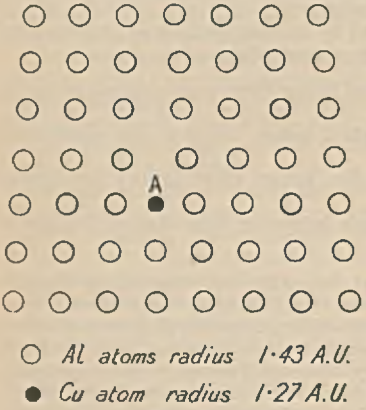

Fig. E.

It is important, however, to bear in mind that the X-ray spectrograph gives a general perspective view and that, while there can be little doubt of the accuracy of present X-ray data and conclusions on age-hardening of Duralumin as affecting the main bulk of the solid solution, it may be that some changes are taking place at the regions near the grain boundaries. Microscopical work on gold–silver, beryllium–copper, and Duralumin leaves one with that impression.

In a recent paper, H. Lay,† refers to the less vigorous age-hardening in cast Duralumin than in wrought and to the still less vigorous age-hardening in single crystal Duralumin. Lay has examined the so-called inhomogeneous (microscopically) precipitation which occurs in the boundary regions in Duralumin aged at temperatures too low to effect general precipitation within the grains.

It appears very remarkable that in this matter of the detection of precipitation in Duralumin, microscopic examination reveals the precipitated constituent before the X-ray spectra have shown appreciable corresponding change of parameter.

The work of Phillips and Brick,‡ on some alloys of the Duralumin type suggests that surface strain reduces solid solubility. The possibility that the strained conditions at crystal boundaries after rapid cooling promote slight rejection of dissolved constituents at the boundary is one that cannot be overlooked. Experience indicates that precipitation at the grain boundary can occur very early and before general precipitation. We should be glad of the author's comment on this point of view.

The Author: In reply to Dr. Callendar, I would say that the broadening and diffuseness of the lines of the X-ray spectra during ageing are indicative that the second stage of the ageing process has set in; this may be associated

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* *Phil. Mag.*, 1933, [vii], **16**, 913–929.
† *Z. Metallkunde*, 1936, **28**, 376–380.
‡ *Metals and Alloys*, 1934, **5**, 204–205.

with rapid growth of molecules and crystallites. No measurable change in the lattice parameter has been detected hitherto during the first stage of the ageing process. The note which has been added to the paper will amplify these remarks.

By means of a chemical method, Dr. Callendar has detected precipitation of silicon in an alloy after annealing, a fact which is most interesting, particularly since the results coincided with a decrease in electrical resistivity; I would suggest that his alloy indicated that the second stage of the ageing process was well advanced. If he had carried out his experiments at a lower (probably critical) temperature, it is highly probable that Dr. Callendar would have detected an initial increase in resistance followed by a decrease; the presence of precipitated silicon, indicated by the latter, being detected also by his chemical method. Unfortunately, such a method cannot be used to detect precipitation in copper–aluminium alloys.

I would refer Dr. Callendar to a recent and very interesting paper on the age-hardening of aluminium–silicon alloys by Helling.*

I regret that Dr. Alexander has been unable to publish the results of his researches on age-hardening, particularly since he advanced a theory, similar to mine, as a working hypothesis. Dr. Alexander considers that before a further discussion of a general theory of age-hardening can take place, a knowledge of diffusion is essential. Would he also suggest that no discussion of the theory of electrical conduction should have taken place before the structure of the atom was fully worked out? It is obvious that the mechanism of diffusion is a problem which is of fundamental importance to age-hardening, and more particularly so since, during the initial stages of age-hardening, concentration of solute atoms occurs contrary to the generally accepted laws of diffusion. The theory of the mechanism of diffusion is a subject to which mathematical physicists are now devoting their attention, and no "certain knowledge" of the problem can be obtained until their results are forthcoming.

Order–disorder transformations are accompanied by an increase in the electrical resistance, and since Dr. Alexander considers that the first stage is a departure from disorder, he expects that during ageing a decrease of electrical resistance should occur. However, a disorder–order transformation such as occurs on heat-treating a copper–gold alloy consisting of Cu_3Au, or an aluminium–iron alloy containing 0–32·5 per cent. aluminium, consists of a re-arrangement of solute atoms from random to regular positions in the lattice. This change is accompanied by a decrease in electrical resistivity, but this change is also indicated by the appearance of *new lines* in the X-ray spectra due to the positions taken up by the ordered arrangement of the atoms.

Considering, therefore, existing data of alloys which age-harden, I think that it is not possible to attribute the physical properties of the alloys whilst ageing to a disorder–order transformation. That an ordered arrangement of particular atoms *ultimately* occurs when a new phase is formed from a single solid solution is undoubted, but I do not consider that the process by which this "ordering" is reached can be compared with that which takes place during the disorder–order transformation, for instance, in gold–copper alloys. The characteristics accompanying such a change, *viz.* decrease in electrical resistivity, and the appearance of new lines in the X-ray spectra, are apparent in alloys which age-harden *after* other changes have first occurred. The appearance of new lines in the X-ray spectra, indicative of the "ordered arrangement," *i.e.* those pertaining to the precipitated phase, are only visible after comparatively prolonged heat-treatment, depending, of course, on the ageing temperature. The changes in the alloys prior to those just mentioned cannot therefore be ascribed entirely to a disorder–order change.

* W. Helling, *Z. Metallkunde*, 1937, **29**, 27.

Dr. Alexander is doubtful about the existence of two maxima on time-hardness curves: such maxima can be seen, however, in the results of Masing and Dahl * on beryllium–copper alloys, of Wiest † on a 5 per cent. copper-silver alloy, as well as in those of Cohen already referred to and to those in his discussion on this paper. More recently still, Lay ‡ has shown that an initial maximum occurs on the hardness–time curve of a nickel–beryllium alloy ageing at 350° C.

Further, the high tensile strength and high ductility of alloys of the Duralumin type aged at room temperature, and also the high tensile strength accompanied by low ductility which occur on ageing alloys at temperatures appreciably higher than room temperature, are additional evidence in favour of the existence of two maxima on the hardness–time curves.

I am very glad that Dr. Cohen and I are in such agreement as to the fundamental mechanism of age-hardening. His data on the ageing of Duralumin is further support of the theory which we have both suggested.

With regard to the idea of " molecules " existing in the solid solution, I have endeavoured to explain my meaning in the note which has been added to the paper. The term " knot " is certainly less definite: it defines such groups in general terms. Merica has postulated that the groups or " knots " . . . are sufficiently distorted and ' rough ' in atomic structure to resist slip and deformation fairly efficiently. They . . . may be considered to act . . . substantially as crystalline particles of $CuAl_2$ would act. . . ." The suggestion that I have put forward, which is amplified in the Note, is that localized stresses are set up in the parent lattice during the first stage of age-hardening and the initial part of the second stage, which results in an increase in hardness caused by " strain-hardening " rather than by " slip-interference " of knots, as suggested by Merica. Heat-treating an alloy in this condition will cause the removal of stresses set up and, consequently, softening will set in. Subsequent hardening on further heat-treatment is caused by the formation of more groups of molecules and crystallites prior to precipitation proper.

I agree with Mr. Bucknall that segregation of solute atoms on a broad scale should be detected by a change in the lattice parameter, whereas localized segregation would not make itself seen in line spectra.

With regard to the evidence submitted in favour of two maxima I hope to submit, in the near future, further experimental data in support of the theory. In the meantime the existing published data (see also reply to Dr. Alexander) indicate that one maximum on the time–hardness curves cannot explain all facts of age-hardening.

I am much interested in Mr. Bucknall's suggestion that the first stage of age-hardening is virtually an example of work-hardening, for I am of a similar opinion. As I have stated more fully in my added note and in the reply to Dr. Cohen, the concentration of solute atoms and the formation of molecules in the early stage cannot take place without localized stresses being set up. Such a conception will account for both the softening which follows on ageing at higher temperatures and for the difference between the mechanical properties of the alloy in either condition (see Note, p. 266).

I regret that Dr. Fink and Mr. Smith consider that I have misinterpreted their statement regarding the time at which visible precipitation had been observed by them, for I fully realize that precipitation must proceed for some time before it is possible to detect signs of it under the microscope. Perhaps my meaning would have been better expressed had I written, " Their results do not show what change has been going on in the alloy before the actual

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* G. Masing and O. Dahl, *Wiss. Veröff. Siemens-Konzern*, 1929, **8**, 103.

† P. Wiest, Ref. 19 in the paper.

‡ H. Lay, *Z. Metallkunde*, 1937, **29**, 32.

precipitation from the solid solution of one or more discrete particles takes place."

Concentration of solute atoms on planes of precipitation does not necessarily imply the formation at once of an ordered arrangement; this point has been discussed in my reply to Dr. Alexander. The concept of molecules and crystallites of a new phase forming prior to precipitation from solid solution has also been more fully explained in an additional note to the paper.

I am indebted to Dr. Harrington for pointing out the agreement between the general principles of age-hardening which we have both striven to establish. I concur with his suggestion that the term "ageing range" is better than "temperature range," and also that the "lower limit" has a measurable meaning only in the practical sense of test data.

The relationship between electrical resistivity and hardness is difficult to interpret, but it seems probable that the maximum hardness of the "diffusion" stage is associated with maximum resistivity, which would indicate that a high degree of localized distortion is present in the lattice, while the maximum hardness of the second stage, *i.e.* precipitation proper, does not appear to be associated with minimum electrical resistivity.

I think that Fig. 2 will apply to all alloys, since temperature is the main factor controlling the existence, or masking of the first stage of the ageing process. Hence, a displacement of the curves in Fig. 2 parallel to the time axis or, rather, an adjustment of the temperature scale to suit known facts, will make them applicable to alloys which age-harden without indication of the first stage.

In Fig. 3, the point C indicates the ageing-temperature at which the maximum hardness due to the first stage of ageing is masked by the rate at which hardening due to the second stage is taking place. The electrical resistivity curves of alloys aged at temperatures below that represented by C will be characterized by an increase to a maximum followed by a decrease: the rate and the time at which this sets in increasing and decreasing, respectively, as the ageing temperature increases. Therefore, on ageing at a temperature C, no first maximum hardness will occur, for the first stage of ageing will be masked by the immediate increase of hardness due to the second stage and, consequently, the electrical resistivity will decrease immediately. High hardness values would be expected in very short periods of heat-treating at the temperature C.

I fully endorse Dr. Harrington's view that further work is necessary to give accurate meaning to a fundamental theory. The queries raised regarding the formation of molecules have been dealt with in the note which has been added at the end of the paper.

Dr. Jenkins writes: "The initial kinks in the various property curves and the characteristically diffuse lines of the X-ray spectra are, I suggest, due to 'positional' hardening in the crystals"; has he not, however, misinterpreted the facts, for the "initial kinks" and "diffuse lines of the X-ray spectra" do not relate to the same stage in the ageing process? The "initial kinks" are correlated with the concentration of solute atoms—prior to any diffuseness in the lines of the X-ray spectra—at definite positions in the aluminium lattice, as shown by intensity measurements. Diffuseness, however, occurs during the later stage of ageing and is indicative of precipitation proper. His criticism that the single curve of age-hardening suggested by himself and Mr. Bucknall represents a "mass" property, while those which I have put forward to express the same relationship are "an expression of the crystalline mechanism" is, therefore, based on a misunderstanding of facts. Dr. Jenkins considers that I have neglected the point: that "hardening is not so much the result of the formation of a new phase, *i.e.* a second constituent, but is set up by the *alterations of the parent lattice* in its attempt to generate the new second phase."

Surely an alteration of the parent lattice is inseparable from the precipitation of a second constituent, since one is the cause and the other the effect. Consideration of the first consequently involves that of the second.

Alloys which harden may be divided into three main types: (*a*) those which form a super-saturated solid solution from which a second phase separates, *i.e.* alloys of the Duralumin type, &c.; (*b*) those which age-harden owing to the decomposition of the entire matrix into two different phases, such as a eutectoid decomposition, *i.e.* steel and alloy steels. Increase of hardening is also caused by further separation of one phase from another owing to differences in their respective solubilities at the ageing temperature; (*c*) alloys which harden owing to the formation of a super-lattice structure, *i.e.* gold-copper alloys.

In alloys of type (*a*) only a portion of the matrix may take part, whilst in those of types (*b*) and (*c*) the whole of the lattice is involved, and hence an immensely greater increase in hardness results, as cited by Dr. Jenkins.

Dr. Jenkins thinks that I consider " that diffused crystallites are the cause of age-hardening," and that this view " does not explain the well-known effect produced in an aluminium alloy if it is cold-worked after solution treatment." Firstly, I have not put forward the view that diffused crystallites are the cause of age-hardening; secondly, the effect of cold-work on an aluminium alloy after solution treatment may be explained as follows: immediately after quenching the alloy, the lattice undergoes distortion in localized areas, due to the concentration of solute atoms and the formation of some " molecules " or " groups of molecules " (see added note to paper for a definition of these terms). According to Le Chatelier's Law, if such an alloy be deformed, it will have an increased tendency to age-harden in order to resist more efficiently the deformation. This simple explanation is sufficient to account for the acceleration of age-hardening produced in an alloy by cold-work.

The consideration of a pseudo-ordered arrangement has been discussed in my reply to Dr. Alexander.

Some of the points raised by Dr. Stockdale in his interesting criticism have been discussed in my replies to Dr. Alexander and Dr. Cohen, and also in the note which I have added to the paper itself.

Preliminary softening may be explained as follows: consider that the hardening of the alloys in the preliminary stage is due to stresses set up in localized areas due to (*a*) concentration of solute atoms, (*b*) the formation of a comparative small number of groups of " molecules." I agree with Dr. Stockdale that the term " molecule " is not a happy one, but neither does the term " knot " satisfy me, for I am trying to describe a process which is built up gradually by the " bonding " together of certain atoms in a more or less definite relationship, such as one atom of copper with two atoms of aluminium. I intend to imply that a definite bonding between an increasing number of atoms takes place gradually (or rapidly according to the ageing temperature), the effect of which will be localized strains in the lattice. This will cause resistance to slip, and will result in an increase in mechanical strength but no decrease in ductility, since the matrix on the broader scale is unaffected.

When the ageing temperature is sufficiently high for softening to be detected prior to the second maximum, I think that the localized strains set up by the " molecules " or " bonded " groups of atoms are removed by prolonged time at the ageing temperature owing to the normal process of diffusion, but that gradually these " bondings " are again re-formed owing to the alloy being still in a metastable condition, and growth takes place until a crystal is precipitated. An analogy for this process may be seen in a metal which self-anneals at the temperature of deformation. Internal stresses are set up, but these are removed on keeping the metal at the same temperature and recrystallization and crystal growth proceeds.

The experimental facts cited by Dr. Stockdale appertain to aluminium–copper alloys ageing at temperatures in which the first stage of the ageing process predominates, since the second maximum hardness is accompanied by change in both lattice parameter as well as in density. Dr. Stockdale's suggestion that Taylor's theory indicates that a lattice in the early stages of age-hardening would have a high yield-point and high electrical resistance is most interesting, particularly since such properties are characteristic of these alloys when aged at room temperature.

Dr. Sutton's and Mr. Willstrop's suggestion that during the first stage of the age-hardening process movement of copper atoms may occur at dislocations is interesting. According to Taylor, there is a temperature T_D (*i.e.* the lowest temperature at which a jump can be made) above which any stress, however small, will cause centres of dislocation to travel. The possibility arises: are the stresses set up in the supersaturated solid solution sufficient to bring about movement of these centres of dislocation, and will the copper rather than the aluminium atoms move, as Dr. Sutton and Mr. Willstrop suggest, owing to their smaller size?

As regards the change in electrical resistivity, I do not think that this is due to a process which may be considered as a disorder–order transformation (cf. reply to Dr. Alexander), though an ordered arrangement is reached during the second stage of the ageing process. The fact that the lines of the X-ray spectra of the alloy in the "as quenched" condition, and also as aged at room temperature for 7 days, are indistinguishable and quite sharp, but that the electrical resistivity increases during this period of ageing, indicates that atomic changes are taking place within the lattice. It is highly probable, therefore, that localized internal stresses are being set up, due to movement of solute atoms, the resultant strain-hardening being indicated by increase in resistivity.

As Dr. Sutton and Mr. Willstrop point out, X-ray line spectra gives us a general view of age-hardening, but the technique used in the past has not been sufficiently sensitive to indicate localized regions where visible changes in the solid solution are taking place.

The work of Phillips and Brick suggesting the possibility that boundary precipitation may be due to the strained condition of the boundary, certainly cannot be overlooked. Too little, however, is known about boundary conditions owing to the impurities generally present; but now that really high-purity metals are available it should be possible to examine more closely the problem suggested above.

THE ESTIMATION OF GRAIN-SIZE IN THE REGION ABOVE 10^{-3} CM.*

By R. A. STEPHEN,† M.Sc., MEMBER, and R. J. BARNES,† Ph.D.

SYNOPSIS.

X-ray methods proposed for determining grain-sizes above 10^{-3} cm. are critically examined. It is shown that to be generally applied in practice any such method must use the same specimens as are used by the metallurgist for microscopic examination. This necessitates the use of back reflection photographs, except in the case of thin sheets.

A new method for determining a value for average grain-size solely from X-ray results is described.

An empirical method too is considered for determining average sizes from a graph. The graph is derived from plotting spots on a given (*hkl*) reflection against the grain-size of standard specimens.

INTRODUCTORY.

THE ordinary method of grain counting is tedious and cannot as a rule be applied non-destructively. As the control of grain-size is becoming of more importance in metallurgical practice, the authors undertook an investigation into an alternative method of grain-size determination. Perusal of the literature showed that various claims in connection with X-ray diffraction methods have been put forward from time to time. These methods have not been applied in industry to any extent, and it was decided, therefore, to examine critically their practical or theoretical disadvantages; these are not always apparent from the opinions expressed in the papers themselves.

Czochralski took Laue photographs through thin specimens, and a qualitative idea of the grain-size was obtained by comparison with pictures of standard specimens. The Laue method cannot be applied generally, except in the case of thin sheet work. It is, too, a qualitative test, and investigation on the counting of spots shows that the method is very difficult to apply quantitatively. The Laue method cannot be regarded, therefore, as practicable for general use.

The diffraction lines in a powder photograph with a grain-size above 10^{-3} cm. become spotted, *i.e.* individual reflections can be sorted

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* Manuscript received August 10, 1936. Presented at the Annual General Meeting, London, March 11, 1937.

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out. Glocker[1] published details in which the sizes of the spots were shown to be proportional to the grain-size, and this was elaborated by Clark and Zimmer.[2] This involves measuring the size of diffraction spots—a difficult task; in fact, it is more tedious than ordinary grain counting with the microscope. It also seems open to objection on the grounds that grains of equal size are not necessarily equally imperfect. This method, too, cannot be considered to be of great utility, except for noting variations of grain-size in the area examined.

Recently Shdanow[3] has published a paper describing another method, which at first sight appears to be more promising. This is based on rather a different view-point; if a large number of crystals are arranged at random and are irradiated by monochromatic X-rays, a certain proportion will be in a position to reflect in accordance with the Bragg law. From the number of reflections, knowing the dimensions of the camera and pinhole system, it is possible to calculate the number of grains irradiated. Since the volume irradiated is known, the grain-size can be deduced. The authors again used thin slips, *i.e.* transmission pictures; it appears that this was done to arrive at an accurate knowledge of the volume irradiated. This method, although theoretically sound, must be rejected in practice on the grounds that transmission pictures necessitate thin slips, and as monochromatic radiation must be used, the exposures are long. The present authors have endeavoured to extend this treatment to reflection pictures.

Short references have been published by the National Physical Laboratory on X-ray methods of determining grain-size, which appear to rest on a similar argument, but in which reflection pictures are obtained. This, of course, is much better, for in practice much shorter exposures result, and the method is non-destructive. A paper dealing with this subject has not apparently been published.

The present authors have been studying this question for some time, and during this period these latter references have appeared. The reflection technique was considered. During the theoretical treatment many difficulties arose in arriving at a rigid formula to be applied quantitatively. To obtain a relation for relative grain-sizes at first appeared easy, but a closer examination showed that it is very difficult to derive a satisfactory relation between grain-size and the number of spots to be used as a basis for relative grain-size determination. A fairly simple method for determining the absolute grain-size of a specimen was evolved.

In Part I of this paper this new method for determining an absolute value for the mean grain-size by X-rays is described. The X-ray data for grain-sizes of samples of aluminium are compared with the microscopic measurements of grain-sizes of the same specimens.

In Part II the determination of relative grain-sizes is considered, and the difficulties in arriving at a rigid expression are discussed. The numbers of spots which can be counted on reflection photographs are plotted against the actual grain-sizes of samples, and a smooth curve obtained. Such a method once standardized can be applied in practice in a simple way, and seems to be less laborious than ordinary grain counting by the microscope. The same photographs, too, yield information on recrystallization, release from internal strain or directionality —information which cannot be obtained by ordinary metallurgical examination.

PART I.

Theoretical.

In this the derivation of the formula relating grain-size to the number of spots in a definite (*hkl*) line for a definite grain-size is given for a back reflection picture.

If a specimen consisting of a large number of small crystals orientated at random be irradiated by a fine pencil of monochromatic X-rays, then, in general, some of the crystals will be so oriented that they give a certain (*hkl*) reflection in accordance with the Bragg law. If the geometrical conditions are chosen correctly, there will, in general, be one spot on the photographic film corresponding to one grain,* and so the number of spots will determine the number of crystals in a position to give this particular (*hkl*) reflection. For certain experimental conditions one can calculate the probability that a single crystal will be in a position to give this (*hkl*) reflection. Combining this probability factor with the number of spots observed on the film for this reflection, it is possible to deduce the total number of grains irradiated. If, therefore, for the same set of experimental conditions the volume of the specimen irradiated is known, the grain-size can be determined.

The calculation of the factor F, expressing the probability of reflection, is impossible for the usual way of taking powder photographs. Shdanow [3] determined this graphically, and took into account the size of the focus of the X-ray tube used and the usual haphazard geometry of the normal pinhole system. This author discussed the general case and mentioned the simplification which results from a long or narrow diaphragm, a method which the present authors use. The use of a long pinhole system whose dimensions and position with respect to the focus of the X-ray tube are such that it is completely filled with X-radiation, simplifies the mathematics and renders easy the calculation of F. Shdanow still utilized the transmission through a

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* It is possible to get two spots from one grain if the divergency of the primary beam be large enough.

thin specimen, a method which has been discarded by the present authors for the reasons previously given, *i.e.* long exposures and rarely applicable in practice.

In Fig. 1 SS is a pinhole system of diameter a placed in such a position with respect to the focus of the X-ray tube that it is completely filled with radiation. CC is the specimen with its plane face perpendicular to the incident rays at a distance D from the front of the diaphragm.

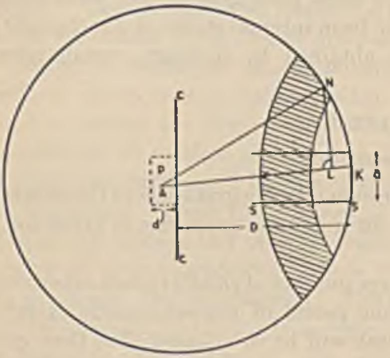

FIG. 1.

Let P be that part of the specimen contained within a cylinder co-axial with the diaphragm, of diameter a and depth d, where d is the effective depth to which the X-rays penetrate the specimen.*

There is incident at any point A in P a solid circular cone of rays defined by the front opening of the diaphragm and the point A; and since d and a are small compared with D the cone can be regarded as right-angled and constant whenever A may be in P. With A as centre, construct a reference sphere of radius D. Let AK be any one of the cone of rays incident at A, let AN be the normal to a set of planes in a crystal at A, and let NL be the normal from N to the ray AK. If angle $KAN = (90° - \theta)$, where θ is the glancing angle of reflection, then a reflection will result, hence if N fall on a circle with $NL = D \sin (90° - \theta)$ as radius, a reflection of the ray AK will occur. Similarly, for any other ray of the cone to be reflected N must lie on the appropriate circle. The envelope of these circles is a belt of area $2\pi D \sin (90° - \theta)a$ around the sphere, so that the probability that this set of planes will reflect one of the rays of the cone is

$$\frac{\text{area of belt}}{\text{area of surface of sphere}}$$

i.e.

$$F = \frac{2\pi D \sin (90° - \theta)a}{4\pi D^2} = \frac{a \cos \theta}{2D}.$$

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* The actual estimation of d is not easy; it may be regarded, however, as that depth beyond which any grain gives a reflection so weak that it cannot be seen on the film by visual observation. This distance d depends on the grain-size, *i.e.* it is possible for a large grain at average depth d below the surface to give a just visible spot, whereas a small grain at average depth d would give a spot which would not be visible owing to its lesser intensity. For one particular grain-size and for a definite time of exposure, d can be regarded as a constant.

If there are N grains in P, then the probable number of reflections from a given plane from the grains in P is

$$\frac{N \cos \theta a}{2D}$$

Let Y be the number of spots for a given (hkl) reflection coming from the grains in zone P.

Then $$Y = \frac{Nj \cos \theta a}{2D}$$

where j is the number of planes in the particular form.

i.e. $$N = \frac{2DY}{ja \cos \theta}.$$

If V is the volume of zone P the volume of 1 grain $= \frac{V}{N}$ and the mean length of the grain edge, G, is given by

$$G = \sqrt[3]{\frac{Vja \cos \theta}{2DY}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the foregoing we have dealt with the central zone P alone, which is easily amenable to mathematical analysis.

With the experimental conditions as depicted in Fig. 1 a limited part, Q, of the specimen lying outside P is irradiated by the more oblique rays passing through the diaphragm, and so Q will also produce spots corresponding to this (hkl) reflection. A little consideration will show that the pencil of rays incident at any point in Q not only varies the further remote the point is from P, but also is of such shape that the factor F expressing the probability of reflection cannot be rigidly calculated. Shdanow used a graphical method to determine F for this zone.

If now the diaphragm is long enough to come practically to the front surface of the specimen, the outer zone Q becomes very small and can be neglected. This is only the case either for a long diaphragm or if a circular " stop " of diameter a is placed concentric with the axis of the diaphragm so that only reflections from P are allowed to register on the film. In the experimental portion to follow the long diaphragm has been mainly used.

Considering expression (1), we find that it is required to know V. Now V is equal to $\frac{\pi a^2}{4} \times d$ (the effective depth). Unfortunately d is not constant, but varies with the grain-size. This introduces the difficulty in deriving a rigid mathematical formula applicable to reflection pictures for different grain-sizes.

For one particular grain-size, however, and a constant exposure time and irradiation conditions, d is a constant. V can therefore be determined if d can be determined. The determination of d is approached by considering the relative intensities of the rays reflected by a small grain at a distance d below the surface of the specimen and of a similar grain on the specimen surface.

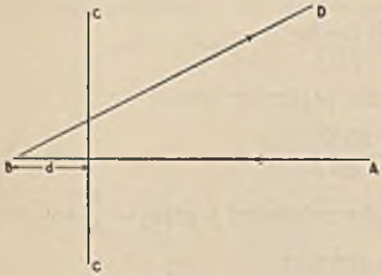

FIG. 2.

Referring to Fig. 2, AB is a ray incident on the specimen CC. Let B be a point distance d below the specimen surface, and let the reflected ray lie along BD.

If I_0 is the intensity of the incident ray, the intensity I_B at B will be given by

$$I_B = I_0 e^{-\mu d}$$

where μ is the linear absorption coefficient of the X-rays in the specimen.

Suppose a fraction, K (depending on the structure factor, &c.), is reflected by a grain at B, then the intensity at B of the reflected ray is

$$KI_0 e^{-\mu d}$$

This ray has to traverse a further distance BD, and since $BD = d/\cos(180 - 2\theta)$ the intensity on emerging from the specimen surface is

$$KI_0 e^{-\mu d\left(1 + \frac{1}{\cos(180 - 2\theta)}\right)}$$

The intensity of a ray reflected by a similar grain at the surface is KI_0,* and the intensities of other reflected beams lie between these two values.

Let the intensity ratio of the strongest and weakest reflected rays be r, then

$$r = e^{\mu d(1 - \sec 2\theta)}$$

i.e.

$$d = \frac{\log_e r}{\mu(1 - \sec 2\theta)}$$

Thus the volume of part P taken as a cylinder of height d radius $\frac{1}{2}a$ is given by

$$\frac{\pi a^2 \log e^r}{4\mu\,(1 - \sec 2\theta)}$$

and the mean length of the grain edge G is given by

$$G = \sqrt[3]{\frac{\pi a^3 j \cos\theta \log e^r}{8DY\,\mu(1 - \sec 2\theta)}} \quad . \quad . \quad . \quad . \quad (2)$$

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* We are here neglecting the absorption in the reflecting grain itself.

Considering this expression, all terms are known except r, the ratio of the intensities of the strongest and weakest spots. There must be a certain minimum blackening for one to see a spot on the film, and the blackening of the strongest spot will depend both on the exposure time and on the grain-size. It is not possible to obtain a measure of the blackening ratio by photometric means, and in any case this procedure can be ruled out from a practical point of view. If it were possible to know the exposure in advance, *i.e.* expose so that the strongest spot has a blackening about equal to unity, then an estimate of r, the intensity range, could be given. This possibility was borne in mind, but a much simpler way of surmounting the difficulty was devised.

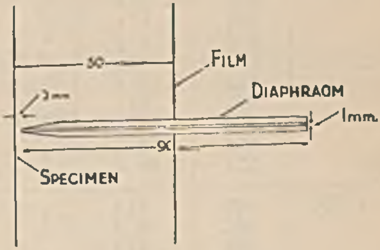

FIG. 3.

A photograph of the specimen was obtained by making the exposure time, t_1, short so that the strongest reflections produce spots of medium blackening B (less than unity). The photograph was repeated using the same part of the specimen with a longer exposure time, t_2. The two photographs are compared side by side, and all spots in the second photograph, which have a blackening equal to or greater than B, must be produced by reflected beams with an intensity range r, where $r = \frac{t_2}{t_1}$.*

If Y_1 is the number of these spots in the second photograph, this is the value of Y, corresponding to r given by the ratio of the times of exposure, to insert in expression (2) for the determination of the absolute grain-size.

The taking of two photographs obviates the need for photometry and permits the evaluation of the actual grain-size using X-ray data alone.

Practical.

The grain-sizes of six specimens of aluminium have been determined by this double picture method. The essential arrangement and dimensions of the apparatus used are shown diagrammatically in Fig. 3. By tapering the end of the diaphragm as shown it can be brought very near the specimen surface without interfering with the required reflected beams. The (331) reflection, conveniently given by CoK_a radiation was observed. The two photographs were compared side

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* This follows from the Schwarzschild law $S = F(it^p)$, where S is the blackening, i the intensity, and t the exposure time. p may be taken as unity for X-rays.

by side on a viewing lantern, and the mean value of two or three of the blackest spots in the first photograph was taken as the value of B.

TABLE I.

Specimen No.	Photo No.	Exposure, Minutes.	$p = \frac{t_2}{t_1}$.	Y.	Grain-Size Calculated, Mm. × 10^{-3}.	Grain-Size by Metallurgical Count, Mm. × 10^{-3}.
P. 445	174 171	1 2½	2½	15	3·3 mean 3·1	2·8
	174 172	1 5	5	33	3·08	
	174 173	1 20	20	72	2·9	
	171 173	2½ 20	8	47	2·96	
	172 173	5 20	4	24	3·24	
P. 732	168 166	2½ 10	4	31	2·98 mean 2·95	3·35
	168 167	2½ 20	8	50	2·92	
	169 167	5 20	4	32	2·95	
P. 431	162 163	1 10	10	20	4·08 mean 4·1	4·2
	162 164	1 30	30	30	4·07	
P. 439	156 161	1 12	12	9	5·48 mean 5·2	6·35
	260 261	1 20	20	15	5·00	
	260 262	1 40	40	20	4·8	
P. 427	216 218	10 2½	4	50	2·54 mean 2·45	2·35
	215 216	45 10	4·5	60	2·46	
	215 217	45 5	9	102	2·34	
P. 554	221 223	10 2½	4	77	2·2 mean 2·15	2·15
	220 221	40 10	4	86	2·12	
	220 222	40 5	8	130	2·12	

In the larger grain-sized samples in particular the α_1 and α_2 reflections cannot be differentiated, so that the total number was counted and halved to get the correct value for Y. Details of the results are given in Table I.

Possible Modifications of Method for Large Grain-Sizes or Highly Absorbing Substances.

Owing to the soft radiations used, *viz.* CuK_a or CoK_a, which are highly absorbed in metals, it was thought at first that the analysis could be treated as if only grains in the surface gave spots which could be counted.

Consider the expression which was obtained in section (1) for G the grain-size

$$G = 3\sqrt{\frac{\pi a^2 \,.\, dja \cos\theta}{8DY}}.$$

If d is smaller than G, one would be justified in treating the whole calculation as if only the grains in the surface give countable reflection spots, and then we should have, simply,

$$G = 2\sqrt{\frac{\pi a^3 \,.\, j \cos\theta}{8DY}}.$$

now

$$d = \sqrt{\frac{\log_e r}{\mu\,(1 - \sec 2\theta)}}$$

in which r is the relative intensity of the weakest and strongest observable spots. Judging from experimental results, r is of the order of 1 to 50, and is bound normally to exceed the ratio of 1 to 10.

Using these values of r, the values of d corresponding to the K_a radiations of Cu and Co for specimens of aluminium, copper, and iron have been calculated. These are given in Table II.

TABLE II.

Specimen.	$d \times 10^{-3}$ cm.	r.
	Radiation CuK_a.	
Al	14·7	1–50
	8·6	1–10
Cu	3·97	1–50
	2·3	1–10
Fe	0·74	1–50
	0·4	1–10
	Radiation CoK_a.	
Al	8·4	1–50
	5·0	1–10
Cu	2·7	1–50
	1·6	1–10
Fe	4·5	1–50
	2·6	1–10

Copper radiation is never used for examination of iron owing to the enhanced incoherent scatter, but cobalt is specially convenient.

Both in the case of aluminium and iron, d for the usual 1–50 intensity ratio is of the order of 5×10^{-3} cm., which is very near the maximum grain-size which it is normally wished to count—it is clear, therefore, that in general for aluminium and iron, grains below the surface layer will give rise to countable spots, and therefore the volume formula must be applied.

Part II.

Determination of Grain-Size from an Empirical Chart.

It is necessary to take two photographs of the same region to determine the absolute value for the mean grain-size. The authors have endeavoured to find whether it was possible to develop a suitable method by which the grain-size can be determined from one picture alone; this would be a considerable advantage in practice. The total amount of X-radiation reflected by small grains is proportional to the volume of the grain. The length of a spot has been shown to be proportional to the grain-size, and the width of a reflected spot is a linear function of the grain-size and the divergency of the beam; it can be seen, therefore, that the intensity of a spot or the blackening of a spot varies approximately with the grain-size. The authors have tried using this as a method of grain-size determination, but there are many difficulties in the practical estimation of the intensities of the spots.

It is fairly easy, however, to derive an empirical relationship between the numbers of spots on photographs taken under standard conditions and the grain-sizes for a given series of specimens. By expressing this relationship in the form of a graph, the grain-size of an unknown specimen can then be read off, after observing the number of spots on a photograph taken under these standard conditions. For constant experimental conditions it is sufficient to realise that Y is some function of G the grain-size.

The graphs relating the total number of observable spots to the grain-size for the same series of aluminium specimens as used before is given in Fig. 4. The (331) reflection given by CoK_a radiation was observed. The source of X-rays was a "Metalix" apparatus for crystal analysis which gives a fairly constant output with a constant size of focal spot.

Curve (1) shows the number of spots plotted against the grain-size determined with the microscope, while in curve (2) they are plotted against the grain-size determined by X-rays. For grain-sizes larger than 5×10^{-3} cm. the method is not very sensitive, but in the useful region down to 10^{-3} cm. results to within 10 per cent. can be obtained.

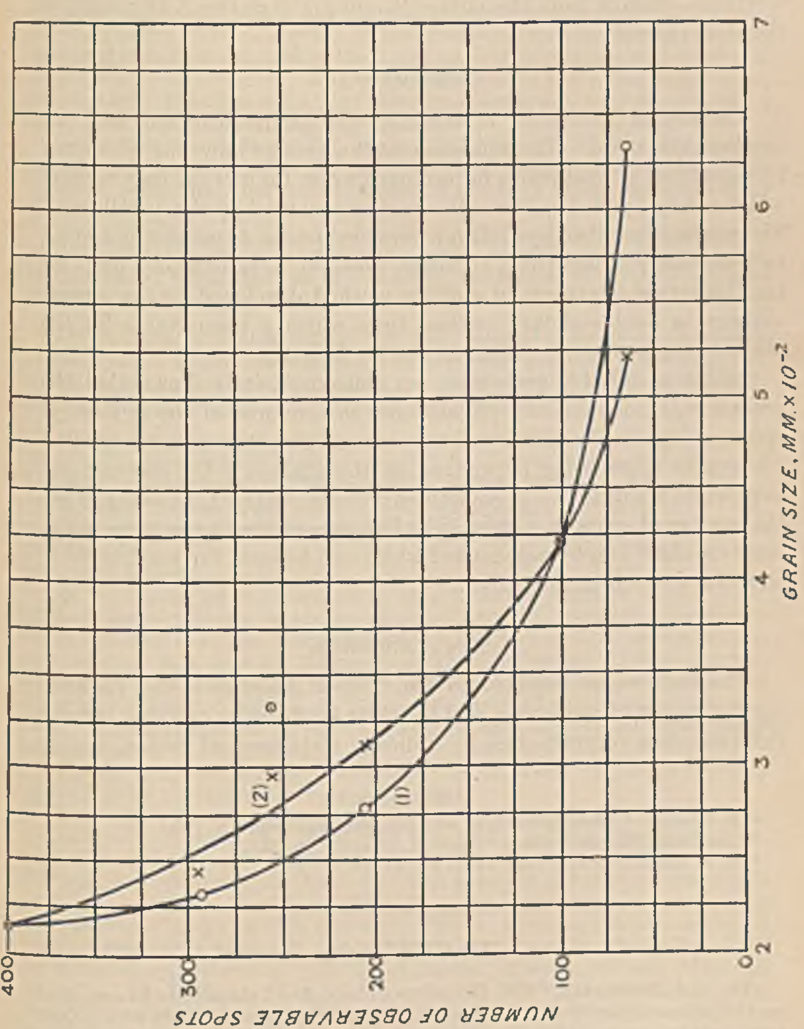
400
300
200
100
0
NUMBER OF OBSERVABLE SPOTS
2
3
4
5
6
7
GRAIN SIZE, MM. × 10⁻²
(1)
(2)

Fig. 4.

With regard to specimen P. 445, there appears to be some discrepancy between the results for grain-size determined by the two methods—judging from the curves it appears that the X-ray result is the more correct.

SUMMARY.

The use of X-rays for determining the grain-size above 10^{-3} cm. has been discussed. The reflection method is the only one which can be considered as practicable for ordinary work, for it is the only method which can be applied on the ordinary specimen used by the metallurgist. The method described by Shdanow for thin specimens cannot be applied to reflection photographs. It forms, however, a satisfactory basis for the theoretical treatment of another method developed by the present authors—a double-picture method from which a mean value for the absolute grain-sizes of specimens can be derived.

So far as relative grain-sizes are concerned, it is shown that the grain-size is not inversely proportional to the cube of the number of spots owing to the relative intensities of the strongest to weakest observable spots being dependent on the grain-size for constant experimental conditions. A smooth curve was obtained, however, when the number of spots on a given (*hkl*) line were plotted against the grain-size. A chart can be constructed which can be used for routine grain-size examination in this region.

ACKNOWLEDGMENT.

The authors are indebted to The British Aluminium Co., Limited, for the supply of specimens, and for their kindness in carrying out the determination of grain-sizes by ordinary metallurgical means.

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[2] Clark and Zimmer, "Clark 'Applied X-rays,'" p. 348.
[3] H. S. Shdanow, *Z. Krist.*, 1935, 90, 82–91.

DISCUSSION.

Dr. C. J. Smithells,* M.C. (Member of Council) : I should like to comment on the extraordinarily small range of grain-sizes which are dealt with; they vary only by a ratio of 3 to 1. This work has been carried out on aluminium. I do not know whether that covers the range required by the makers of aluminium, but in metals in which I am interested I have a range of grain-size of 50 to 1, and sometimes 100 to 1, and, if this method is confined to a range of grain-size of 3 to 1, it is too small for many purposes.

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Another point is that if that range is enough to be of interest, presumably the method must be accurate in that range. If one is really bothered by a variation in grain-size from 2½ to 3 or 4, the measurements must be accurate. From the figures in Table I, one can take the grain-size as determined metallurgically as 3·67 ± 40 per cent. If the grain-size by metallurgical count is compared with that obtained by the X-ray method, in one case a divergence of 30 per cent. will be found; this is almost equal to the actual range being investigated. It seems to me that the agreement is not good enough, and I should like more information on this point.

Again, only the surface grains are examined and the depth of penetration is apparently something like 10^{-3} cm. In a great many specimens the surface structure is definitely not representative of the body of the material. That seems to me to be a possible drawback.

This method might have very useful applications in routine testing of certain types of material, but unless it can be extended to cover wider ranges of grain-size, I think that the application is too limited to be very generally valuable.

Dr. E. VOCE [*] (Member): Does the X-ray method count twins as separate grains or not? I think that this is a very important question. The American standard method of grain counting,[†] a metallographic method, definitely specifies that twins should not be counted as separate grains.

Mr. STEPHEN (*in reply*): In answer to Dr. Smithells' first question, the range with which we have dealt was from 10^{-3} to the maximum grain which we had for these specimens, which was about $6·35 \times 10^{-3}$ cm. I think that it can be taken that the X-ray method covers a range from 10^{-2} down to 10^{-3} cm., which is satisfactory for most deep-drawing problems. The comparison of one divergence of 30 per cent. with the extent of the range 300 per cent. is somewhat intrepid.

Dr. Smithells' second question seems not only a criticism of the X-ray method, but a criticism of the metallurgical method, which is even more a surface method than the X-ray method. A surface has to be studied in any case, whether it is done by X-rays or metallurgical means. The X-ray does at least get a little below the skin; its big advantage is that there is no need for a highly polished surface; a rough etch gives all that is necessary, and other valuable information is obtained which cannot be given by metallurgical examination.

We are now studying the point raised by Dr. Voce. When twinning is present, twins are counted as separate grains.

The work was really an attempt to see whether we could get order from the many claims which had previously been made, and it seems, in our view, that this method can be applied usefully within the region of 10^{-2} down to 10^{-3} cm., but I do not think that a very high accuracy will ever be obtained in that region, either by metallurgical means or by X-ray; nor does there seem any point in aiming at a high accuracy. The big advantage of this method is that a variation in grain-size can be seen easily, since the blackening of the spots varies approximately with the grain-size. If spots are seen which are larger and much blacker than others, some idea is obtained of the variation from their relative number. It should be possible to find out what is really meant by an average grain-size, which, we would imagine can only be truly expressed in the form of a distribution curve, about some mean value. I have found it very difficult to get order from the statements previously made for average grain-size determinations, and it seems to be a very difficult subject indeed.

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[†] *Amer. Soc. Test. Mat. Standards*, **1936**, (I), 765.

CORRESPONDENCE.

Dr. W. Betteridge,* B.Sc.: While the authors' X-ray method agrees excellently with metallographic methods for the specimens examined, it should be pointed out that its accuracy depends to a great extent on the freedom from distortion of the grains. Two types of distortion of the crystal lattice can affect the accuracy of the measurements: (1) bending of the lattice, which causes a reflection from any given plane to occur over a range of positions of the lattice relative to the incident X-rays, although the reflection angle θ remains constant; and (2) variation in the spacing of the reflecting planes, which causes reflections to occur for a range of values of θ.

Bending of the lattice, in effect, makes the normal to the reflecting plane become a cone of small angle instead of a line (AN in Fig. 1 of the paper), and a reflection will then occur if any part of that cone intersects the belt of area $2\pi Da \cdot \cos\theta$ on the sphere. If ϕ be the angle of the cone the effective area of the belt becomes $2\pi D(a + \phi D) \cdot \cos\theta$ and the probability of a reflection occurring is increased to $\frac{(a + \phi D) \cdot \cos\theta}{2D}$. If this distortion of the lattice is at all large it immediately becomes apparent since the reflected spots will be elongated in a circumferential direction and also it is possible for $K\alpha_1$ and $K\alpha_2$ reflections to be obtained from a single grain. Fig. A (Plate XLIV) which shows the reflection of the $K\alpha$ radiation of iron by the (400) plane of the lattice of a sample of fully heat-treated R.R. 59 alloy, is an extreme example of such distortion. For high order reflections the minimum angle between planes reflecting α_1 and α_2 rays becomes relatively large, and in the example quoted by the authors (a reflection of cobalt radiation by the (330) plane of aluminium) it is 27′; grains with less spread of the reflecting planes than this cannot give a double reflection plainly to reveal their distortion and yet the probability of reflection can be increased by as much as 1·71 times. The elongation of the spots would be in a similar ratio, which would probably escape detection, and if all the grains had the same degree of distortion the grain-size measurement would be too low, in the ratio of $1 : \sqrt[3]{1\cdot71}$ or $0\cdot83 : 1$.

The second type of lattice distortion giving reflections over a range of values of θ also increases the probability of reflection, for if a variation of $d\theta$ from the mean value can occur, the normal to the plane may move within a range of $2d\theta$ while still reflecting; the probability in this case is increased to $\frac{(a + 2d\theta \cdot D) \cdot \cos\theta}{2D}$. Distortion of this type causes the spots to be extended radially, and frequently makes the α_1 and α_2 reflections irresolvable. If, in the same example, the doublet is just irresolvable the probability of reflection is again increased 1·71 times. It is also incorrect with such irresolvable reflections to halve the total number of spots, for any one may represent both α_1 and α_2 reflections.

Care must therefore be taken in applying this method of grain-size measurement, and if the reflected spots show any signs of spreading, discretion must be exercised in considering the values obtained.

Messrs. H. W. L. Phillips,† B.A. (Member) and **P. C. Varley,**‡ M.A. (Member): For some years we have been interested in the possibilities of applying X-ray methods to the determination of grain-size, particularly in

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PLATE XLIV.

FIG. A.

[*To face p.* 298.

view of the well-known limitations of the metallurgical methods. We were very pleased, therefore, to lend the authors some specimens when they informed us that they were undertaking these experiments. We were disappointed, however, to see from this paper that they have by no means overcome all the difficulties involved in such methods.

In the first place in calculating the mean grain diameter from the X-ray and metallurgical counts, the authors have assumed that the crystals are cubic, whereas in fact they are irregular polyhedra, and with the finer-grained samples probably approximate more closely to spheres.

We have recalculated the figures in Table I of the paper, on the basis of spheres, and we find that not only are the absolute values for the grain-size altered, but also their relative magnitudes. In order to calculate the mean grain diameter from the metallurgical count we have assumed that the individual crystals are spherical in shape, but that they may show considerable variation in size, the spacial arrangement being random so that the spaces between the large spheres are filled up with smaller ones. The metallurgical counts were done by the well-known intercept method, and it can readily be shown that if a sphere of radius r is cut at random by a line the expected length of the intercept will be $4r/3$. Hence, if D is the mean grain diameter the intercept count n will be equal to $3/2D$. The figures given by the authors in the last column of Table I are equal to $1/n$ so that on this basis they are two-thirds of the mean grain diameter. For comparison purposes, the X-ray count must also be recalculated on the same basis; this is readily done by multiplying the figures given in the paper by $3\sqrt{\frac{6}{\pi}}$.

Taking specimen No. P. 445 as an example, we find that the mean grain diameter from the metallurgical count is $4{\cdot}22 \times 10^{-2}$ mm. and from the X-ray count $3{\cdot}84 \times 10^{-2}$ mm., giving a ratio of metallurgical to X-ray count of 1·10 instead of 0·90. Similarly, different values were found for the other specimens, and the mean ratio worked out at 1·26 as against 1·04 from the figures given in the paper, so that on this basis there appears to be a discrepancy of 25 per cent. between the two methods. Further, we are not satisfied that, even assuming the grains to be cubes, the figures given in the last column of Table I really represent the mean grain edge as calculated from the metallurgical counts. The figures supplied by us were expressed in grains/mm.^{2} in the conventional manner, and the authors have used the reciprocals of the square roots of these figures as equivalent to the mean grain edge as calculated from the X-ray data. This, in effect, assumes that the cube-shaped crystals are all nicely arranged with one face of each cube in the plane of polishing, which is certainly not the case.

There is one other point which should be mentioned here. In making their calculations, the authors have neglected the effect of the oblique rays passing through the pinhole, on the grounds that the area irradiated by such rays under the conditions of their experiment was small. Actual calculation shows that the area of the specimen irradiated by such rays is about 8 per cent. of the total, and even allowing for the diminution of intensity with increasing obliquity will introduce an error of about 4 per cent. in the number of spots observed.

We have attempted to carry out grain counts by the methods described in the paper, but we have met several difficulties which are not mentioned by the authors. The difficulty of determining the number of spots on a given ring is increased by two factors. In the first place not all crystals show both the α_1 and α_2 reflections. There is a region round the periphery of the irradiated area where only one of these reflections is possible and a correction should be made for this. Secondly, the normal X-ray film used for such work is double coated, and owing to the thickness of the base and the obliquity of the reflected rays each spot appears double, one image being on each side of the film.

This difficulty can, of course, be readily overcome, but may be a trap to the unwary.

In considering the relative merits of the metallurgical and X-ray methods of determining grain-size, attention should be paid to the cost of obtaining a given accuracy by the two methods. So far as we can discover, the time taken in exposing the two X-ray films is approximately the same as that required to prepare and polish a specimen for a metallurgical count and the time of counting cannot be very different. We normally carry out ten counts on each specimen and under these conditions the standard error of the figure in the last column of Table I works out at ±0·10, whereas the standard error of a single X-ray determination, calculated from the figures given by the authors, works out at ±0·16. In order to obtain the same accuracy as is normally obtained by the metallurgical method, three X-ray determinations would have to be made. The empirical method described later in the paper has an even lower accuracy, the authors only claiming 10 per cent. which is about one-third that of the metallurgical method, and nine determinations would be necessary to obtain a similar degree of precision.

Thus while the methods described in the paper are of great interest and may be of value in providing a useful check, they cannot claim any advantages over the normal metallurgical methods.

The AUTHORS (*in reply*): We greatly appreciate Dr. Betteridge's remarks—the validity of the X-ray method is indeed affected by the distortion or "coring" of the type illustrated in the picture. It is clear, however, that estimations of the number of spots from such pictures can hardly be attempted. In any case, the appearance of the spot enables one immediately to identify either peripheral or radial elongation which factor is of value for instance in evaluating the amount of elongation in a slightly worked sample. It is highly questionable, too, whether a definite grain-size should be indicated for such pictures, as the X-ray results show the presence of large numbers of "crystallites."

With regard to the contribution of Messrs. Phillips and Varley, the X-ray method gives us the number of grains per unit volume irrespective of shape and is therefore independent of any assumption as to the variation in grain-size.

The difficulty occurs in the basis of comparison of the metallurgical with the X-ray results, since the former are based purely on surface observations. To compare the results accurately both the shape and distribution of sizes must be known. The grain-sizes examined are in our opinion far too large to allow of an assumption of spheres, especially as there is no evidence from X-ray pictures that there exist small grains filling up the interstices between larger grains. Because of this and other considerations, we chose the simplest case, assuming that the grains were cubic. Without a knowledge of the shape and distribution, it was thought worthless to attempt any ultra accurate comparison basis. It should be emphasized that the X-ray pictures make it possible to see at a glance whether there is any great variation in grain-size and, in the examples examined, this was not the case.

The X-ray method places the grain-sizes in their right order, purely on the number of grains per unit volume, taken as a physical observation, devoid of any assumption. The metallurgical observations on the surface interceptions reverse the order of P445 and P732, which results cannot be correct.

Spots occurring on α_1 and α_2 rings, only occur in pairs even if the divergency is great enough to permit this, so that there should be no difficulty in deciding whether a grain gives two spots or one. Incidentally, observations of these doublets provides evidence of great value regarding perfection of grains or lattice distortion—information inaccessible to the microscope.

In making our calculation, we decided to neglect the effect of the oblique rays; the error involved depends on the product of the area neglected, and the average probability of reflection for the area. This explains an error of about 4 per cent. in the number of spots or the number of grains per unit volume, which leads to an error of 1·3 per cent. in the mean grain diameter.

We do not wish to claim any great advantage over the normal metallurgical method. The X-ray method is rather an auxiliary method, as it provides a check and gives a qualitative idea of the variation in sizes. The fact that it can be used non-destructively, too, is of importance, *e.g.* when investigating the grain-size of the base or coating in coated sheets.

We are certainly of the opinion that attempts at too high accuracy by either method without further information are in general worthless.

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THE CONTROL OF COMPOSITION IN THE APPLICATION OF THE DEBYE–SCHERRER METHOD OF X-RAY CRYSTAL ANALYSIS TO THE STUDY OF ALLOYS.*

By WILLIAM HUME-ROTHERY,† M.A., D.Sc., MEMBER, and PETER WILLIAM REYNOLDS, B.A., B.Sc.‡

SYNOPSIS.

The application of the Debye–Scherrer method to the study of alloys is discussed critically with special reference to errors due to uncertainty of the exact composition of the filings comprising the specimen. It is concluded that where practicable it is desirable to analyze the actual filings from which the representative small sample used in the preparation of the specimen has been sieved. Methods are described for the preparation of perfectly clean filings suitable for accurate chemical analysis. It is shown that, in the determination of phase boundaries from lattice spacing measurements of two-phase alloys, misleading results may be obtained if the temperature of the preliminary anneal of the material in lump form is not suitably related to that of the final annealing of the filings.

(1) INTRODUCTORY.

THE Debye–Scherrer or powder method of X-ray crystal analysis is now used extensively in metallurgy, both for the investigation of crystal structures and the determination of solid solubility curves. On the side of X-ray technique a satisfactory standard of accuracy has been attained provided that certain essential precautions are taken. Of these the most important are: (*a*) the use of suitable radiation to obtain "high angle lines," (*b*) allowance for film shrinkage, and (*c*) the use of some extrapolation method such as that of Bradley and Jay [1] in order to allow for errors introduced by absorption, eccentricity of the specimen, &c. If these precautions are taken the lattice constants of alloys can be measured to an accuracy of the order 1 part in 10,000 to 1 part in 50,000, or even to 1 part in 100,000 in specially favourable cases. The defect of the method lies in the uncertainty of the exact composition of the filings comprising the specimen. This point has received comparatively little attention from investigators, with the result that in

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* Manuscript received May 21, 1936. Presented at the Annual General Meeting, London, March 11, 1937.

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‡ Jesus College, Oxford.

many papers where lattice constants are claimed to be measured to an accuracy varying from 1 part in 5000 to 1 part in 50,000, the results are represented by smooth curves from which individual points may differ by 1 part in 5000 or even 1 part in 500. The present paper discusses methods by which these discrepancies may be reduced, since it is clearly unsatisfactory for the accuracy on the one axis of co-ordinates to be out of all proportion to that on the other. The matter is of great importance in determinations of solid solubility limits in view of the increasing tendency to determine these from lattice spacing-composition curves with very few points in the critical region of the homogeneous solid solution; in such cases unless the few points in the homogeneous area are entirely reliable, the whole series of solid solubility limits may be deduced wrongly. Further, as shown later, if the annealing treatment is not suitably chosen, quite incorrect values for the solubility curves may be deduced from measurements of the lattice constants of filings quenched from a temperature in the two-phase region.

(2) THE CHOICE OF ANNEALING TEMPERATURES.

In all but a minority of cases the preliminary treatment of an alloy should consist of an anneal in lump form, because the cored structure of a cast alloy is usually coarser than the fine filings used for the X-ray specimen. Consequently, unless one metal in a binary alloy is volatile, annealing of filings from the casting will not produce true equilibrium unless sintering and coalescence occur. Where the cast alloy is two-phase this difficulty is accentuated, since the two phases may have to react to produce equilibrium, whilst individual particles of the filings will often consist of one phase only.

After the preliminary anneal of the material in lump form, the filings are prepared, and have then to be annealed in order to relieve mechanical strain, and may be slowly cooled, or quenched from a particular temperature according to the requirements of the experiment. If the alloy contains no volatile metals, and is homogeneous at both high and low temperatures, the preliminary anneal can be carried out most quickly at a temperature as near to the melting point as possible. If the cast alloy contains constituents of low melting point which are absorbed in the annealing process, it is advisable to heat the alloy slowly to the final high temperature in order to avoid temporary fusion of the low-melting constituent with the production of a very coarse structure from which true equilibrium is only obtained after prolonged annealing. If, however, the alloy contains a volatile constituent, it is frequently advisable to anneal the lump of alloy for a comparatively long time at a moderately high temperature, rather than for a short time at a higher temperature.

This is because a short anneal at a very high temperature results in the loss of the volatile constituent from the surface, and although in some alloys, as shown by Owen and Pickup,[2] this difficulty can be overcome by removing a comparatively thin surface layer, there are other cases in which a longer annealing at a lower temperature is more satisfactory.

Where two-phase alloys are concerned, as in the determination of solid solubility limits, the position is much more difficult. We may consider an equilibrium diagram of two metals *A* and *B* where a primary solid solution α exists in equilibrium at different temperatures with two phases β and β′, the form of the solubility curves being as shown in Fig. 1. We may suppose that it is desired to determine the solubility limits of the α and β or β′ phases at the temperatures t_1, t_2, t_3, and t_4 from lattice constant measurements of filings of a two-phase alloy of composition x. We may suppose first that the preliminary lump anneal is at t_1, resulting in the production of α-phase of composition a_1, and β-phase of composition b_1, the structure being coarser the higher the annealing temperature. Filing of this alloy will produce fine particles most of which will consist entirely of one phase. When re-annealed at t_2, the particles of the β-phase have merely to precipitate some of the α-phase so that their composition changes from b_1 to b_2, with the production of α-phase particles of composition a_2. The particles of α-phase of composition a_1 have, however, to take up more of the solute element *B* in order to reach the equilibrium composition a_2, and this they are normally unable to do, although if the element *B* is volatile true equilibrium may be obtained.* This combination of heat-treatments may, therefore, result in the production of α-phase particles of composition a_1 and a_2. If the relative amounts of these two kinds of

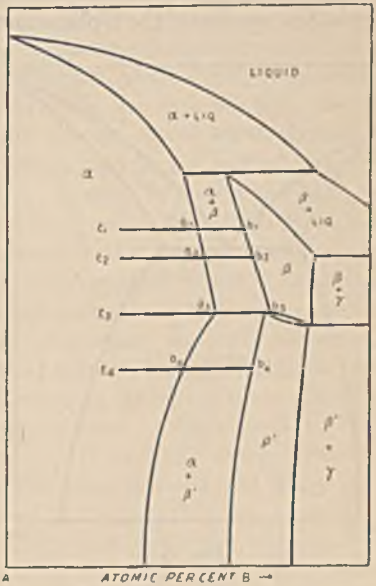

FIG. 1.

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* With non-volatile metals equilibrium may be reached if sintering or coalescence of the filings occurs, but the resulting mass is, of course, generally useless.

α-phase particles are comparable, and their lattice spacings are sufficiently different, definitely fuzzy or double lines will be produced in the X-ray diffraction photograph. If, however, the compositions a_1 and a_2 do not differ widely, slightly broader lines will result, the centres of darkening of which will correspond with some point between a_1 and a_2, whilst completely misleading results may be obtained if the relative amount of a_2 is so small compared with that of a_1 that the particles of a_2 are too few to produce a line of appreciable intensity; unless care is taken this may easily be the case.

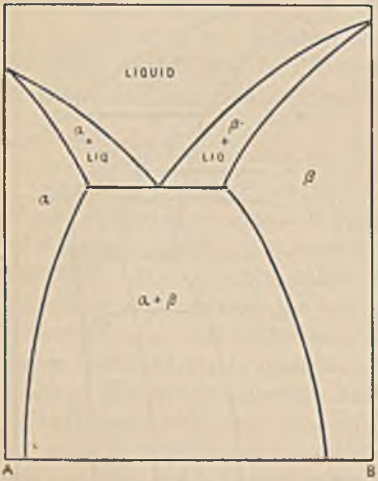

Fig. 2.

The above heat-treatment, therefore, makes it possible to determine the lattice spacing of the β-phase on the solubility curve at t_2, but leads to difficulties with the α-phase. Similar reasoning shows clearly that if the preliminary lump anneal is at t_3, the position is reversed. In this case if the filings are subsequently annealed at t_1, t_2, or t_4 the α-phase particles of composition a_3 have merely to precipitate the β-phase in order to reach the equilibrium compositions a_1, a_2, or a_4, whilst the β-phase particles of composition b_3 have to take up into solution some of the element A, and this may be impossible unless this element is volatile. This reasoning is quite general, and the conclusion may be summarized by saying that if the preliminary lump anneal is not at the same temperature as that of the filings, the two must be adjusted so that, in the final anneal, the particles of the phase under investigation precipitate a second constituent, and do not take one up into solid solution. This implies that in an equilibrium diagram of the type of Fig. 2, a single intermediate two-phase alloy annealed at a high temperature will serve for the determination of both solubility curves at lower temperatures, whereas in the diagram of Fig. 1 considerable care is necessary if misleading results are to be avoided. A critical examination has shown that in several recent papers where solid solubility curves of the type represented in Fig. 1 have been determined by X-ray methods, parts of the curves may be affected by errors of the kind referred to above. These difficulties may be more pronounced in alloys where the filing process produces a surface film of oxide which may completely prevent interaction between different particles on annealing.

(3) The Determination of the Composition of the Specimen.

There has been a general tendency to assume that the composition of the filings in the specimen may be determined by lump analysis of the original alloy, although in cases where a volatile constituent is present the necessity for analysis of filings receiving the same heat-treatment as those of the specimen has been recognized. Even with non-volatile metals, however, the former method frequently leads to misleading results, and the authors, therefore, recommend that, where practicable, analysis should be made of the actual filings from which the representative small portion used in the preparation of the specimen has been sieved.*

In the first place, if segregation is present, errors due to differences between the compositions of the portions used for the specimen and the analysis are avoided by this method. It must be emphasized that the mere fact that sharp diffraction lines are given by a specimen made from a small quantity of filings is no indication that segregation effects are absent. It is commonly but erroneously supposed that if sharp diffraction lines are given by filings prepared from a complete cross-section of a cylindrical rod, the material is satisfactory, but this assumption ignores the possibility of longitudinal segregation. The authors have encountered this phenomenon particularly in the case of silver–tin alloys in the form of $\frac{5}{16}$-in. diameter drawn rods. Filings prepared from complete cross-sections of these rods gave perfectly sharp diffraction lines, and it was only by repeating the measurements with filings from different sections along the rod that the segregation was discovered. The rods were prepared for the authors with great care, the cast bars being subjected to a prolonged annealing treatment before being drawn down into rods. All this batch of silver–tin alloys showed this type of segregation, but there seemed to be no obvious fault in preparation, since other rods of silver alloys prepared by the same firm under supposedly identical conditions were quite free from this defect. The extent of the longitudinal segregation in the silver–tin alloys was such that if filings were prepared from a complete cross-section, and the composition determined from 1 grm. of the adjacent material, the error involved was of the order ± 0·1 per cent. by weight, whereas completely misleading

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* It is important that filings used for the specimen shall be representative of the whole sample used for analysis. In practice the specimen is usually made from very fine particles sieved out from the main bulk, whilst the analysis is carried out on a mixture of those which pass through the sieve and those retained. It is important, therefore, that the whole mass used for analysis shall have been shaken on the sieve so that the fine particles are thoroughly representative.

results could be obtained if the analysis were carried out on material from another part of the rod. In other silver alloys, and also in certain copper alloys, the segregation is usually of the transverse type, and here the best results are obtained by preparing filings from a zone of material equidistant from the centre of the rod.

An indication of uniformity in the composition of the specimen is given by the resolution of the K_a doublets in *low angle* diffraction lines, provided that the specimens are of the correct thickness, and that the camera and specimen are accurately adjusted. These conditions are essential, since variations in the X-ray slit system, or faulty centering of the specimen affect the resolution considerably. In the α-solid solutions in silver, the use of cobalt radiation gives 024 and 133 lines at approximately 78° and 72°, respectively, but it is difficult to estimate the extent of segregation from these high-angle lines since the doublets are resolved in all but extreme cases. With homogeneous specimens the 400 lines at approximately 60° are distinct and well resolved, whilst the 222 and 113 lines at 49° and 46° are also definitely resolved. Resolution of these last two lines in a sample prepared from 0·5 to 1·0 grm. of material is, however, exceptional for alloys, although a satisfactorily homogeneous sample will give well resolved 400 lines.

Since accurate chemical analysis requires from 0·5 to 1·0 grm. of material, any marked segregation will usually be revealed by a fuzziness of the diffraction lines if the X-ray specimen is made from filings representative of the whole quantity prepared. The sensitivity of this test naturally depends on the extent to which the lattice spacing varies with the composition, and it must be emphasized that visual observation will not reveal segregation if the limiting compositions correspond with a difference in lattice spacing of less than 0·0005 A. The existence and direction of segregation in an alloy may often be conveniently determined by preparing an X-ray specimen from a mixture of minute amounts of filings obtained from two positions in the original specimen, this method being particularly useful in the case of rare metallic alloys where economy of material is important. The direction of segregation being known, the procedure to obtain the most homogeneous sample possible is readily determined.

If a slight inhomogeneity of the specimen cannot be avoided, analysis of the actual filings gives the most accurate results obtainable, since both the chemical analysis and the X-ray measurement tend to give a mean value. This may not apply, however, if the segregation is of such a type that the rod consists mainly of one composition (x), with a thin layer of distinctly different composition (y). In this case if the diffraction line corresponding to (y) is faint, and sufficiently different from (x), the darkest parts of the lines may correspond with the composition (x), and not with the mean value given by chemical analysis. It is for this reason that the outermost surface layer of a lump should always be discarded.

Apart from the effects due to macroscopic segregation in an alloy, fuzziness of diffraction lines may also be due to insufficient annealing of the lump alloy. In this case fuzziness persists when the specimen is made from a minute amount of material, in contrast to fuzziness due to segregation, which can be reduced by preparing the specimen from a very small volume. In a one-phase alloy * slight fuzziness of line due to insufficient annealing is much less serious than fuzziness due to segregation. This may be illustrated by Table I which shows results obtained [4] with a second series of silver–tin alloys. In alloys 2*a*, 3*a*, and 4*a* the preliminary lump-annealing treatments were not quite sufficient to give well-resolved 400 lines, whilst in alloys 2*b*, 3*b*, and 4*b*, the resolution

TABLE I.—*Lattice Spacings of Silver–Tin Alloys* (α *Solid Solution in Silver*).

No. of Alloy.	Atomic Per Cent. Sn.	Lattice Spacing at 21° C.
2*a*	4·13	4·0945(9)
2*b*	4·13	4·0945(9)
3*a*	6·24	4·1032(5)
3*b*	6·26	4·1032(6)
4*a*	8·17	4·1122(3)
4*b*	8·20	4·1122(4)

Annealing Treatments.

Lump anneals. No. 2*a*. 20 hrs. at 650° C. + 40 hrs. at 780° C., + 11 hrs. at 860° C.
Nos. 3*a* and 4*a*. 20 hrs. at 650° C. + 4 hrs. at 780° C.
Nos. 2*b*, 3*b*, and 4*b*. 5 days at 725° C.

Filing anneals. 15 hrs. at 520° C. in all cases.

The camera was calibrated with quartz and copper radiation as described by Bradley and Jay,[3] and the alloy diffraction photographs taken with cobalt radiation. The constants involved are:

Calibration of camera.

Cu. $\lambda k\alpha_1 = 1537{\cdot}395$ X.U.
$\lambda K\alpha_2 = 1541{\cdot}232$ X.U.
Quartz at 27° $a = 4246{\cdot}53$ X.U.
$c/a = 1{\cdot}09996(5)$.

Lattice spacing measurements.

Co. $\lambda K\alpha_1 = 1785{\cdot}29$ X.U.
$\lambda K\alpha_2 = 1789{\cdot}19$ X.U.

As in the work of Bradley and Jay, the results from the α_1 and α_2 lines were averaged in the ratio $2\alpha_1 : 1\alpha_2$.

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* This does not necessarily apply to two-phase alloys where the two phases have to react in order to reach equilibrium.

was satisfactory. When allowance is made for the slight differences in composition of the filings from the two portions of alloys 3 and 4, the maximum discrepancy between the two series of results is equivalent to 0·0001(1) A., so that the error introduced is less than 1 part in 40,000. This indicates that any slight fuzziness of lines not detected visually will be without effect, but it must be emphasized that the use of films with slightly fuzzy lines is justifiable only when there is conclusive proof that the fuzziness is not due to macroscopic segregation effects.

(4) THE PREPARATION OF FILINGS.

The considerations mentioned above suggest that results based on the analysis of filings are to be preferred, and since this involves the preparation of from 0·5 to 1·0 grm. of filings from each specimen, an automatic filing machine has been devised in order to minimize the labour involved. This machine, made by Messrs. Alfred Herbert, Ltd., of Coventry, is a modification of a small hack-saw machine. The hack-saw blade is replaced by a suitable file holder, and the specimen held in a clamp is surrounded by a paper tray to collect the filings. A long lever supports a moveable weight, by means of which the load on the file can be adjusted to suit the particular alloy concerned. The machine has been very satisfactory, and has saved much time and labour, since the filing can be accomplished with little attention whilst other work is in progress. The authors must express their thanks to Professor F. Soddy, F.R.S., for his kind interest in developing this machine, and for placing it at their disposal.

The contamination of filings with foreign matter may give rise to difficulties in analysis. It is perhaps significant that no details of complete analyses of filings appear to have been published, many investigators relying on the determination of one constituent only, even though the second metal determined by difference is present in small amount. The authors have examined this point in detail, and find that errors of the order 0·1–0·2 per cent. may easily be introduced in this way.

In the early work on silver and copper alloys, filings were prepared by hand, and it was found that even with the most careful precautions to exclude dust and other foreign matter, the sums of the percentages of the metals as determined by analysis varied between 99·8 and 100·0, whilst another investigator obtained totals as low as 99·6. This source of error has been overcome by taking the utmost precaution in the preparation, and by cleansing the filings from foreign material which even then contaminates the product. To avoid metallic contamination it is practically essential to use a new file for each specimen. The files are washed in benzene to remove grease, and are carefully freed from foreign material by the use of a camel-hair brush; a cloth or rag must not be used for this purpose. The specimen, after removal of the surface layer, is clamped in the holder of the machine, or in a vice if hand-filing is used, and, if necessary, is cleaned with benzene. The filings are collected in a glazed-card tray, and are transferred to a stoppered weighing bottle where they are shaken up with benzene. Even after the most careful preparation, the amount of foreign material which is floated off in the benzene is often astonishing. The benzene is decanted together with suspended and dissolved impurities, and the process is repeated twice. In extreme cases carbon tetrachloride may be more suitable on account of its higher density (approximately 1·5), but, in general, benzene is more satisfactory. The filings are then washed with six successive portions of ether, and are dried in a vacuum or in a gentle current of warm air according to the nature of the product. Finally the filings are magnetted in order to remove iron particles which may have been introduced from the file, unless, of course, the filings are themselves magnetic.

By adopting these methods the authors have succeeded in preparing filings the total metallic content of which is not less than 99·90 per cent., the usual totals of the analytical percentages being about 99·98 per cent. Under these conditions a difference figure is accurate to within 0·1 per cent. if impurities are absent, but experience suggests that determination of both metals is always advisable since it gives warning of contamination, and many other possible sources of error. Filings of magnesium alloys, for example, when prepared in air may contain from 0·5 to 5·0 per cent. of oxygen and nitrogen. The filings may, however, still be used for analysis if both metals are determined, since the *ratios* of the metallic constituents will be the same as in the original lump. Experiment alone can determine whether such filings can justifiably be annealed and used for X-ray investigations, since the annealing process may produce concentration gradients in the particles, or may produce a complex alloy with the oxide or nitride, in which case the filings must be prepared out of contact with air. A further advantage of making a complete analysis of the filings is that where a particular metal is liable to contain small but variable amounts of a certain impurity, a complete analysis may enable the lattice constants of a binary alloy containing this impurity to be corrected so as to give the value for the pure alloy. Thus the effects of traces of copper on the lattice constants of solid solutions in silver can sometimes be allowed for, assuming an additive relation, from a knowledge of the effect of copper in the system copper–silver. Where a solvent metal cannot be obtained free from a particular impurity, this method may be very valuable.

CONCLUSION.

It is hoped that the methods outlined above may be of value in helping to improve the relative accuracy on the composition axis of lattice spacing–composition curves, and thus enable full advantage to be taken of the high accuracy which the X-ray methods afford in the determination of equilibrium diagrams. The authors do not mean, of course, to suggest that it is always advisable to base results on the analysis of from 0·5–1·0 grm. of filings. Exceptions are clearly presented by very hard alloys which cannot readily be filed, and by some ferromagnetic alloys where particles of iron from a file cannot be removed by a magnet, and may interfere with the analysis. In some cases the precautions that have been described are undoubtedly unnecessary, but, in general, this can only be proved by such extensive duplication of lattice spacing measurements or chemical analyses that the complete analysis of the actual filings is eventually the shortest method, quite apart from the numerous safeguards which it supplies. The authors' experience has shown that with copper and silver alloys, difficulties of the kind referred to above are so often encountered, that the rather common tendency to consider X-ray measurements of phase-boundaries as replacing older determinations may be criticized. The X-ray method has great potentialities, but the older microscopic and conductivity methods use larger quantities of material, and thus avoid errors which may vitiate the X-ray results unless precautions are taken which appear to be neglected in many published investigations.

ACKNOWLEDGMENTS.

The authors desire to express their gratitude to Professor F. Soddy, F.R.S., for his kindness in providing laboratory accommodation and many other facilities which have encouraged them in this work. One of the authors (W. H.-R.) must thank the Council of the Royal Society for election to a Research Fellowship, and for generous grants towards the cost of X-ray apparatus, materials, and fees for chemical analyses. Grateful acknowledgment is also made to the Department of Scientific and Industrial Research and to the Aeronautical Research Committee for financial assistance in connection with the general research work of which this forms a part.

THE OLD CHEMISTRY DEPARTMENT,
THE UNIVERSITY MUSEUM,
OXFORD.

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DISCUSSION.

Dr. C. H. Desch,* F.R.S. (Vice-President): The authors have rendered a great service by directing attention to these difficulties in the application of the powder method of X-ray investigation. There is a difficulty, of course, in any method which involves the use of filings; in the process of annealing and quenching it is almost impossible to avoid changes, and the ideal method is one which does not involve the preparation of filings at all. Where an alloy can be drawn into a wire, the X-ray work can, of course, usually be carried out without filing, but with non-ductile alloys that is much more difficult. It would seem, however, that the main aim should be to develop a technique which would not involve the annealing and particularly the quenching of filings.

The authors have shown how, by taking very great precautions, most of these objections can be overcome, but everyone is aware that, even when working with inert gases or with a good vacuum, surface changes take place, and as the surface of filings is so very large compared with the surface of a mass of metal those changes may become appreciable.

The authors have also referred to segregation in alloys; that is often very much more than is supposed, and it is surprising, when very careful analyses are made of different portions of small ingots—we have noticed it particularly in the light alloys—how great are the differences which may be found in what appears to be a quite homogeneous alloy. Those differences will make a very appreciable error in the determination of lattice parameters.

I said that in the process of quenching of filings there were certain difficulties, and that is why it seems undesirable to base equilibrium diagrams on the X-ray examination of quenched alloys only. In the authors' case they avoid that very thoroughly by carrying out a thermal investigation of each system alongside the X-ray investigation. Dr. Hume-Rothery's own work and that of his colleagues is beyond reproach in that respect, but wherever quenching processes are involved errors are introduced which it seems to me are really unavoidable, and even with the precautions described in the paper there may be some doubt in the interpretation unless checked by the thermal method.

The paper should be very carefully studied by all who have to determine a new equilibrium diagram.

Dr. D. Stockdale † (Member of Council): I think that metallurgists are well aware of the difficulties to be overcome in preparing a pure, uniform alloy and in keeping it pure and uniform, but chemists and physicists sometimes think that all that is necessary when making an alloy is to melt some metal, put in a little of another metal, give it a stir and pour it into something. Segregation and the unwitting introduction of impurities are traps which are continually lying in wait for the unwary.

I am in complete agreement with almost everything that the authors have said, except that I do not think that they stress sufficiently the importance of correct sampling. The risk of getting separation when working with fine filings and rather coarser filings is very great. The method of filing suggested by the authors seems satisfactory, but it might be slightly improved if the filing were carried out under benzene. Filing under benzene would tend to keep the alloy cleaner and it would also eliminate the slight risk of getting oxygen into the alloys.

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Dr. Hume-Rothery, when introducing this paper, mentioned the importance of an exact determination of the lattice parameter–composition curve. Hume-Rothery, Lewin, and Reynolds * have shown that this curve is not always a straight line. It follows that, in very accurate work, any considerable extrapolation is unjustified. The experimental determination must be carried right up to the limits of the solid solution. If the formation of a solid solution produces an expansion of the lattice which at high concentrations is progressively greater than that required by a linear relationship, the extrapolation of the earlier portion of the curve as a straight line will give solubilities greater than the true values. It is noteworthy that more often than not these curves are shown as straight lines and that solubilities as measured by X-rays are nearly always slightly larger than those as measured by the older methods.

For a long time I have been suspicious about the efficiency of the X-ray method and I am still not convinced of its accuracy. Discrepancies are always cropping up in the literature. I will give one example. Owen and Yates found that the parameter of copper is 3·6077 A. If the density of copper is worked out from those figures, it will be found to come out at 8·9291 at 20° C. Now, Maier † has shown by direct determination that the density of a single crystal of copper is 8·9528. There is a discrepancy of 2·7 parts per 1000. The uncertainty in the mass of the hydrogen atom will account for 1 part per 1000, but a substantial difference still remains. The parameter of 3·6077 A. is too large. It would be expected, of course, that X-ray measurements would eliminate all the grosser imperfections in the metal, and that the density calculated from X-ray measurements would be higher than the density determined experimentally. Maier himself suggests that such discrepancies are due to insufficient annealing, and believes that temperatures considerably in excess of 600° C. are required for the complete recrystallization of copper. If this is so, I think that it follows that when the filings are annealed, in many cases they are annealed at a temperature too low to get rid of all the strains.

Dr. C. Sykes ‡ (Member): The X-ray diffraction photograph is probably a much more sensitive method for detecting certain forms of inhomogeneity, such as coring, than any other at present available, and its application often reveals that annealing treatments normally considered to be satisfactory are quite inadequate. This point is well illustrated by experience with the alloy Cu_3Au: diffusion can be detected in this material at temperatures as low as 60° C., yet to produce a structure free from coring it is necessary to anneal hard drawn 1 mm. wire for 6 hrs. at 10° C. below the solidus.

I have two suggestions to make in connection with this paper, with regard to the production of suitable samples of volatile metals. Dr. Desch has already made one of them by suggesting that in certain circumstances it may be worth while to try to produce the material in the form of wire. My other suggestion concerns the production of filings of volatile alloys. What is the objection to annealing the filings in a large lump of the same material which is closed by another piece? I should imagine that any change in composition due to volatilization in those circumstances ought to be very small.

I have one minor criticism to make of the paper which may be considered to be merely a bandying of words. On p. 304, the authors state "it is clearly unsatisfactory for the accuracy on the one axis of co-ordinates to be out of all proportion to that on the other." I know what the authors mean, and most

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* *Proc. Roy. Soc.*, 1936, [A], 157, 167.

† C. G. Maier, *Trans. Amer. Inst. Min. Met. Eng.*, 1936, **122**, 121.

‡ Physicist, Research Department, Metropolitan-Vickers Electrical Company, Ltd., Trafford Park.

of those here to-day know also, but I would emphasize that, whilst it is possible to measure lattice spacings to 1 part in 100,000, what the authors are really concerned with in this work is the difference in lattice spacings produced by change in composition, and that is usually quite small. In Table I it will be found that for a change in composition of 4 atomic per cent. tin, there is a change of 177 parts in 40,000, which means—assuming the accuracy of X-ray measurements to be about 1 in 40,000—that if one can analyze to 0·02 per cent. of tin the accuracy on the two axes is roughly equal. In short, I do not agree with the phrase " out of all proportion." I mention this because there are many people, particularly in industry, who have only a very limited knowledge of the application of X-ray crystal analysis, and they hear of figures of accuracy of 1 part in 100,000 and do not appreciate the qualifications which have to go with that statement.

Mr. E. H. **Bucknall** * (Member): Dr. Stockdale has already directed attention to the implications in constitutional work of systematic departures from Vegard's law. An example is afforded by the nickel–chromium alloys, which form a simple eutectiferous series, the eutectic lying at about 50 per cent. chromium. A recent X-ray investigation indicated that the solubility of chromium in nickel below the eutectic temperature exceeds this value, but this inference is based on the straight line law of change of parameter with composition, which was apparently established only up to 34 per cent. chromium. Departure from the linear relationship, to a quite ordinary extent, beyond this point would invalidate the authors' conclusion. This is one example of the confusion which can arise from lengthy extrapolation of X-ray data.

Is there any real merit in filings which is not shared by lump material? If one can induce a grain-size corresponding with the dimensions of filings is there any point in comminution? Are we justified in taking one stage further a suggestion made by Dr. Sykes, and saying that the best way to treat filings is to leave them in the lump? On p. 311 it is stated that although filings of magnesium alloys may pick up oxygen and nitrogen, " the filings may, however, still be used for analysis if both metals are determined, since the ratios of the metallic constituents will be the same as in the original lump." That is true, of course, but the use of contaminated filings must often result in deceptive X-ray measurements, as ternary or more complex alloys do not usually have structures corresponding to the binary alloys of the main constituents in the same proportions.

Dr. **Marie Gayler** † (Member): Dr. Desch has referred to the difficulties of high-temperature treatment of filings, a point on which, unfortunately, the authors have not touched, for it is a problem which is of very great urgency. The X-ray examination of the alloys will have to be carried out at the temperature of heat-treatment and, instead of taking the alloy to the X-ray apparatus, it may be necessary to take the apparatus to the alloy.

The authors have dealt with the quenching of powders, but it is not easy to obtain powders unchanged on quenching from temperatures appreciably higher than those used in the case of magnesium or silver alloys. For instance, with iron–manganese alloys I have experienced the greatest difficulty in retaining the structure of the alloys quenched from temperatures above 1200° C. X-ray analysis in the case of one of the specimens heat-treated

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thus, showed the true structure, but not otherwise. This problem needs very careful study.

I understood Mr. Bucknall to suggest that powders should be made of definite grain-size and annealed, as Dr. Sykes has said, in a lump of the material at the high temperature. I agree that that is a suitable method if no marked change is expected to take place in the alloy, such as the authors have shown in Fig. 1. With reference to that diagram, I heartily agree with the authors regarding the difficulties which they have pointed out, and particularly when the same method is applied to ternary alloys. I have investigated various, and by no means simple, ternary systems, changes in the solid taking place over a very long period of time: *e.g.* the aluminium–copper–zinc system, in which reactions take place across solubility lines of the type shown by the authors, and where annealing alloys for weeks does not produce equilibrium. In such cases the greatest care should be taken by the physicist, or by the metallurgist working with the physicist, to ensure that the sample X-rayed is really in equilibrium, and I doubt whether the annealing of powders would be suitable. The lump should be annealed and then filed, but care would have to be taken to ensure that the lump was in equilibrium before filing.

Mr. Reynolds (*in reply*): At Oxford we are very sceptical concerning the X-ray method of determining phase diagrams, and we have never yet employed it, though we now intend to use it in the determination of certain boundaries in the AgGe and CuGe systems. Even here, however, the method is being used only on account of the rarity of Ge, which renders the microscopic determination of phase boundaries an expensive process. In general, there are so many sources of error which may creep in to vitiate the accuracy of the results of the X-ray method, that it seems preferable to use the older microscopic method.

In agreement with Dr. Gayler, we also would emphasize the necessity of annealing the lump to equilibrium at the temperature concerned before the filings are prepared for X-ray examination. If then the lump is examined microscopically just before filing, one may be certain that the filings are indeed those intended, and that the alloy is in equilibrium—a condition which is not satisfactorily established by visual examination of the sharpness of diffraction lines. For example, an originally 2-phase alloy approaching homogeneous equilibrium when examined microscopically often exhibits a few still unabsorbed crystals of the second constituent which, though they must affect the determined composition of the alloy, may constitute too small a portion of the whole mass to affect appreciably the X-ray diffraction measurements. The importance of the composition error is frequently made obvious in the parameter/composition diagrams in which the agreement is excellent in the 2-phase regions, where exact composition is unimportant, but is bad in the homogeneous region.

Dr. Stockdale has suggested that it would be preferable to prepare all filings under benzene or some such liquid in order completely to exclude atmospheric contamination. Work has already been done at Oxford on the filing of magnesium alloys under benzene, but filing with a rotary file in an inert gas atmosphere seems to offer the greater advantages.

CORRESPONDENCE.

The Authors (*in further reply*): Dr. Stockdale's remarks on the density of copper are most interesting, and it is perhaps significant that our own value for the lattice spacing of copper * was 3·6070(5) at 18° C., which is somewhat lower than that of Owen.

Dr. Sykes' suggestion of annealing filings inside a lump of the same alloy is most attractive, and we hope that we may be able to use this method with alloys of common metals. As regards the relative accuracy on the two axes of the diagram, we agree with Dr. Sykes that if proper precautions are taken the accuracy on the two axes is roughly equal; but our own experience of segregation and other effects, together with a critical reading of many published papers suggests that in many cases the errors involved are of the order of several tenths of 1 atomic per cent. rather than the value 0·02 atomic per cent. given by Dr. Sykes.

In reply to Mr. Bucknall we fully agree that results from filings containing oxygen and nitrogen must be looked on with suspicion, and have ourselves pointed this out on p. 311.

* W. Hume-Rothery and P. W. Reynolds, *Proc. Roy. Soc.*, 1936, [A], 157, 167.

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AN X-RAY STUDY OF THE CHROMIUM–ALUMINIUM EQUILIBRIUM DIAGRAM.*

By A. J. BRADLEY,† D.Sc., Member, and S. S. LU,‡ Ph.D.

SYNOPSIS.

X-ray powder photographs were made from more than 70 slowly cooled and quenched chromium–aluminium alloys. These were used to provide a basis for a tentative equilibrium diagram. Nine phases exist after slow cooling from 800° C. to room temperature, and two other phases were found in alloys quenched from 1000° and 1100° C. The α body-centred cubic structure formed by the solution of aluminium in chromium exists from 0 to 30 weight per cent. of aluminium at temperatures above 850° C. Below this temperature alloys containing about 75 per cent. of chromium change to a tetragonal β-structure. This is a superlattice made by stacking three body-centred cubes above each other.

Three phases with crystal structures resembling that of γ-brass were found after slow cooling to room temperature, and a fourth phase of similar type was found in alloys quenched from 1100° C. These all appear to be distorted forms of the γ-type of structure. γ_2 exists around the composition Cr_5Al_8, which formula agrees with structure analysis. This phase is derived from a body-centred cubic structure of the γ-type by elongation in the direction of a trigonal axis, so that the symmetry is rhombohedral. It decomposes at about 890° C. γ_3 exists around the composition Cr_4Al_9 at temperatures between 700° and 870° C. Below 700° C. it gradually transforms into the related γ_4 structure. At still lower temperatures, the composition range of γ_3 is more limited, whereas that of γ_4 increases, until at room temperature γ_3 is restricted to a very narrow range of compositions. At each temperature below 700° C., γ_3 contains just a little more chromium than γ_4.

There are three closely related phases θ, η, and ϵ, with the approximate formulæ $CrAl_7$, Cr_2Al_{11}, and $CrAl_4$. They melt at 725°, 900°, and 1011° C., respectively. A phase with the approximate formula $CrAl_3$ exists in alloys quenched from temperatures exceeding 850° C., and melts at 1180° C.

INTRODUCTION.

The chromium–aluminium system has been investigated by Hindrichs,[1] Guillet,[2] Gotō and Dōgane,[3] Fink and Freche,[4] and Hori,[5] but hitherto no consistent scheme has been proposed to show either the complete phase-sequence at room temperature or to give any account of transition temperatures. Guillet suggested a phase diagram based on Hindrich's experiments, which showed a solidus horizontal at 644° C. stretching from pure aluminium up to 85 per cent. of chromium, and a liquidus at 980° C. up to 55 per cent. of chromium. Above 980° C. a two-liquid

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* Manuscript received December 21, 1936.

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region was indicated, and an intermetallic compound Cr_3Al was proposed. The diagram published in the International Critical Tables (Fig. 1) also shows two liquid phases, but omits some of the other features of Guillet's diagram. The present authors have found no evidence to support these diagrams, but the more recent work of Gotō and Dōgane is, on the whole, in good agreement with the present experiments. They showed the liquidus rising from 654° C. at 1 per cent. chromium to 1170° C. for 36 per cent. chromium. The general outline for this curve is probably correct, but requires some modification to fit in with the accurate measurements made by Fink and Freche on a large number of aluminium-rich alloys. These authors found a peritectic horizontal at 661° C., instead of the eutectic horizontal at 654° C., and found that the liquidus rose more steeply than in Gotō and Dōgane's diagram. At 2 per cent. of chromium, this line has already reached 790° C.

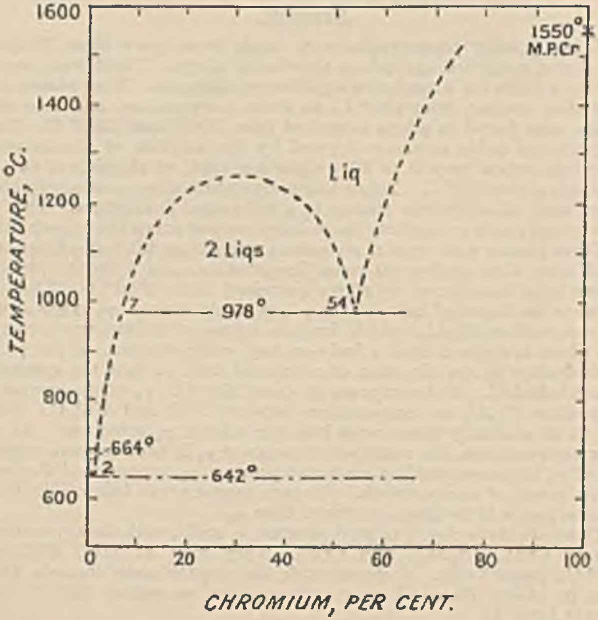

Fig. 1.—Aluminium–Chromium (From the International Critical Tables).

Gotō and Dōgane found two intermetallic compounds. $CrAl_7$ was formed by a peritectic reaction at 725° C., and $CrAl_4$ by a peritectic reaction at 1011° C. Both observations are perfectly consistent with the present authors' results, who, however, find some solid solubility and a change of phase boundaries with temperature.

More recently Hori has determined the phase boundaries up to 50 per cent. chromium. The 660° C. peritectic of Fink and Freche is confirmed, and two compounds Al_2Cr and Al_4Cr were observed. These are reported to form at 1018° and 803° C., respectively, but this is not consistent either with the work of Gotō and Dōgane, or with the present authors' results, which give much higher temperatures.

PRESENT INVESTIGATIONS.

The present investigation offers, for the first time, a basis for a complete equilibrium diagram. In Fig. 2 are shown nine phases in alloys slowly cooled to room temperatures, and two other phases only found in quenched alloys. Each of these was identified by means of its X-ray powder pattern. Approximate limits of temperature and composition were found for each phase, and from these the diagram has been constructed. It is not within the scope of this work to investigate the complete phase equilibria at high temperatures, but the authors consider that the phase boundaries are probably accurate to about 1·0 per cent. just below 850° C. The solidus and liquidus lines are to some extent speculative, although the authors have experimental evidence for a temperature as high as 1350° C. for the solidus. For the liquidus, the results of Gotō and Dōgane and of Fink and Freche have been taken, extrapolating to the known melting point of pure chromium[6].

The most important feature of the present work is the phase sequence below 600° C., obtained from the slowly-cooled alloys. Nine types of structure are found, each separated from its neighbours by clearly marked two-phase regions. Each phase exists over a range of compositions, the widest of which is the solid solution of aluminium in chromium. This solid solution, which is body-centred cubic, has been termed the α-phase. Above 850° C. its range of compositions is considerably extended, the phase boundary at 900° C. being about 72 per cent. of chromium, whereas at 830° C. it is placed at 82 per cent. of chromium.

At about 850° C. the α body-centred cubic structure in the phase range between 75 per cent. and 81 per cent. of chromium is transformed into the tetragonal β-phase. This is a deformed body-centred cubic structure, due to an ordering of the chromium and aluminium atoms. Three body-centred cubes, stacked one above another, form a tetragonal unit, in which two planes of chromium atoms alternate with one plane of aluminium atoms.[7] The ideal composition of the phase corresponding to Cr_2Al lies in the two-phase $\alpha + \beta$ region whatever the heat-treatment below 850° C. The phase range is greatest after slow cooling, which increases the excess of aluminium which may be taken into solid solution.

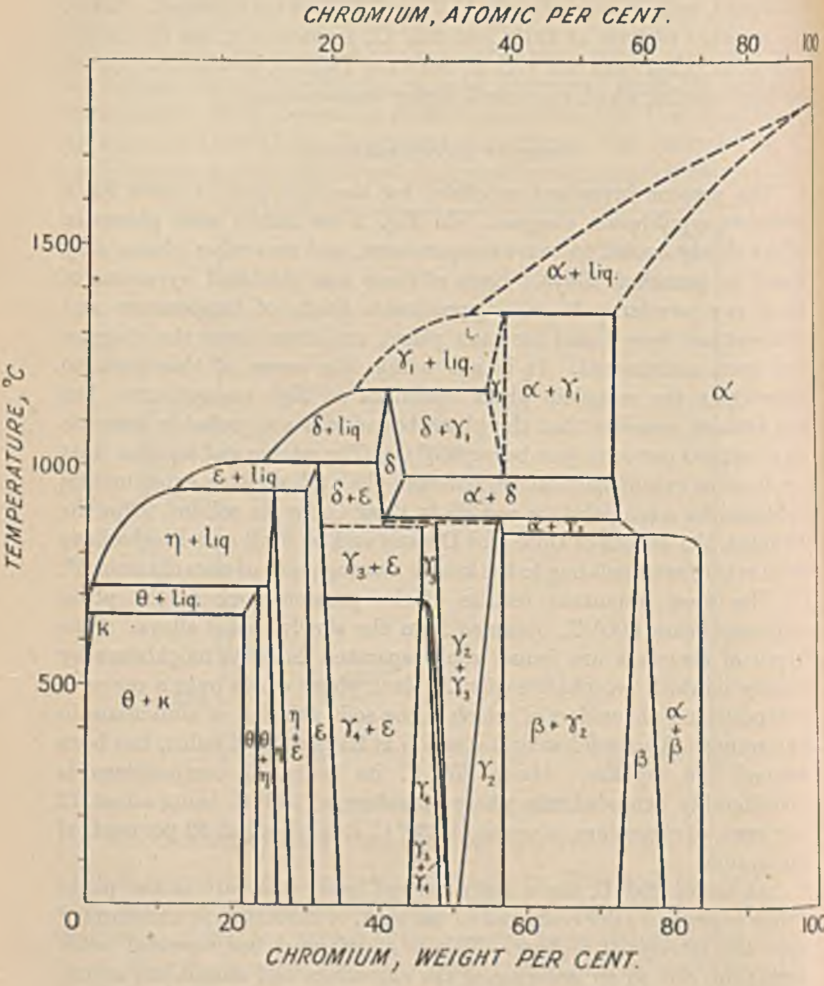

Fig. 2.—Chromium–Aluminium Equilibrium Diagram.

No fewer than four phases have crystal structures which in their general form resemble that of γ-brass. The powder photographs are so difficult to differentiate that we have called them γ_1, γ_2, γ_3, and γ_4, although they are apparently quite distinct phases. γ_1 is only found in alloys quenched from 1100° C. γ_2, γ_3, and γ_4 are present in slowly cooled alloys. γ_2 has a composition corresponding to the formula Cr_5Al_8, which agrees with the crystal structure data. After slowly cooling, it dissolves excess of either chromium or aluminium. The structure is rhombohedral, but the positions of the atoms are almost identical with those in γ-brass, Cu_5Zn_8. The atomic distribution, which follows a rhombohedral plan, is responsible for the distortion from cubic symmetry. Cr_5Al_8 is formed by a peritectoid reaction at about 890° C.

γ_3, which is formed at about 870° C., corresponding to the approximate composition Cr_4Al_9, begins to be transformed at about 700° C. into γ_4, while below this temperature the two phases may coexist over a small composition range. In the slowly cooled alloys, γ_3 has not been found as a single phase, but occurs mixed with either γ_2 or γ_4, so that its composition range at room temperatures is extremely small.

δ, $CrAl_3$ is found in alloys quenched from temperatures between 900° and 1100° C., but it is always associated with decomposition products, or with the two neighbouring phases. The pattern is fairly simple, but cannot be solved easily on account of the admixture with impurities, from other phases.

ε, $CrAl_4$, is obtained by slow cooling or quenching from any temperature up to 1000° C. η, Cr_2Al_{11}, forms below 1000° C., and θ, $CrAl_7$, between 700° and 800° C. Each of these phases has a range of solid solubility which varies with the temperature. From the powder photographs, the structures appear to be very complicated. θ, $CrAl_7$, forms single crystals, which have been shown by the oscillation, Laue, and Weissenberg methods to have an orthorhombic (pseudo-hexagonal) structure. κ, the solid solution of chromium in aluminium has a very narrow range of solid solubility after slow cooling.

The Preparation of the Alloys for X-Ray Examination.

Alloys of chromium and aluminium were melted in alumina-lined crucibles, in a high-frequency induction furnace under a small pressure of hydrogen, which was pumped off before solidification. The presence of the hydrogen is essential to prevent the chromium from boiling off during heating.

The purest possible ingredients were employed. The chromium was kindly supplied by the courtesy of Dr. C. H. Desch of the National Physical Laboratory, and Mr. C. C. Paterson of The General Electrical

Company, Ltd. The authors are deeply indebted to them, and also to The British Aluminium Company, Ltd., and to Aluminium Française, who supplied them with pure aluminium. The work was begun before the purest materials were obtained, but all the vital results recorded here were obtained from material exceeding 99·9 per cent. in purity. Test analyses proved that the chromium content agreed to within 0·2 per cent. of the weighed proportion, *e.g.*

Chromium Weighed Out, Per Cent.	Chromium Analyzed, Per Cent.
27	26·81
49·5	49·55

The heat-treatments of the alloys were made in lump and in powder form. The lump annealing serves two purposes: to eliminate coring, and to complete peritectic and peritectoid reactions; while quenching may be required to prevent the decomposition of high temperature phases. Owing to the complicated nature of the diagram, the heat-treatments had to be varied considerably from one alloy to another, but in general the process was as follows.

The alloy was heated for 1–3 days in a Nichrome-wound furnace at as high a temperature as possible without being melted.* It was then reheated within a temperature range where a single phase was anticipated, and, if necessary, quenched from a suitable temperature. All these heat-treatments were carried out *in vacuo.* Finally, having obtained the alloy in as homogeneous a form as possible, it was broken into powder and subjected to a further heat-treatment *in vacuo*, being either slowly cooled from about 800° C. down to room temperature at about 10° C. per hour, or quenched from a definite temperature. A special arrangement was used for quenching, where the powder was cooled in less than $\frac{1}{1000}$ second, after several hours heating at the stated temperature.

In all, over seventy alloys were prepared. The composition intervals did not exceed 1 per cent. by weight, except where there were no features of especial interest. Where necessary for the investigation of narrow-phase regions, extra alloys were made up, reducing the intervals to less than 0·5 per cent. All the specimens were heat-treated by slow cooling in powder form, and in each case a powder photograph was taken using chromium radiation with a vanadium screen to filter out the K_β radiation. A 9 cm. diameter powder camera was used. Where possible the unit cell was found and the lattice dimensions were measured accurately to one part in 30,000. The structure of the γ_2 phase

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* 800° C. for less than 32·5 per cent. chromium. 1000° C. for more than 32·5 per cent. chromium.

PLATE XLV.

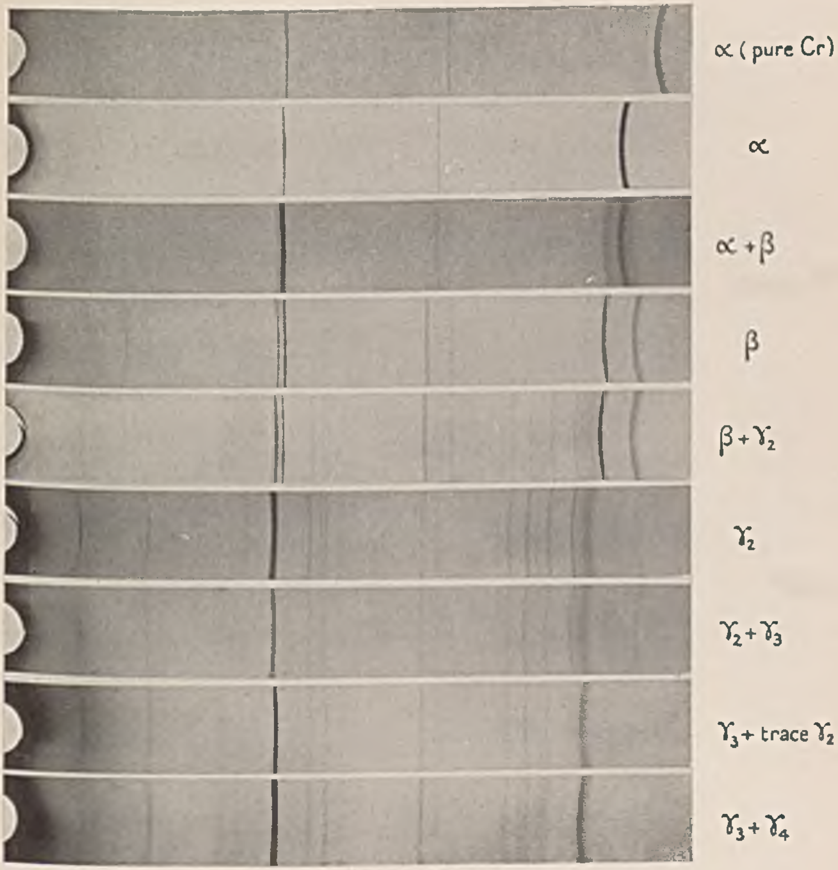


FIG. 3.—Powder Photographs of Slowly-Cooled Chromium–Aluminium Alloys.

[*To face p.* 324.

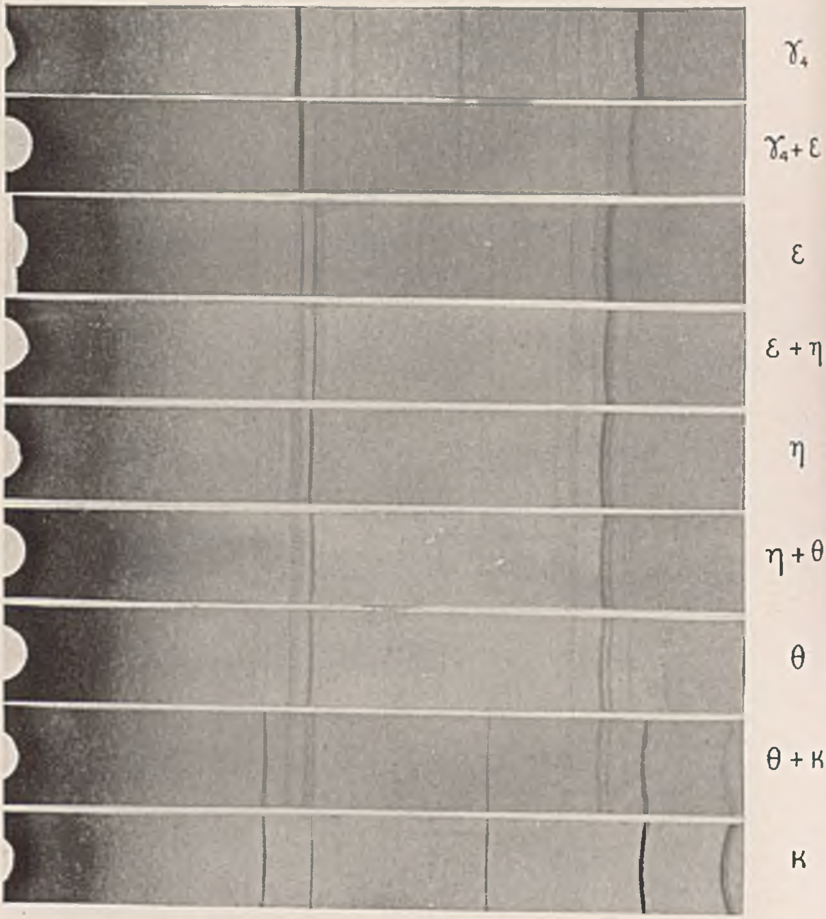


FIG. 4.—Powder Photographs of Slowly-Cooled Chromium–Aluminium Alloys.

PLATE XLVII.

FIG. 5.—The Four γ-Phases Compared with γ-Brass (Copper K_α Radiation).

(Cr_5Al_8) which could not be solved in this way was found from a powder photograph taken in a 19 cm. diameter camera.

Certain of the alloy powders were quenched from 600°, 710°, 800°, 850°, 890°, 930°, 1000°, or 1100° C. In each case, only those specimens were used which would help to fix the positions of the phase boundaries. The powder photographs from the quenched alloys were in some instances quite as clear as from the slowly cooled alloys, but in most of the quenching experiments from 890° or 930° C. they contained a mixture of many patterns, caused by the partial decomposition of the high-temperature phases.

The Results of X-Ray Analysis.

The phase sequence in the slowly cooled alloys was deduced from powder photographs taken with chromium radiation, some of which are reproduced in Figs. 3 and 4 (Plates XLV and XLVI). The nomenclature of the phases has been chosen to indicate the close relationship of the four γ-phases. The similarities in structure lead to resemblances in the strong lines of these patterns, but there are definite characteristics by which each phase may be identified. The differences are more pronounced in photographs taken with copper radiation, owing to the presence of higher order reflections, which are much influenced by small changes in the atomic positions. This may be seen from Fig. 5 (Plate XLVII), which gives a comparison of the patterns of the four γ-alloys with that of γ-brass.

The single-phase patterns are distinguished from the neighbouring two-phase patterns by the constancy of the relative intensities of the lines. Each two-phase photograph can be analyzed into two sets of lines due to the two neighbouring phases, the relative intensities of which vary with the composition. It is impossible, however, to reproduce here the whole series of photographs which were used to prove the sequence of the phases. In the neighbourhood of the phase boundaries, alloys were examined at intervals of 0·5–1 per cent., but the final decision might depend on faint lines which are difficult to show as reproductions.

The results of the X-ray analysis are summarized in Fig. 6. This diagram gives a tabulation of the phase patterns found on all the powder photographs, both from slowly-cooled and from quenched alloys. The constituents of a given alloy after a specific heat-treatment are written one below another and enclosed in a small rectangle. Where one phase predominates, it is shown in heavier type. The figures 1, 2, 3, and 4 are abbreviations for γ_1, γ_2, γ_3, and γ_4. The composition of the alloy corresponds to the centre of the rectangle, except where two or more

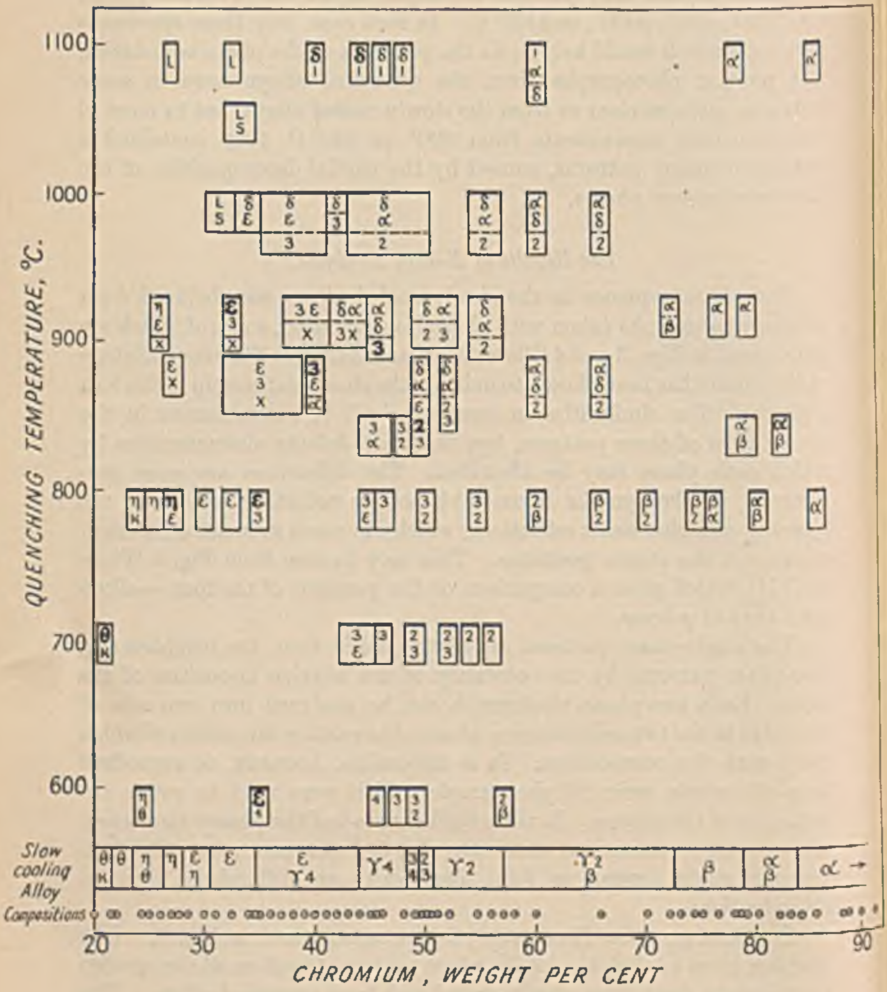


Fig. 6.—The Phases Shown by the Powder Photographs.

alloys were examined at intervals closer than 1 per cent. In such cases the rectangles enclose all alloys which were found to have the same constituents after the same heat-treatment, the boundary of the rectangle then corresponding to the phase boundary. So many slowly cooled alloys were examined that the results were virtually continuous, and the diagram at the foot of Fig. 6 records the complete phase sequence. The positions of the boundaries after slow-cooling should be accurate to within 0·5 per cent. The exact compositions of the alloys are indicated by circles.

In the quenching experiments, only selected alloys were used to fix the positions of the phase boundaries and the transition temperatures. The thick upper line of each rectangle shows the temperature of the alloys before quenching. The powder photographs may correspond to a whole range of temperatures below the initial temperature, as the alloys may change during the process of quenching. Up to 850° C., this causes no difficulty. Each photograph shows either a single phase, or a mixture of two phases, and may be interpreted directly in accordance with the phase rule. The equilibrium diagram given in Fig. 2 is therefore absolutely satisfactory as a representation of the X-ray results below 850° C. Above 850° C. the results must be accepted with some caution.

At all quenching temperatures above 850° C., the powder photographs cause difficulties. They often show more than two phases, and in several cases as many as five phase patterns have been identified on a single photograph. This is due to partial decomposition on quenching; the low-temperature phases stable at 800° C. are formed, mixed with new high-temperature structures. In Fig. 6 the high-temperature phases are placed immediately below the quenching temperature, and separated from the decomposition products by a dotted line. The complications are worst after quenching from 890° and 930° C., because, as is shown in Fig. 2, there are at least four transition temperatures just below 890° C. During quenching some of the high-temperature phases are preserved, but part of the material undergoes each of the possible transformations between 890° and 850° C. The quenches from higher temperatures than 930° C. were on the whole more satisfactory. Above 1000° C. the patterns are still simpler, but there is again some decomposition. A serious difficulty arises from the resemblance of the γ_1 pattern to the low-temperature γ patterns, which makes it difficult to distinguish them from each other. It is not always possible to be sure whether γ_1 is present alone, or mixed with decomposition products including γ_2 or γ_3.

The existence of the two high-temperature phases γ_1 and δ was confirmed by some observations made during the solidification of the alloys in the induction furnace. It was found that the alloys near the composition of γ_1 solidified at over 1300° C. Hindrich's arrest point observed in a 60 per cent. alloy at 1180° C. cannot possibly have been due to the liquidus, as was suggested by Guillet. The horizontal at 980° C. given by Hindrich's thermal arrest points may at first correspond to the peritectic temperature of the ε phase, given by Gotō and Dōgane as 1011° C. Beyond 40 per cent. chromium it reappears as a eutectoid temperature of γ_1, and might easily be taken for a continuous horizontal. The presence of melted portions after quenching the alloy powders is indicated by *L* or *LS* in Fig. 6. The 1011° C. solidus is obviously interrupted before passing 40 per cent. chromium.

An alloy containing 58 per cent. of chromium solidified at about 1350° C. An alloy containing 40 per cent. of chromium solidified at about 1180° C. These temperatures were found by means of an optical pyrometer, which was calibrated against the melting points of copper and nickel. The two metals were allowed to cool in the induction furnace under the same conditions as the alloys. It was found that the apparent temperature was far below the true temperature, but the differences were consistent and a correction could be applied. The values should be accurate to 25° C., which is quite enough for the qualitative purpose of the present investigation.

The α-Phase (Solid Solution of Aluminium in Chromium).

The body-centred cubic α-phase is a solid solution of aluminium in chromium with the atoms distributed at random. The lattice spacing increases steadily with the replacement of chromium by aluminium. Without aiming at high accuracy, an approximate determination has been made of the phase boundary at different temperatures, by following the changes in lattice spacing, in the two-phase quenched alloys. In Fig. 7 the lattice spacing is plotted against the weight per cent. of chromium. The values for slowly cooled alloys increase linearly from 100 per cent. chromium to 83 per cent. chromium. The next result, at 82 per cent. chromium is from a two-phase alloy after slow cooling, the other constituent being the β-phase. The lattice spacing indicates that after slow cooling the phase boundary is at about 83 per cent. of chromium.

The results of the quenching experiments must be interpreted with caution. Since there is nearly always some decomposition of the high-temperature phases, the measurements are subject to a correction. The lattice spacings probably refer to a temperature somewhat below the actual temperature of quenching. As an arbitrary assumption, it is supposed that in the neighbourhood of 900° C. the true temperature is about 20° C. below the recorded quenching temperature. This arbitrary correction leads to a consistent interpretation of the results.

Fig. 7 shows that the lattice spacings of the α-phase in the quenched alloys of the two-phase region always exceed those of the slowly-cooled alloys. The higher the quenching temperature, the higher is the lattice spacing. Since increase of spacing corresponds to increase of aluminium content, it follows that a greater amount of aluminium is taken into solution at high temperatures than at low temperatures. The position of the phase boundary at a given temperature is shown by the points of intersection of the dotted lines with the spacing–composition curve. The procedure is confirmed by estimates of the amount of the α-constituent in two-phase alloys. Fig. 8 gives the position of the α-boundary derived from Fig. 7. The circles, which denote the observed values, fall on a curve with two breaks. One, at 75 per cent. of chromium, corresponds to the decomposition of the α-phase. The other, at 72 per cent. of chromium, may be due to the peritectoid horizontal of the γ_2-phase.

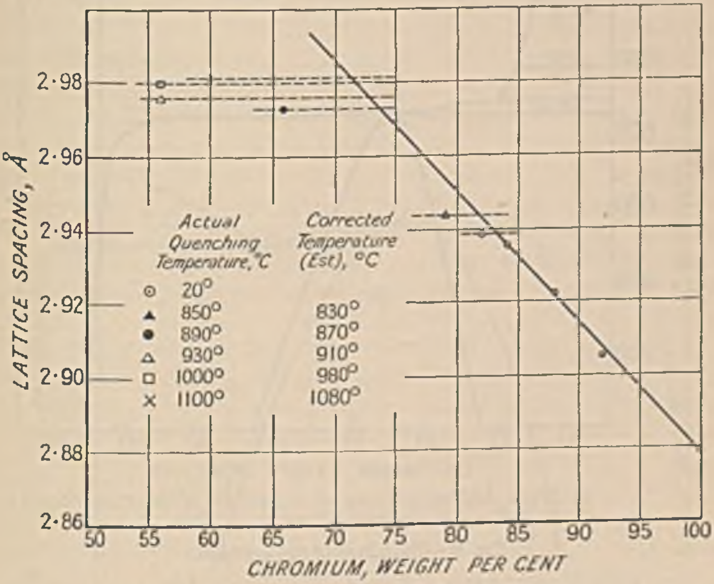
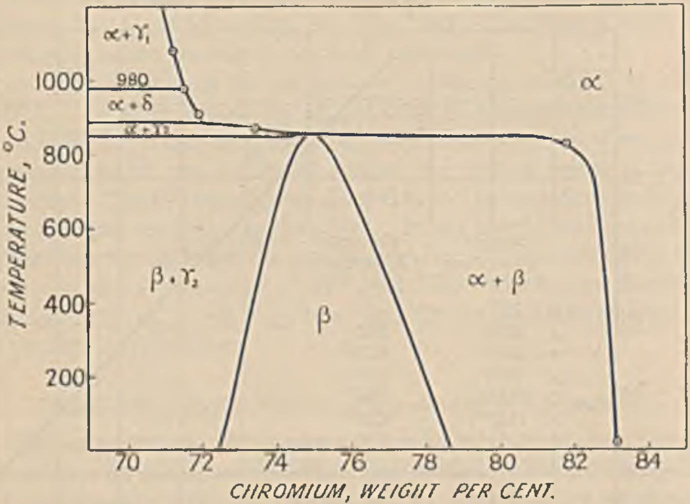


Fig. 7.—Lattice Spacings of the α-Phase.

The transformation of β to α as given in Fig. 8 appears to be rather complicated. This is due to the close approach of two points on the phase diagram. Consequently, it appears that five lines meet at one point. Although it is not possible to represent the exact details on the scale of Fig. 8, this may be done schematically as in Fig. 9, which shows the most probable mechanism for the transformation. Since the change from the β-phase to the α-phase is essentially a disordering process, it probably takes place by the tangential contact of the two-phase boundaries at the maximum temperature of the β-phase. The lower boundary is between the β and the α + β-fields. The upper boundary is between the α and the α + β-fields. Independently of this mechanism, we may have a eutectoid decomposition of the α-phase on the aluminium-rich side of the β-phase. At high temperatures we have an α-field and an α + γ-field. At lower temperatures there is a β-field and a β + γ-field. It is necessary for the validity of this eutectoid theory, to assume the existence of a small α + β-region on the aluminium-rich side of the β-phase. The area of this field is so small that it cannot be represented on the scale of Fig. 8, and it would be difficult to establish experimentally.



⊙ *From lattice spacing measurement of the α constituent in 2 phase quenched alloys.*

Fig. 8.—Boundary of the α-Phase.

The β-Phase (Cr_2Al).

A complete account of the structure analysis of the tetragonal β-phase has been published elsewhere.[7] This phase may be considered to be derived from the body-centred cubic α-phase by a process of ordering. The unit cell is formed by stacking three body-centred cubes one above another. The axial ratio is not quite 3 : 1, as there is some deformation, and the atoms are displaced in accordance with tetragonal symmetry. There are places in the structure for four chromium atoms and two aluminium atoms, but there is always a slight excess of aluminium atoms, which replace some of the chromium.

The limits of the β-phase were fixed from the quenching experiments. It is not formed in alloys quenched from as high as 890° C., but appears in those quenched from 850° C., and lower temperatures, and is always present after slow cooling. The β-phase therefore decomposes between 850° and 890° C. The exact temperature is probably near 850° C., since there is no sign of the incipient formation of the phase in the alloys quenched from 890° C., except in one case. On the other hand, the γ_2, γ_3, and ε-phases all occur as decomposition products in a number of different alloys quenched from 890° C. It seems probable from this that the β-phase is formed at a slightly lower temperature than these other phases. The α-phase lattice spacing measurements confirm the view that the β-phase finally decomposes at 850°–860° C. The

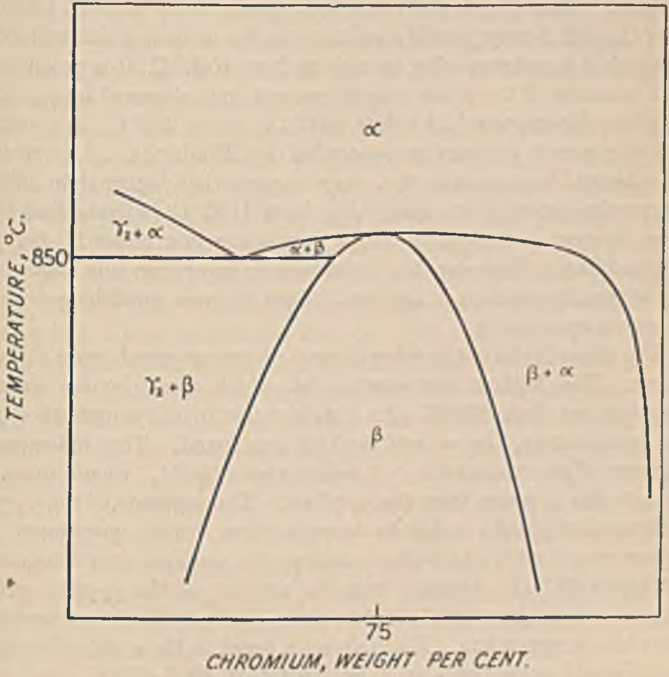


Fig. 9.—The α–β Transformations.

qualitative examination of the quenched alloys, recorded in Fig. 6, indicates that an alloy containing 75 per cent. of chromium preserves the β-phase at a higher temperature than any other composition. The theoretical composition for the formula Cr_2Al is 79·39 per cent. of chromium.

The γ-Phases (γ_1, γ_2, γ_3, *and* γ_4).

The four γ-phases are so similar in structure type that it is not easy to fix the phase limits, especially in the case of the high-temperature γ_1-phase. From Fig. 6, this phase seems to be stable between 1000° and 1100° C., and it may possibly exist up to the melting point at 1350° C. Although it is not seen after quenching from 1000° C., it is possible that small amounts of the phase may be present, but obscured by γ_2. If so, the phase decomposes just below 1000° C., say at 980° C., in agreement with the arrest temperature recorded by Hindrichs. Alternatively, the eutectoid temperature of γ_1 may be somewhat higher than 1000° C. The results recorded for quenching from 1100° C. indicate that the γ_1 phase is most prevalent in alloys containing just below 60 per cent. of chromium. However, the information regarding this phase is so scanty that its position in the equilibrium diagram must be regarded as somewhat speculative.

The phase limits of the other three γ-phases are much more definitely known. The highest temperature at which the γ_2-phase exists is probably less than 890° C. In a wide range of alloys quenched from this temperature, the α- and δ-phase are found. This indicates the existence of an extensive $\alpha + \delta$ region above 890° C., which appears to separate the γ_2-phase from the γ_1-phase. The presence of the γ_2-phase in these photographs is due to decomposition during quenching. The α-phase reacts with the δ-phase to give the γ_2-phase at a temperature just below 890° C. Judging from the amount of the γ_2-phase present after quenching from 890° C., it is probably formed only a few degrees below this temperature. Fig. 8 shows a break in the α-phase boundary, which would correspond to a horizontal at 880°–890° C., and in all probability this corresponds to the peritectoid temperature of γ_2.

An account of the structure of the γ_2-phase is published together with that of Cr_2Al. The ideal formula, Cr_5Al_8, agrees closely with the range of homogeneity. The theoretical composition is 54·68 per cent. of chromium, and an alloy of this composition is homogeneous after slow cooling, when the phase is found to extend from 51 to 57 weight per cent. of chromium. On quenching from 600° C., a 57 per cent. chromium alloy contains some of the β-phase, and on quenching from 800° C. a 54·5 per cent. alloy contains some of the γ_3-phase. On slowly cooling, the homogeneous γ_2-phase is widening so rapidly that it seems possible that prolonged annealing will be required to get phase equilibrium just below 51 per cent. and just above 57 per cent. chromium, but this is beyond the scope of the present work.

γ_3, on the contrary, occupies a more extended range of compositions at high temperatures than at room temperature, where it is replaced by γ_4. Up to the present, γ_3 has not been found as a single phase, except after quenching. In the slowly cooled alloys, it is found mixed with γ_4 at 49 per cent. of chromium, and mixed with γ_2 at 49·5 per cent. of chromium. On quenching from 600° C., both these alloys are found to consist of $\gamma_2 + \gamma_3$. The single-phase γ_3 region is first reached on quenching a 48 per cent. alloy from 600° C. At 710° and 800° C., a 46 per cent. alloy gives γ_3. Both the 46 and the 48 per cent. alloys are converted into pure γ_4 on slow cooling.

The γ_3-phase, like the γ_2-phase, appears to be formed by the interaction of the α- and δ-phases, at temperatures between 850° and 890° C. In alloys quenched from between 890° and 1000° C., it is present side by side with the original $\alpha + \delta$, as a decomposition product. Since there is less γ_3 than γ_2 in most of the 890° C. quenches, it seems probable that γ_3 is formed at a somewhat lower temperature than γ_2, say at 870° C. In this case there should be a narrow range between 880° and 870° C., where δ is in equilibrium with γ_2. The authors have no definite evidence on this point, which must remain in doubt for the present.

The γ_4-phase does not occur above 700° C., but the range of homogeneity gradually widens on cooling. An alloy with 48 per cent. chromium gives the γ_3-pattern on quenching, but the γ_4-pattern is found after slow cooling. No alloy has been found to give the γ_4-pattern after quenching from 710° C., where γ_3 is found to be in equilibrium with ε in alloys containing 43 per cent. and 45 per cent. of chromium. The γ_4-phase is definitely present at 600° C., and from that point down to room temperature is found in equilibrium with ε and γ_3. It may be seen from Fig. 5 that no evidence was found for any transformation in this or any other part of the system below 600° C.

The composition ranges of γ_4 and γ_3 are so nearly the same that they must be represented by the same formula. Cr_4Al_9 corresponds exactly with the centre of these phases, and agrees with the preliminary results of structure analysis, though later work may possibly suggest some modification of this formula.

The transformation of γ_4 to γ_3 cannot be adequately explained by Fig. 2. An enlargement has therefore been made in Fig. 10, which gives a possible explanation of the mechanism of the γ_3–γ_4 transformation. Since this is essentially an order–disorder change, somewhat analogous to the α–β transformation, a similar mechanism is proposed. The

γ_3 and $\gamma_4 + \gamma_3$ boundary meets the γ_4 and $\gamma_4 + \gamma_3$ boundary tangentially. This is in agreement with the experimental data, since the $\gamma_3 + \gamma_4$ region narrows with increasing temperature. The eutectoid decomposition of γ_3 on the aluminium-rich side of γ_4 would explain the occurrence of pure γ_3 at 46 per cent. of chromium after quenching from 850° and 800° C., and its transformation to γ_4 on slow cooling. The intermediate state $\gamma_3 + \gamma_4$ is too small to observe on the aluminium-rich side of γ_4.

The δ-Phase ($CrAl_3$).

The δ-phase is found at about 40 per cent. of chromium. At lower chromium contents quenching from 1000° C. gives an admixture with the ε-phase. At higher chromium contents the α-phase is always present. The phase diagram (Fig. 2) is drawn to explain these facts. The presence of γ_2 or γ_3 in these quenched alloys, which is due to the incipient reaction of the α- and δ-phases during quenching, only occurs where there is more than 40 per cent. of chromium. The formula $CrAl_3$, which was chosen empirically, corresponds to 39·12 per cent. of chromium.

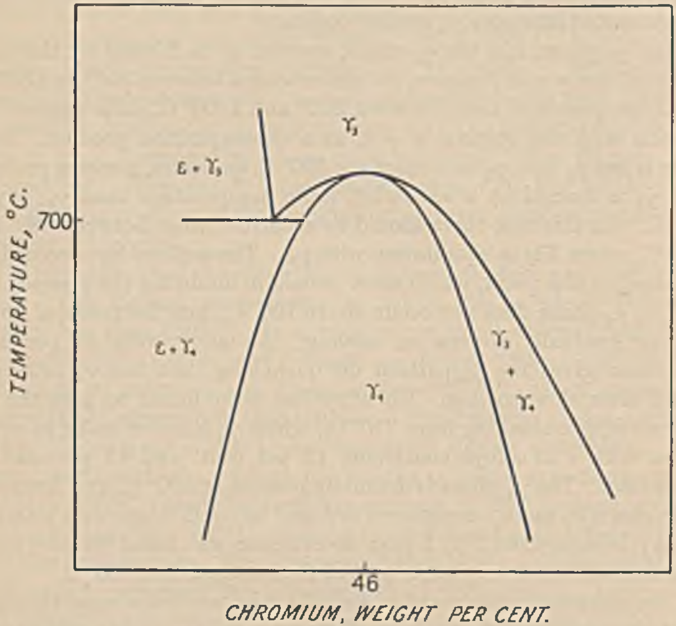


Fig. 10.—The γ_3–γ_4 Transformation.

Quenching from 1100° C. prevents the decomposition of the δ-phase, but the presence of γ_1 in all photographs shows that it has only a narrow range of composition. The solidus in this region is well over 1100° C., since powders heated above this temperature did not begin to melt. Measurements made during solidification in the induction furnace gave 1180° C. as the temperature of solidification. On the other hand, a 32·5 per cent. chromium alloy was found to have melted after heat-treatment at 1100° C. In Fig. 2 this alloy is placed in the δ + liquid region at 1100° C.

Quenching from 890° C. leads to so much decomposition that it would appear that this temperature is near the lower limit of the phase, and this conclusion is confirmed by the absence of any trace of the δ-phase from alloys quenched from 850° C. It is difficult to explain the results obtained by quenching alloys containing 32·5 to 40 per cent. of chromium from 930° C. No δ-phase is found, but γ_3 is present together with a trace of a new constituent x. It seems likely that the δ-phase has reacted with the ε-phase during quenching to give an unstable intermediate product which has no place on the phase diagram. This intermediate product x then begins to decompose into $\varepsilon + \gamma_3$, at temperatures between 900° and 800° C., so that only a small amount of the x-phase is found on examination by X-rays.

The ε-Phase ($CrAl_4$).

Gotō and Dōgane found that an alloy of this composition melted at 1011° C. This is in agreement with the present authors' heat-treatment experiments, where alloys containing 32 and 33 per cent. of chromium were quenched from 1000° C. They withstood this temperature successfully, except when they were previously heated to 1060° C., which caused them partially to melt. The range of the ε-phase is displaced towards the aluminium end at high temperatures. A 30 per cent. chromium alloy, which is $\varepsilon + \eta$ at room temperatures, becomes pure ε on quenching from 800° C., whereas a 34 per cent. alloy, which is pure ε after slow cooling, becomes $\varepsilon + \gamma_3$ after quenching from 800° C. On quenching from 930° C., a 32·5 per cent. alloy also becomes two-phase. The ε-phase coexists with the η-phase when the composition is on the aluminium side, and with the δ, γ_3, and γ_4 phases on the chromium-rich side. The empirical formula $CrAl_4$ corresponds to 32·52 per cent. of chromium, and is near the centre of the phase at low temperatures.

The η-Phase (Cr_2Al_{11}).

No phase of this composition was found by Gotō and Dōgane, but the X-ray evidence is clear as to its existence, range of compositions, and approximate melting point. It has been found in slowly cooled alloys and in those quenched from as high as 930° C. Since alloys containing less than 32 per cent. of chromium were found to have partially melted at 1000° C., it would seem that the η-phase decomposes between 930° and 1000° C. The range of homogeneity varies with the temperature, being slightly displaced towards the aluminium end at high temperatures. The empirical formula Cr_2Al_{11} corresponds to 25·96 per cent. of chromium, which agrees closely with the narrow range of the phase.

The θ*-Phase* ($CrAl_7$).

Gotō and Dōgane found that $CrAl_7$ decomposed at 725° C. The formula corresponds closely to the aluminium-rich boundary of the phase at 21·6 per cent. of chromium, and is in agreement with the work of Fink and Freche on the two-phase alloys. After dissolving out the aluminium solid-solution, the residue which was analyzed was found to be $CrAl_7$.

In the present experiments, a two-phase $\theta + \eta$ alloy was obtained by quenching a 24 per cent. alloy from 600° C., and a two-phase $\theta + \kappa$ alloy was obtained by quenching a 21 per cent. alloy from 710° C.; this confirms the existence of the θ-phase up to 710° C. After quenching from 800° C., a 24 per cent. alloy contained the η-phase mixed with κ, the aluminium solid-solution; this proves that the θ-phase decomposes between 710° and 800° C., in agreement with Gotō and Dōgane. At 800° C. the alloy must have been composed of η mixed with a small amount of the liquid phase, which was held in the interstices of the alloy. During the process of quenching, this aluminium-rich liquid solidifies as a mixture of η and κ without reacting to form θ.

The θ-phase ($CrAl_7$) crystallizes from the melt in the form of pseudo-hexagonal needles. These were examined by the oscillation and Laue methods, which showed that the crystals were orthorhombic (pseudo-hexagonal).

$$a = 19{\cdot}99 \text{ A.} \qquad b = 34{\cdot}51 \text{ A.} \qquad c = 12{\cdot}47 \text{ A.}$$

The authors are indebted to Dr. I. Fankuchen for Weissenberg photographs which confirm these measurements. The pseudo-hexagonal symmetry was also confirmed by goniometer measurements, kindly made by Dr. H. E. Buckley.

The κ*-Phase (Aluminium Solid-Solution) and the Liquidus.*

According to Fink and Freche, pure aluminium dissolves up to 0·8 per cent. of chromium depending on the temperature. These results are incorporated in the phase diagram (Fig. 2), and their observations give the liquidus up to 790° C. Beyond this temperature the present authors have followed approximately the work of Gotō and Dōgane, who give the liquidus up to 1170° C. This temperature is attained by an alloy with 36 per cent. of chromium, and beyond this composition there is no more satisfactory information.

In conclusion, it is interesting to note the extraordinary resemblance between all the powder photographs of the chromium–aluminium system. The positions of the strongest lines fall at nearly the same angles in every phase. In particular, a line corresponding to 110 of a body-centred cubic lattice is present in every one of the photographs. This behaviour may perhaps be explained by the Jones–Brillouin [8] theory of alloy phases.

ACKNOWLEDGMENTS.

The authors are greatly indebted to Professor W. L. Bragg, F.R.S., for his very great interest in the work, which was carried out in the Physical Laboratories of the University of Manchester.

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ALLOYS OF MAGNESIUM. PART V.—THE CONSTITUTION OF THE MAGNESIUM-RICH ALLOYS OF MAGNESIUM AND CERIUM.* 756

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T. H. SCHOFIELD,‡ M.Sc., Member.

Synopsis.

The constitution of the magnesium-rich alloys of magnesium and cerium has been re-determined. The eutectic point is found to be at 21 per cent. cerium and 590° C. Magnesium dissolves about 1·6 per cent. cerium at the eutectic temperature and probably less than 0·15 per cent. at 337° C.

I. Introduction.

This report is Part V of the investigation of the constitution and mechanical properties of magnesium alloys which is being conducted at the National Physical Laboratory under the direction of Dr. C. H. Desch, F.R.S., for the Metallurgy Research Board of the Department of Scientific and Industrial Research.[1, 2, 3, 4]

Recent research has shown that the mechanical properties of some magnesium alloys at elevated temperatures are improved by the addition of small amounts of cerium. The present work has been carried out to confirm, and possibly supplement, existing information on the constitution of the cerium–magnesium alloys and has been extended to alloys containing up to about 40 per cent. cerium in order to establish the composition of the eutectic and to confirm the existence of a peritectic reaction. The solid solubility of cerium in magnesium has also been determined.

II. Previous Work.

Although Muthmann and Beck[5] were probably the first to prepare cerium–magnesium alloys, the only systematic study carried out was that by Vogel,[6] who investigated the constitution in some detail. Using fairly pure magnesium and cerium containing 6·5 per cent. of

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* Manuscript received August 22, 1936. Presented at the Annual General Meeting, London, March 11, 1937.

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impurities, he found the eutectic point to be about 27 per cent. cerium and 585° C. No evidence of solid solubility was given.

III. Present Work.

Preparation of the Alloys.

The magnesium was supplied by British Maxium, Ltd., and contained as impurities: aluminium 0·018; iron 0·020; silicon 0·013 per cent.

The cerium, kindly given by La Société de Produits Chimiques des Terres Rares, contained 97·7 per cent. cerium and 1·25 per cent. iron.

The alloys were prepared by adding cerium in small quantities to molten magnesium under a flux in a stainless steel crucible. They were cast into smaller stainless iron crucibles of the type previously described[1]; the excess was cast into iron moulds, and a vertical slice cut from the ingots was used for chemical analysis; in some cases the remainder was used for the preparation of other alloys and for microscopical examination. The flux had the same composition as that employed previously, and a minimum quantity was used for each melt.

Thermal Analysis.

Heating and cooling curves of nine alloys were recorded. Because of the large difference in specific gravity between cerium and magnesium, it was deemed advisable to carry out the thermal analysis in the stirring apparatus designed by Payne.[7] Most of the thermal curves were recorded on an inverse-rate recorder by means of manual signals depending on observations of a deflection potentiometer, but some were recorded automatically on the recorder by means of an automatic potentiometer [8] actuated by a photoelectric cell.

Two heating and two cooling curves of each alloy were recorded, and as the temperature arrest of the liquidus taken from the first and second pair of curves agreed closely it was assumed that no appreciable change in composition had taken place during the taking of the curves. After the curves had been taken, the metal was remelted in the crucible and cast into an iron chill. In certain cases the ingots thus obtained were analyzed, and the cerium content was always less than that of the alloy before taking thermal curves. This discrepancy was probably due to losses caused by adding new flux when remelting the alloy from the thermal curve crucible. That considerable loss could be caused in this way was shown by the analysis of the flux from one of the rich cerium alloys which gave 18·5 per cent. cerium. Cooling curves of two alloys were taken down to 360° C., but no arrest points were observed below the eutectic temperature.

The results of the present work and of Vogel's work are embodied in Figs. 1 and 2, respectively.

Microscopical Examination.

The specimens were rubbed down by hand on emery paper and polished on velvet with metal polish. Specimens of cerium content near and beyond the eutectic were brittle and were mounted in Bakelite before polishing.

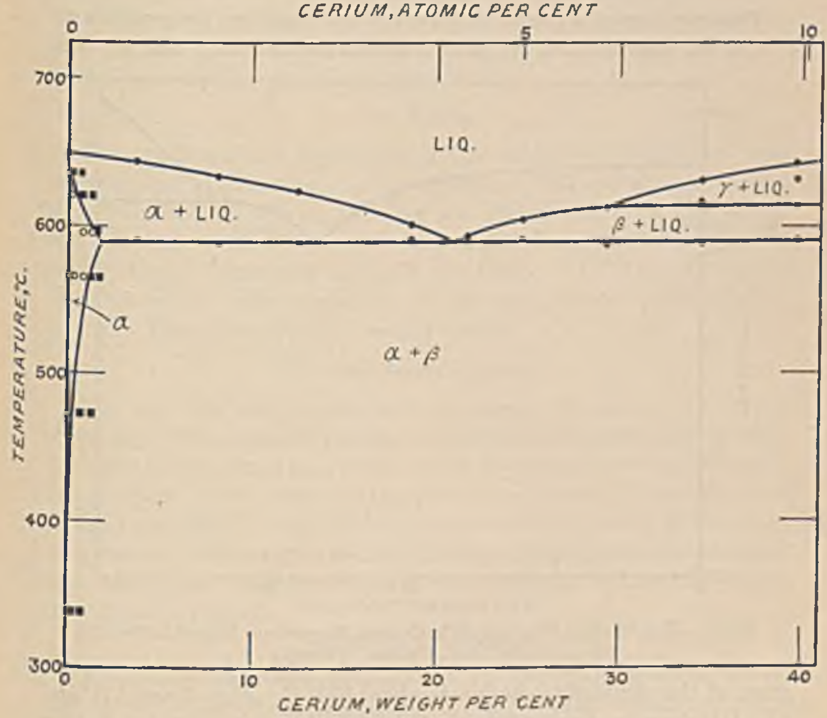

Fig. 1.

Fig. 1.—Equilibrium Diagram of the Cerium–Magnesium Alloys Containing up to 40 Per Cent. Cerium. (Haughton and Schofield.)

The specimens were etched either in a 4 per cent. solution of nitric acid in alcohol or in a mixture of citric acid, nitric acid, and glycerine. All specimens used for the determination of the solidus and solid solubility were annealed in hydrogen contained in sealed tubes of Pyrex glass. Quenching was done by pushing the tube containing the specimens directly into cold water.

The Liquidus.

The liquidus differs in temperature and form from that plotted from Vogel's data; the former falls less steeply and is below the latter. It should be noted that the temperature of the melting point of magnesium given by Vogel is high (661° C.).

The Peritectic Reaction.

The existence of a peritectic observed by Vogel has been confirmed by thermal analysis and by microscopical examination. The temperature of the peritectic reaction is about 614° C. Figs. 3 and 4 (Plate XLVIII) show an alloy containing 39·7 per cent. cerium as cast and after annealing at 565° C. for 6 hrs., respectively. The cooling curves of this alloy showed four definite arrests, one of which was close to the peritectic; no explanation is put forward for one arrest point which suggests increasing complexity of the system. Investigation of the diagram beyond this point, however, lies outside the scope of the present work.

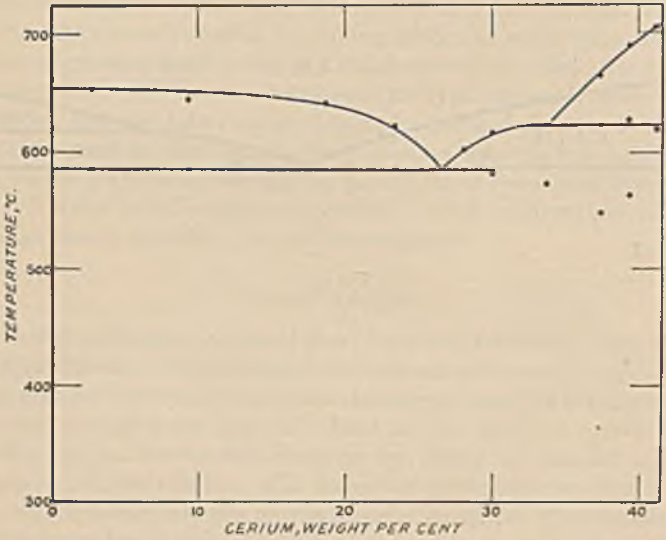

Fig. 2.—Equilibrium Diagram of the Cerium-Magnesium Alloys Containing up to 40 Per Cent. Cerium. (Vogel.)

The Eutectic.

From thermal evidence, the eutectic point was found to be at 21 per cent. cerium and 590° C., compared with about 27 per cent. cerium and 585° C. from Vogel's data. Confirmation of this was obtained by microscopical evidence. Figs. 6 and 7 (Plates XLVIII and XLIX) show the structure of alloys containing 24·7 and 18·6 per cent. cerium, respectively, and illustrate the primary separation on either side of the eutectic. Fig. 8 (Plate XLIX) shows the structure of an alloy containing 21·6 per cent. cerium and shows that it contains a small amount of hypereutectic primary. It was possible to distinguish between the two primaries by etching in boiling water which stained the α primary brown but left the β primary unchanged. Photographs illustrating the etch are not reproduced because liquid exuding from the numerous holes in the specimen caused a tarnish film to spread over the surface and rapidly spoiled its appearance.

The Solidus.

The position of the sloping part of the solidus was determined from microscopical examination of alloys quenched after annealing at various temperatures. All alloys, both for the determination of the solidus and the solid solubility line, were first annealed at 565° C. for 6½ hrs. to render them homogeneous. Fig. 5 (Plate XLVIII) shows the structure of an alloy containing 1·7 per cent. cerium quenched from 595° C. The chilled liquid is readily visible.

The Solid Solubility Line.

The solid solubility of cerium in magnesium was determined microscopically. Specimens of suitable composition were annealed at 565°, 472°, and 337° C. for 12 hrs., 40 hrs., and 5 weeks, respectively. Although microscopical examination led to conclusive evidence of the amount of solubility at 565° C., some doubt exists as to the solubility at the lower temperature; this was due to the difficulty in identifying small amounts of a second phase in the presence of small amounts of impurity originating from the cerium.

Magnetic Properties.

It has been discovered that some of the cerium–magnesium alloys, and certainly those containing about 20–40 per cent. cerium, are magnetic in that they are feebly attracted by a strong permanent magnet. It seems improbable that the magnetism can be solely due to the iron in the cerium because the latter is not attracted by a magnet.

IV. Conclusions.

The constitution of the magnesium-rich alloys of magnesium and cerium has been determined. The eutectic point is found to be at 21 per cent. cerium and 590° C., compared with about 27 per cent. and 585° C. observed by Vogel, who used much less pure metals than were employed in the present investigation. Vogel did not determine the solubility of cerium in magnesium, which is now shown to be about

1·6 per cent. at the eutectic temperature, and probably less than 0·15 per cent. at 337° C. The existence of the peritectic observed by Vogel has been confirmed, though at a slightly lower temperature (614° C.). Some of the alloys are found to be very feebly magnetic.

V. Acknowledgments.

The authors wish to express their thanks to Dr. C. H. Desch, F.R.S., under whose supervision the work was carried out. They are also indebted to Messrs. P. Ward, B.Sc., and W. H. Withey, B.A., for carrying out the analyses of the alloys. They would also like to express their gratitude to the Société de Produits Chimiques des Terres Rares who have, on several occasions, supplied them, gratis, with both cerium and "Mischmetall" for this work and for the work on mechanical properties referred to at the beginning of this paper.

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[2] W. E. Prytherch, *J. Inst. Metals*, 1935, **56**, 133.
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[5] W. Muthmann and H. Beck, *Liebig's Ann.*, **331**, 46.
[6] R. Vogel, *Z. anorg. Chem.*, 1915, **91**, 277.
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DISCUSSION.

Mr. A. J. Murphy,* M.Sc. (Member): The relation between the work on the magnesium alloys at Teddington and that on the mechanical properties may obviously lead to great developments, particularly in the use of these alloys at elevated temperatures, from which applications magnesium alloys generally have been excluded up to the present. Presumably we must wait some time longer before we have an indication, based on the constitutional diagram or diagrams, of the reasons for the good properties of these new alloys at high temperatures.

Throughout the paper the material is described as cerium; on p. 340 it is stated to contain 97·7 per cent. cerium and 1·25 per cent. iron. Does that mean precisely what it says? The cerium most readily obtainable is actually "Mischmetall," which rarely contains more than 60 per cent. of cerium, the remainder being closely related metals. Possibly, and indeed probably, in the present case that does not much matter, because no doubt all the other metals can be counted as cerium. One never knows, however, when it may be necessary to differentiate between their effects, and it would be useful if it were indicated whether the true cerium content of the metal used was 97·7 per cent. or whether 97·7 per cent. represents the total of the rare earth metals.

Mr. Schofield (*in reply*): A specially pure sample of cerium was given for this work by La Société de Produits Chimiques des Terres Rares, who stated that it was almost free from other rare earth metals, which we have made no attempt, however, to estimate. Most of the alloys for the work on the mechanical properties were prepared from "Mischmetall" containing about 55 per cent. cerium.

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* Chief Metallurgist, J. Stone and Company, Ltd., Deptford.

PLATE XLVIII.

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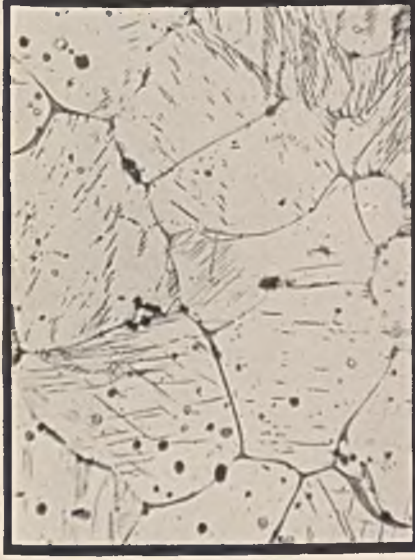

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FIG. 3.—39·7% Cerium, As Cast. Etched in 4% Nitric Acid in Alcohol. × 500.

FIG. 4.—39·7% Cerium, Annealed at 565° C. for 6 Hrs. and Quenched. Etched in 4% Nitric Acid in Alcohol. × 300.

FIG. 5.—1·7% Cerium, Quenched from 595° C. Etched in Citric Acid, Nitric Acid, and Glycerine. × 150.

FIG. 6.—24·7% Cerium, As Cast. Etched in Citric Acid, Nitric Acid, and Glycerine. × 150.

[*To face p.* 344.

PLATE XLIX.

7

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FIG. 7.—18·6% Cerium, As Cast. Etched in Citric Acid, Nitric Acid, and Glycerine. × 150.

FIG. 8.—21·6% Cerium, As Cast. Etched in Citric Acid, Nitric Acid, and Glycerine. × 150.

THE SOLUBILITY OF SILVER AND GOLD IN SOLID MAGNESIUM.* 752

By WILLIAM HUME-ROTHERY,† M.A., D.Sc., MEMBER, and EWART BUTCHERS,‡ B.A., B.Sc.

SYNOPSIS.

The solid solubility of silver in solid magnesium has been investigated above 300° C., and the solidus and solid solubility curves of the magnesium-rich solid solution have been determined. The maximum solubility of silver in magnesium is 3·9 atomic per cent. (15·3 per cent. by weight) at the eutectic temperature (471° C.), and the solubility decreases with decreasing temperature to 0·9 atomic per cent. (3·9 per cent. by weight) at 300° C. The maximum solubility of gold in solid magnesium is of the order 0·1 atomic per cent. at 576° C., and the solubility decreases with decreasing temperature.

INTRODUCTION.

PREVIOUS work on alloys of copper and silver with the elements of the B Sub-Groups, including those of the first two Short Periods, led to the hypothesis of the "relative valency effect."[1] According to this, in a binary system where the metals have different valencies, the primary solid solution in the element of lower valency tends to be of greater extent than that in the element of higher valency. The object of the present investigation was to test this hypothesis for the systems silver–magnesium and gold–magnesium, where the "size-factors"[2] are favourable. The work of Schemtschushny[3] and Saeftel[4] on magnesium–silver alloys, and of Vogel[5] and Urasow[6, 7] on magnesium–gold alloys shows that silver and gold take up at least 20–30 atomic per cent.§ of magnesium into solid solution. The results obtained in the present work confirm the hypothesis of the relative valency effect, since the maximum solubilities of gold and silver in magnesium are only 3·9 and < 0·2 atomic per cent. respectively.

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* Manuscript received June 3, 1936. Presented at the Annual General Meeting, London, March 11, 1937.

† Royal Society Warren Research Fellow, Oxford.

‡ Keble College, Oxford.

§ The form of the magnesium–silver equilibrium diagram is at present in dispute since Saeftel claims that the *α* solid solution in silver extends up to 65 atomic per cent. of magnesium.

EXPERIMENTAL METHODS.

General.

By the kindness of the Aeronautical Research Committee and the National Physical Laboratory, the authors were presented with magnesium of 99·95 per cent. purity, and with a magnesium–gold ingot from which the magnesium–gold alloys were prepared. For the magnesium–silver alloys the magnesium was melted with 99·99 per cent. silver grain supplied by Messrs. Johnson, Matthey & Company, Ltd. The alloys were melted under flux in crucibles lined with alumina and fluorspar, and prepared by the Morgan Crucible Company, Ltd. The flux used contained 896 parts by weight of anhydrous magnesium chloride, 320 parts potassium chloride, 60 parts sodium chloride, and 40 parts calcium fluoride. The alloys were then cast into heavy copper moulds giving cylindrical ingots of $\frac{3}{8}$ in. and $\frac{1}{4}$ in. diameter, with a very fine microstructure.

For the annealing experiments the alloys were enclosed in sealed evacuated glass tubes, and heated in tubular resistance furnaces controlled by a Foster temperature regulator, by means of which the temperature was kept constant to within ± 2° C. in all the critical experiments. At the end of each annealing treatment the alloys were quenched in cold water. In the determination of the solidus curve in the system magnesium–silver, the specimens, after a preliminary annealing treatment, were heated for 30 minutes at the desired temperature before quenching; in this work the temperature was controlled by hand adjustment of the resistances in the furnace circuit, and the constancy of the control was gradually increased from ± 0·8° to ± 0·3° C. The temperature was measured by an Alumel–Chromel thermocouple with its tip touching the sealed tube containing the alloy, the thermocouple being calibrated against the melting points of aluminium, the aluminium–copper eutectic, zinc, lead, and tin.

Microscopic Examination.

After grinding on emery papers, the specimens were polished on a cloth smeared with oil and magnesia. The structures of the magnesium–gold alloys, and of the two-phase magnesium–silver alloys were easily revealed by etching with a solution containing four drops of Tinofeff's reagent * in 10 c.c. of alcohol. For the homogeneous magnesium–silver alloys the best results were obtained by repeated etching in a more concentrated solution containing 18 drops of Tinofeff's reagent to each 10 c.c. of alcohol, the specimen being polished lightly after

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* This reagent consists of a mixture of 4 parts of chromic acid and 96 parts of nitric acid.

each immersion. Although this treatment revealed the crystal grains clearly, it tended also to produce etch pits, but these could readily be distinguished from the bluish particles of the second constituent in the two-phase alloys. Photomicrographs are not reproduced, since the alloys showed quite typical homogeneous or two-phase structures.

Chemical Analysis.

The magnesium–silver alloys were analyzed by one of the authors (E. B.), the silver being determined gravimetrically as chloride, and the magnesium as pyrophosphate. The sum of the percentages of the two metals determined by analysis varied between the limits 99·95 and 100·09 in all the alloys of critical composition. The magnesium–gold alloys were analyzed by Mr. R. G. Johnston of the Midland Laboratory Guild, Ltd.; the gold was weighed as metal after precipitation from solution in hydrochloric acid by means of sulphur dioxide, and the magnesium determined as pyrophosphate. The sum of the percentages of the two metals determined by analysis varied from 99·90 to 99·95.

EXPERIMENTAL RESULTS.

(a) *Magnesium–Silver.*

TABLE I.—*The Solidus Curve.*

Preliminary Treatment.—Before being used for the experiments described in this Table, the alloys received a preliminary annealing treatment of at least 9½ days at 450°–460° C., and all except the first and last mentioned alloys had previously been annealed for 6 days at 420° C. or 8 days at 440° C.

Silver.		Quenching Temperature, ° C.	Microstructure.
Weight Per Cent.	Atomic Per Cent.		
2·63	0·60	613	α + a little chilled liquid
		601·5	α
4·37	1·02	588·5	α + chilled liquid
		581	α
5·26	1·23	575·5	α + a little chilled liquid
		563·5	α
8·77	2·12	542	α + chilled liquid
		532	α
10·13	2·48	522·5	α + a little chilled liquid
		512	α
12·33	3·07	504	α + chilled liquid
		493	α
13·92	3·51	483·5	α + a little chilled liquid
		473	α

This system was investigated by Schemtschushny,[3] who observed no solid solution in magnesium, but obtained an equilibrium diagram in which pure magnesium formed a eutectic with the compound Mg_3Ag, the eutectic horizontal being at 469° C. The present work confirms the eutectic temperature as lying between the limits 470° and 473° C., but shows that a definite solid solution exists, the limits of which decrease from a maximum of 3·9 atomic per cent. of silver (15·3 per cent. by weight) at the eutectic temperature to 0·9 atomic per cent. of silver (3·9 per cent. by weight) at 300° C.

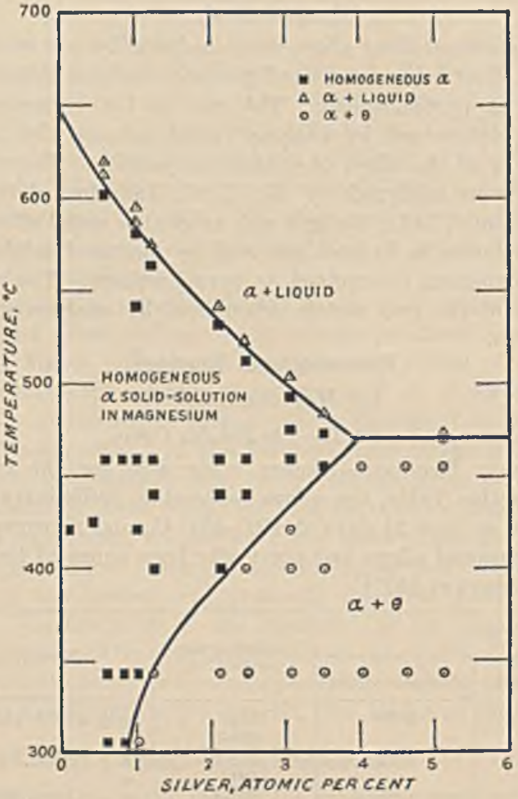

Fig. 1.

The results of the solidus determinations are shown in Table I, and are included in Fig. 1 which also shows the results of the annealing experiments given in Table II. For brevity, only the critical points near to the solubility and solidus curves are given in these Tables, but the additional points obtained in the course of the work are included in Fig. 1. The Tables are self-explanatory, and the results confirm that the solubility of silver in solid magnesium is very much less than that of magnesium in solid silver.

TABLE II.—*The Solid Solubility Curve.*

Silver Composition.		Annealing Treatment.		Micro-structure.	Remarks.
Weight Per Cent.	Atomic Per Cent.	Preliminary.	Final.		
15·68	4·02	none	13 days, 455° C.	$\alpha + \theta$	This alloy remained two-phase when re-annealed at 400°, 343°, and 306° C. after the above high-temperature treatment.
13·92 13·92	3·51 3·51	none *	13 days, 455° C. 5 days, 400° C.	α $\alpha + \theta$	This alloy remained two-phase when re-annealed at 313° and 306° C. after being made homogeneous by a preliminary anneal at 450°–460° C.
12·33 12·33	3·07 3·07	6 days, 421° C. none	9½ days, 459° C. 6 days, 421° C.	α $\alpha + \theta$	
10·13 10·13	2·48 2·48	none *	8 days, 440° C. 5 days, 400° C.	α $\alpha + \theta$	
8·77 8·77	2·12 2·12	* 8 days, 400° + 9½ days, 459° C.	5 days, 400° C. 8 days, 343° C.	α $\alpha + \theta$	
5·26 5·26	1·23 1·23	* 8 days, 440° + 9½ days, 459° C.	5 days, 400° C. 8 days, 343° C.	α $\alpha + \theta$	
4·37 4·37	1·02 1·02	6 days, 421° + 9½ days, 459° C. †	8 days, 343° C. 8 days, 306° C.	α $\alpha + \theta$	
3·59	0·83	9½ days, 459° C. + 8 days, 343° C.	8 days, 306° C.	α	

In this Table, the primary solid solution in magnesium is denoted α, and the second phase θ; if the diagram of Schemtschushny is correct, the θ phase is the compound Mg_3Ag.

* After being used for the series of experiments at 343° C., these alloys were made homogeneous by annealing at 404° C. for 5 days followed by 2 days at 460° C., and were then used for the final experiments at 400° C.

† This experiment was made with the specimen found to be homogeneous after quenching from 343° C.

Magnesium–Gold.

The equilibrium diagrams of Vogel[5] and Urasow[6] show no solid solution in magnesium, and indicate that pure magnesium forms a eutectic with the compound $AuMg_3$, the eutectic horizontal being at 576° C. In the present work the eutectic horizontal was determined by the quenching method as lying between the limits 575·5° and 580° C., in good agreement with the previous data. For the solid solubility determinations alloys containing 0·21 and 0·33 atomic per cent. of gold were prepared together with others of higher gold content. These were given a preliminary annealing treatment of 2 days at 400° C.

followed by 5 days at 518° C., and were then annealed at 567° for 10 days. After this treatment all the alloys were two-phase. The same specimens were then re-annealed at 459° for 10 days, examined microscopically, and annealed again at 343° C. for a further 8 days. The amounts of the second phase present in the alloys increased slightly, but definitely, after the final annealing treatments at the lower temperatures. From the relative amounts of the second phase in the different alloys, it was concluded that the solid solubility of gold in magnesium is of the order 0·1 atomic per cent. at the eutectic temperature, and decreases to even smaller amounts at lower temperatures. The microscopic method is not well suited to the determination of such very narrow ranges of solid solution in magnesium, and since the relative valency effect is clearly confirmed the subject was not investigated further.

ACKNOWLEDGMENTS.

The authors express their gratitude to Professor F. Soddy, F.R.S., for kindly providing laboratory accommodation and many other facilities which greatly helped the work described in this paper. Grateful acknowledgment is also made to the Council of the Royal Society for the election of one of the authors (W. H.-R.) to a Research Fellowship, and to the Aeronautical Research Committee and the Fellows of Keble College, Oxford, for grants towards the expenses of the research. Special thanks are also due to Dr. C. H. Desch, F.R.S., and to Dr. J. L. Haughton for their help in obtaining materials, and to Mr. R. G. Johnstone for his skill in connection with the analysis.

THE OLD CHEMISTRY DEPARTMENT,
THE UNIVERSITY MUSEUM,
OXFORD.

April, 1936.

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ALLOYS OF MAGNESIUM. PART IV.—THE CONSTITUTION OF THE MAGNESIUM-RICH ALLOYS OF MAGNESIUM AND SILVER.*

By R. J. M. PAYNE,† B.Sc., Member, and J. L. HAUGHTON,‡ D.Sc., Member of Council.

Synopsis.

The form of the liquidus and the values obtained for the eutectic and peritectic temperatures by other workers have been checked in magnesium–silver alloys containing up to 60 weight per cent. of silver. It was found that solid magnesium can hold in solution up to 15 weight per cent. of silver at the eutectic temperature, but less than 1 weight per cent. of silver at 200° C. The alloys should, therefore, be capable of precipitation-hardening.

This report forms Part IV [1] of the investigation into the constitution and mechanical properties of magnesium alloys which is being conducted at the National Physical Laboratory, under the direction of Dr. C. H. Desch, F.R.S., for the Metallurgy Research Board of the Department of Scientific and Industrial Research; the three previous reports were published in this *Journal*.[1,2,3]

The addition of small proportions of silver to some magnesium alloys has been found to have good effects, particularly in maintaining the tensile strength at high temperatures, and this research was carried out to confirm and to supplement existing information on the constitution of the binary alloys of magnesium and silver.

The investigation was limited at the outset to include only alloys necessary for checking the composition of the eutectic. The alloy richest in silver which was dealt with contained 59·57 weight per cent. silver.

Previous Work.

The system magnesium–silver has been studied, as a whole or in part, by Schemtschushny, by Smirnow and Kurnakow, and by Saeftel.

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* Manuscript received June 19, 1936. Presented at the Annual General Meeting, London, March 11, 1937.

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‡ Principal Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

Schemtschushny [4] studied the complete range of alloys by the methods of thermal analysis and microscopic examination; his results, up to about 65 per cent. silver, are given in Fig. 1. With regard to the magnesium-rich end of the diagram, he found the eutectic point at 17·3 atomic per cent. silver (= 48·14 weight per cent.) and at 469° C. No evidence was given for the existence of solid solubility.

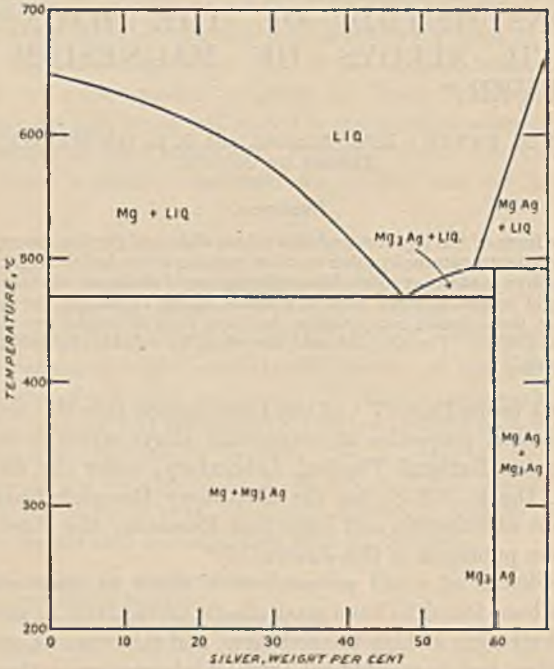

FIG. 1.—Equilibrium Diagram of the Magnesium–Silver Alloys Containing up to 65 Per Cent. Silver. (Schemtschushny.)

Smirnow and Kurnakow [5] studied the electrical properties and hardness of the alloys, and indicated that silver was soluble in solid magnesium to the extent of about 12 weight per cent. silver.

Saeftel [6] confined his investigation to the silver-rich alloys.

PREPARATION OF THE ALLOYS.

The magnesium used contained about 99·95 per cent. magnesium; the impurities being: copper 0·006, iron 0·038, and aluminium 0·010 per cent.

The silver used was supplied by the Sheffield Smelting Company, Ltd., and contained 0·0005 per cent. lead as the only impurity.

The alloys were prepared by melting the magnesium in a stainless-steel crucible under flux, and adding the silver to it. It was found necessary to exercise care to keep the surface of the alloys from contact with the air. When molten the alloys were cast into stainless-iron thermal-curve crucibles and the surface covered with a little flux, composed of magnesium chloride 450, sodium fluoride 30, calcium fluoride 20, and potassium chloride 160 grm. After making the thermal curves, the alloys were carefully remelted in the crucibles and cast into a horizontal chill ingot mould. The ingots thus obtained were analyzed, and were afterwards used to provide samples for microscopic study. Analysis showed that there was no contamination of the alloys by the material of the crucibles.

The figure given by the analysis of the material after melting and casting was considered to be as near an estimate as could be obtained of the composition of the alloy at the time when the curves were being made, in spite of a slight loss of silver which occurred during the re-melting operation. It was thought inadvisable to sample the alloys by taking drillings from the metal while it was still in the crucible, owing to the possibility of segregation.

THERMAL ANALYSIS.

Five alloys were examined by the method of thermal analysis to check the accuracy of the work of Schemtschushny. These alloys contained 19·72, 33·31, 42·88, 50·83, and 59·57 per cent. by weight of silver. It was anticipated that with alloys made from two metals of widely different densities, such as magnesium and silver, some trouble due to segregation of the silver compound would be encountered (cf. the report on alloys of magnesium and nickel).[1] The thermal analysis of these five alloys was carried out, therefore, in the apparatus which was used for the study of the magnesium–nickel alloys[7] and which was designed to minimize the effects of segregation on thermal curve samples. As will be seen, the results obtained on stirred specimens agree fairly well with those of Schemtschushny who used no stirring. The employment of the apparatus occasioned little additional trouble whether essential to accuracy or not.

The thermal curves were plotted by means of the deflection potentiometer and inverse-rate recorder. Two heating and two cooling curves were obtained for each alloy, and the close agreement between the temperatures of the liquidus arrest taken from the first and the second curve of each kind indicated that no appreciable change of composition had occurred during the making of the curves. The results are shown in Fig. 2. The liquidus for the hyper-eutectic alloys

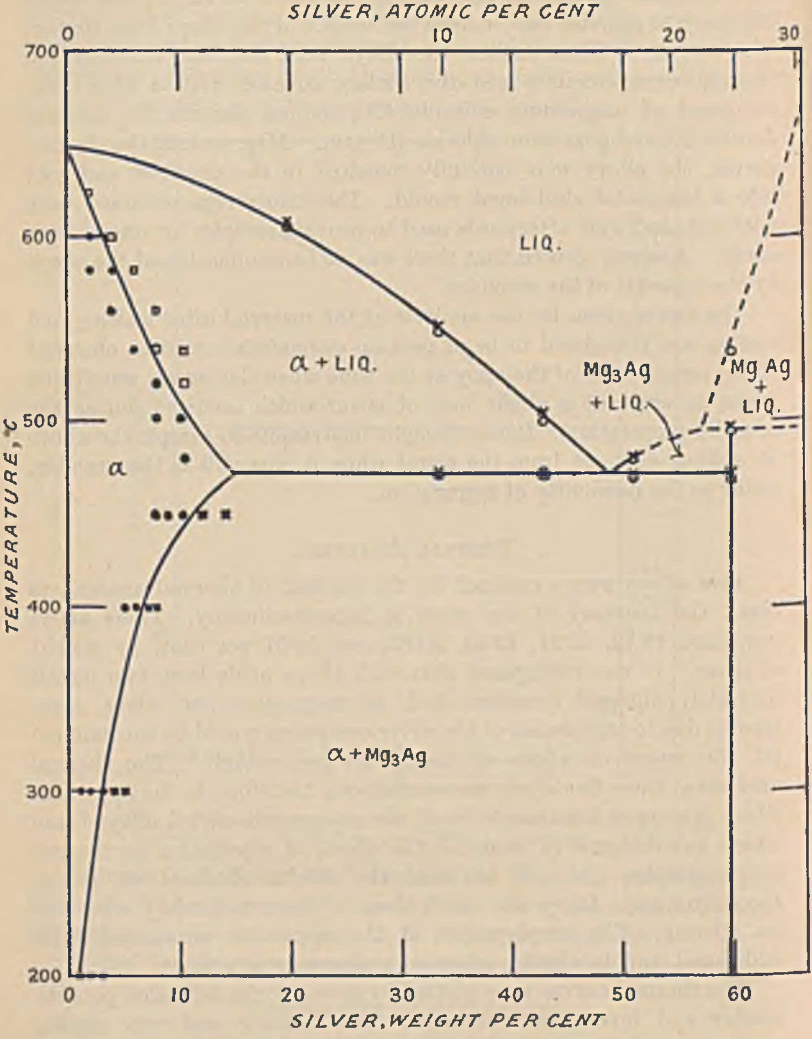

FIG. 2.—Equilibrium Diagram of the Magnesium–Silver Alloys Containing up to 65 Per Cent. Silver. (Haughton and Payne.)

(shown by a broken line) is taken from the work of Schemtschushny. Curves were taken for one alloy containing 19·72 per cent. silver down to room temperature, but no arrests were found below the eutectic temperature.

MICROEXAMINATION.

The microspecimens were polished by hand with metal polish on velvet. The etching of duplex alloys presented little difficulty, a dilute solution of nitric acid in alcohol staining the α solid solution brown whilst leaving the compound Mg_3Ag unaffected. With homogeneous alloys it was found impossible to etch grain boundaries, all the reagents tried giving only the (often irregular) brown tarnish film. Moreover, reagents such as alcoholic nitric acid were found to be unreliable in action. However, when trying the effect of organic acids it was found that by adding hydrogen peroxide to a concentrated solution of tartaric acid in alcohol, an etching reagent was obtained which gave more consistent results. This mixture also stained the solid solution and enabled any compound present to be distinguished by colour contrast, but it produced a more uniform film than the nitric acid and gave more reproducible results. If no white patches were to be seen when a specimen had been etched with this mixture, properly prepared,* it could safely be concluded that the specimen was homogeneous. It was found afterwards that Smirnow and Kurnakow had recommended the use of a similar reagent (hydrogen peroxide plus alcoholic citric acid) for these alloys. The reagent was also found suitable for detecting fusion spots in those alloys which were used in determining the solidus.

THE LIQUIDUS.

The liquidus plotted from these observations will be seen to agree quite well with that of Schemtschushny: perhaps rather surprisingly well in view of the fact that no consideration was given by him to the effects of segregation. No arrest was obtained on heating curves with the alloys containing 59·57 per cent. silver.

THE PERITECTIC REACTION.

The mean of the temperatures of the peritectic reaction obtained on heating and on cooling the only alloy which falls within this range is 495·5 C.

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* This reagent was prepared by placing crystals of tartaric acid in excess in industrial methylated spirit and adding hydrogen peroxide (40 vol./c.c.) to the saturated solution in sufficient quantity to produce the film. The action of the combination is complicated by the fact that the hydrogen peroxide itself contains free acid.

THE EUTECTIC.

Although the present work does not really establish the liquidus for hyper-eutectic alloys nor, consequently, the composition of the eutectic alloy, the liquidus point for the only hyper-eutectic alloy examined (50·83 per cent. Ag) fell exactly on the liquidus curve obtained by Schemtschushny. This was considered to be sufficient evidence that the latter was substantially correct over the part under consideration, and, taking this in conjunction with the authors' determination of the hypo-eutectic branch of the liquidus, the eutectic between magnesium and Mg_3Ag was found to occur at 48·6 per cent. silver and at 472° C. The temperature of the eutectic arrest obtained from the heating curves of the different alloys vary less from a mean value than do those obtained from cooling curves. The maximum difference between the temperatures of the arrests on heating and cooling for any one alloy is 4° C.

THE REMAINING BRANCH OF THE SOLIDUS.

This was determined by quenching samples of alloys which had been annealed at temperatures above that of the eutectic.

Alloys intended for this purpose were first annealed for 6 days at 450° C. to render them homogeneous. The high temperature annealings were (with one exception) carried out in a bath of molten flux, and specimens were held at the required temperature for 15 minutes before quenching. Fusion spots were readily detected microscopically.

THE SOLID SOLUBILITY OF SILVER IN MAGNESIUM.

This was determined by microscopic methods at 450°, 400°, 300°, and 200° C. Preliminary annealings showed that a period of 7 days was sufficient for equilibrium conditions to be attained at 400° C. A period of 4½ days was adjudged to be adequate for annealings carried out at 450° C. Specimens for annealing at 300° and 200° C. were given an initial solution treatment of 7 days at 400° C., and were slowly cooled to the final annealing temperature. All annealings were carried out *in vacuo*.

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JOINT DISCUSSION.

Dr. S. W. Smith,* C.B.E., A.R.S.M. (Member): Mr. Payne and Dr. Haughton have confirmed and supplemented the work of the well-known Russian investigator Schemtschushny. How close is the confirmation of that work which was carried out 30 years ago, is shown by the fact that whereas Schemtschushny found the eutectic at 48·14 per cent. of silver, the present authors put it—rather by computation and not, I think, by exact determination—at 48·6 per cent., while the corresponding temperatures of solidification were, in the earlier work 469° C. and according to the present authors 472° C., a difference of only 3° C., which is actually 1° less than the difference which the authors themselves say may occur between the arrests of heating and of cooling, namely 4° C.

With regard to the preparation of the alloys, the authors adopt the procedure of melting in a stainless steel crucible and then, for the purpose of their thermal curves, they transfer a portion to a stainless iron thermal-curve crucible. To obtain specimens for annealing and quenching they cast in a horizontal chill mould. The fact that they have given no indication of how they sampled the alloys leaves a little doubt in my mind as to whether they are fully aware of the very considerable variations which may occur in such alloys when chill-cast in this way. They mention, however, a slight loss of silver which occurred during the re-meltings. One would rather expect, of course, that there would be a loss of magnesium and that the silver content would increase, and I think, therefore, that that must mean only that the loss of silver exceeded that of magnesium, because it seems most unlikely that they did not lose some magnesium. Perhaps it is unwise to speculate on why the loss of silver may be greater than that of magnesium, but we have had some such experience in trying to use magnesium in silver alloys in attempting to obtain sounder castings. Those particular trials were not very successful. A certain amount of silver–magnesium alloy certainly comes away from such alloys and may be left in the pot as a shell or a scum. That may explain perhaps why the investigation of this series at the silver-rich end does not appear to have received much attention. I have no wish, however, to be too critical of the technique which Mr. Payne and Dr. Haughton have used, because I know only too well the difficulties of obtaining, in small melts particularly, compositions which are aimed at, and also the difficulties of sampling them accurately. With regard to the thermal analysis, the authors took considerable precautions with regard to stirring with the object of avoiding any possible segregation, and they have a special apparatus for that purpose which they have described in an earlier paper and into which I need not go. In the paragraph headed "The Liquidus" they say "The liquidus plotted from these observations will be seen to agree quite well with that of Schemtschushny: perhaps rather surprisingly well in view of the fact that no consideration was given by him to the effects of segregation." On reading that, I wondered whether the authors quite realized where segregation comes in. I do not feel that in taking a cooling curve the effects of segregation are very much to be feared. There is probably no temperature gradient in a small mass of this kind, and it is difficult to see how a small amount of segregation, should it occur, can affect the initial freezing point or the final freezing point. When it comes to casting the metal in a chill mould, however, the effects of segregation may be very considerable.

It may be, of course, that the silver–magnesium alloys resemble the silver–zinc alloys, which do not segregate very much. I have no experience of this particular series, but looking at the diagram I should say that there

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* Royal Mint, London.

is possibly some liability to segregation, and that on the magnesium side of the eutectic it will be in the direction of an enrichment of the silver on the outside of the castings; *i.e.* the central and last portions to solidify are likely to be low in silver. I will not go into the grounds for making that suggestion.

I should like to say a word, however, about casting specimens in chill moulds. I rather prefer the method, adopted by Mr. Reynolds and Dr. Hume-Rothery in their study of the silver-rich silver–antimony alloys, of casting these specimens in a sand mould. There they have attempted to approximate to conditions in which there is very little temperature gradient, and they say that they have practically overcome the effects of segregation by casting in this way. I think that that is probably correct, because it is consistent with our experience. I should like, however, to go still further than that, and suggest that the metal might be left in the pot in which it was melted and allowed to solidify without any pouring or casting at all. We have found a great advantage in making use of that procedure in examining alloys of many compositions, *i.e.* we allow the metal to solidify as slowly as possible in the crucible without pouring. The fears of segregation under those conditions are not so great as might be imagined, and certainly not so great as when the metal is cast into a chill mould. There is the further advantage that by slow solidification the structure develops to its fullest extent. I often think that much of the long annealing to which specimens are subjected, running up to 7 or 8 days, might be partially obviated at any rate by starting with specimens which have been very slowly solidified.

Dr. D. STOCKDALE, M.A.[*] (Member): The work described in the paper by Mr. Payne and Dr. Haughton appears to be accurate, but anyone making a detailed study of this system can get his information only from Fig. 2. The points on the diagram must therefore be translated back into terms of percentages of silver and degrees before they can be used. This process must necessarily introduce some inaccuracy. I ask the authors, therefore, whether they could use equations to preserve their work. It may be easy to find equations for the solidus and α-phase boundary. These, and small deviations from them, could be given in four or five lines. If funds permit us to have tables such as Dr. Hume-Rothery and Mr. Butchers have given, so much the better.

A minor point is that Dr. Haughton is of the opinion that formulæ should not be introduced into equilibrium diagrams, as has been done here.[†]

Dr. M. HANSEN[‡] (Member): As I was not able to read these papers until this morning, I can make only a few general comments. Very little can be said on these two papers, because no real criticism can be made of modern work on these lines, especially when it is of the high standard of that presented this morning.

I am very much impressed by the fact that in the last 2 or 3 years a great deal of work has been done on magnesium alloys by the Department of Scientific and Industrial Research in this country, and I very much appreciate the fact that this work has been done so systematically. No doubt there is a very grave need for such research work, because magnesium will become more and more important in certain branches of engineering, and particularly in aircraft work. Unfortunately, magnesium is rather a base metal, and therefore the possibility of finding appropriate alloying elements is small. Zinc and aluminium are the two most important ones, and that is why in nearly all industrial alloys of magnesium such as those developed in Germany

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[†] *Monthly J. Inst. Metals*, 1937, 4, 79.

[‡] Dürener Metallwerk A.G. Hauptverwaltung, Berlin-Borsigwalde, Germany.

these two metals are present. I believe, therefore, that these two papers are more important from the scientific point of view.

If we compare the behaviour of copper, silver, and gold towards magnesium, and especially the solid solubility, we find that silver is soluble in solid magnesium to a rather high content, whereas copper and gold are practically insoluble and very little soluble, respectively. This is, I think, very remarkable, and the reason is worth seeking, because copper, silver, and gold form an allied group in the periodic system of elements. There is another example of the fact that silver may behave quite differently from copper and gold in alloying with a second metal. Copper and gold can form real alloys with iron; there is complete solubility of the two metals in iron in the liquid state, and both copper and gold can replace iron atoms in the α and γ iron lattices. Silver, on the other hand, cannot form an alloy with iron, and therefore in consequence of this there is no solubility of silver in iron.

Mr. REYNOLDS: Dr. Smith referred to our work on the silver–antimony alloys, in which we cast in sand moulds. We did that because it is generally recognized that if inverse segregation is suspected it is better to cast in sand than in a chilled mould. Since then, however, we have come to wonder, because, for instance, silver–aluminium can be cast beautifully in a steel or copper mould and there is no segregation, and I have since then cast silver–indium in a copper mould with no segregation, although, to be perfectly fair, I ought to add that I had to throw away two antimony alloys because they were badly inverse segregated. The only explanation that I can think of is that the principles have been worked out for larger quantities and that they will not apply to ingots ½ in. in diameter and 1½ in. long.

Dr. C. J. SMITHELLS,* M.C. (Member of Council): I think that Dr. Stockdale criticized the paper by Mr. Payne and Dr. Haughton on the ground that it was not possible to read from the diagram some of the points with sufficient accuracy where they really matter, whereas in the paper by Dr. Hume-Rothery and Mr. Butchers there is a table which gives the data for the points which are really important. The Publications Committee is quite prepared to publish both tables and curves when it is desirable and necessary to do so; there is no hard and fast rule; we do not, however, wish to publish tables and curves which merely duplicate each other. When, however, a diagram, and particularly an equilibrium diagram, cannot give information sufficiently accurately, there is no reason why a table giving the exact data at the really critical points should not also be included.

I should also like to point out that until recently, diagrams reproduced in the *Journal* were not reproduced to any definite scale. Now all diagrams are drawn so that the ordinates are simple multiples of either an inch or a centimetre; that enables one to read very much more accurately and easily than would otherwise be possible the exact position of points on these curves.

Mr. PAYNE (*in reply*): The question of the sampling of these alloys for analysis is bound up with the point about the loss of silver, which was, of course, due to dissolution in the protective fluxes used. The flux protected the alloy from oxidation, and therefore from appreciable loss of magnesium, but at the same time caused a loss of silver by the attack of the fluorides and chlorides of which it is composed. The thermal curve ingots were melted in the crucible and then poured into small horizontal chill moulds which were sectioned vertically, a parallel slice being taken from the centre of the ingot, for chemical analysis, and this I think gives a representative sample of the material.

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Dr. Smith is rather sceptical about the necessity for stirring, whereas we have found in previous work, particularly in our study of the magnesium–nickel alloys, that this stirring is very necessary. With these alloys we obtained liquidus arrest points when, starting from pure magnesium, we approached the eutectic, but they faded away about half way before the eutectic composition was reached. On the other branch of the liquidus, and working backwards from the compound Mg_2Ni we obtained one or two points which became again very diffuse when the eutectic was approached. By simple stirring methods sharp liquidus arrests were obtained over the whole range, and it was possible to complete the diagram. It was with some surprise, therefore, that we found agreement between our own results, using stirred specimens, and the results of Schemtschushny. This segregation is due, I think, to the fact that if a crucible of alloy is cooled slowly there is a tendency for the primary crystallization, if of magnesium, to seek the top of the pot (being lighter than the mother liquor from which it separates), or, if the alloy is beyond the eutectic, for the primary separation (which in this case might be heavier than the mother liquor), to sink to the bottom. In both cases it will become removed from the junction of the couple, and will not have its due effect on the curve recorded.

Dr. Smithells has relieved me of the necessity of replying to Dr. Stockdale with regard to the publication of both diagrams and tables.

Dr. Hume-Rothery (*in reply*): Dr. Smith has suggested that the agreement between the National Physical Laboratory work and the old Russian work which was done with unstirred alloys can be taken as indicating that the need for stirring is not so very vital. I think, however, that if the evidence of other systems is taken as a whole, that is a very dangerous conclusion to reach, and certainly in a large number of cases the stirring is absolutely essential. It is essential, first of all, in order to obtain a homogeneous alloy, and it is essential secondly to prevent under-cooling or super-cooling effects. We have examined these effects at Oxford in very great detail for silver alloys, and have found that for accurate freezing point determinations thorough stirring is essential. Errors of several degrees may easily be introduced if under-cooling occurs in an unstirred alloy, but if it is stirred the effects are to a great extent removed. If a curve is drawn for an alloy which is thoroughly stirred to prevent under-cooling, the true arrest point is obtained. If the same alloy is entirely unstirred, a lower arrest point may be obtained with little or no recalescence. When the freezing begins, presumably it starts at the outside of the alloy, and so the frozen layer at the outside stops the thermal effect from reaching the thermocouple. We have carried out an experiment with an alloy of known freezing point which we deliberately allowed to undercool, and as soon as we saw that the freezing had started we stirred. We obtained a curve, in which there was recalescence and half the under-cooling effect was recovered by stirring, but one can never recover it all, whereas by stirring in a suitable way one can obtain the true arrest point.

CORRESPONDENCE.

Dr. Haughton (*in further reply to the oral discussion*): Most of the points raised in the discussion have been effectively answered by Mr. Payne or by other speakers. I should, however, like to refer in more detail to the question of segregation. It is well known that there are two forms in which this can occur: inverse segregation and what, for want of a better term, we can call "gravity

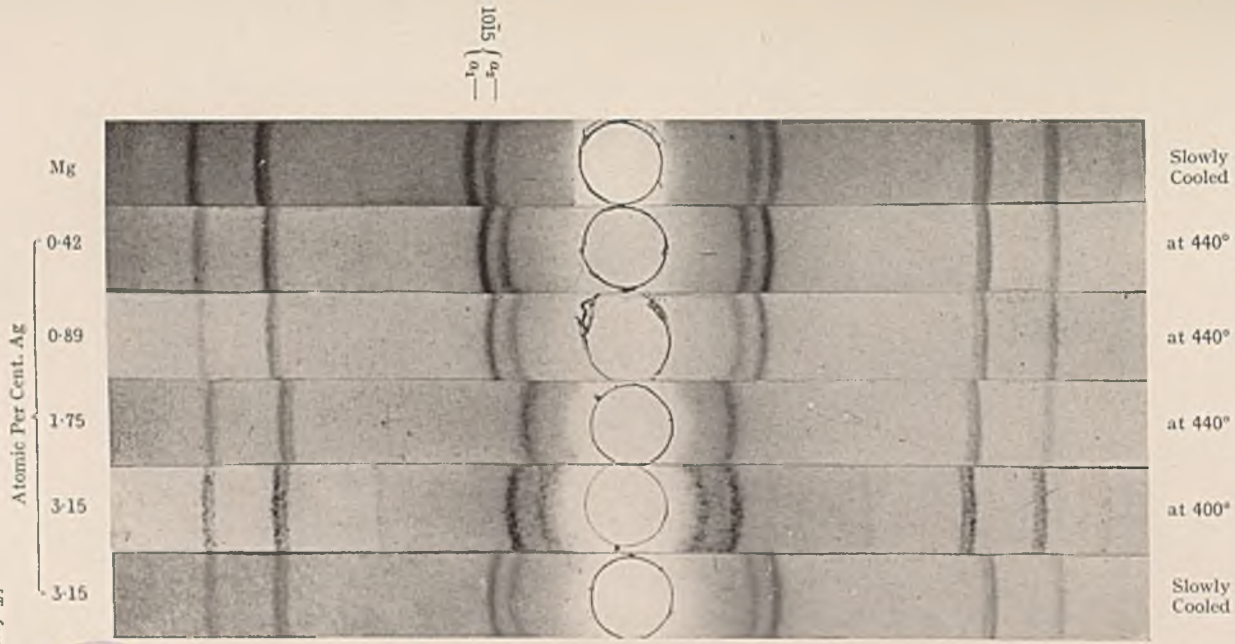

FIG. A.—X-Ray Photographs of Magnesium-Rich Silver-Magnesium Alloys.

[To face p. 360.

segregation." In general, treatment that is a cure for one aggravates the other. Thus, rapid chilling will completely overcome gravity segregation, while really slow cooling will, I believe, reduce inverse segregation to a minimum. In taking thermal curves, cooling has to be very slow, and therefore gravity segregation is the *bête noir*, especially where there is a great difference between the densities of the phases. It is therefore necessary to adopt some device, such as stirring, to overcome it. The chill-cast ingots used for analysis, on the other hand, will only be affected by inverse segregation. Perhaps sand-cast specimens, which would cool more slowly, would have been less segregated, as there would almost certainly have been less inverse segregation and probably not very much gravity segregation. However, as pointed out by Mr. Payne, a complete cross-section of the chill-cast ingot was analyzed, which should give an accurate representation of the composition.

Dr. Stockdale would like to see equations for the curves. This is an interesting suggestion, but I rather doubt that more really accurate results would be obtained from them than from a diagram drawn on the scale of Fig. 2. It is easy to determine a point to ± 2° on this figure, which is about the accuracy of the experimental work. The composition is not quite so satisfactory—about ± 0·2 per cent., but I wonder if the equation would agree better with the facts than this. As regards tables, it is very unlikely that anyone would want to use the exact alloys employed by the investigator, so he would have to replot their results, without having the guidance from practical experience with the individual thermal curves that the author had.

With reference to Dr. Stockdale's point about the introduction of formulæ, I must cry *peccavi*. However, the paper was written about fifteen months before the letter in the *Monthly Journal*, and I will see that it does not occur again.

Dr. N. AGEEW,* Met. Eng. (Member), and Mr. V. G. KUZNEZOW*: We have carried out some experiments in an X-ray study of the equilibrium diagram of the silver–magnesium alloys, the results of which may be compared with those of two papers now under discussion.

Our determination of the solubility of silver in magnesium was based on the X-ray precision measurement of the lattice spacing in a Preston camera. After preparation, the alloys were annealed for 5 days at 400° C. and slowly cooled to room temperature. The annealed alloys were made into powder for the X-ray investigation and again annealed and quenched in petroleum, which had been treated with metallic sodium and cooled to 2°–5° C., for the determination of the solubility curve. At 260° C. annealing lasted for 12–15 days, at 390° C. for 6 days, and at 440° C. for 5 days.

Fig. A (Plate L) shows some of the X-ray photographs; the results of the calculations of the lattice spacing for $(10\bar{1}5)$ are given in Table A and Fig. B. It is remarkable that the solubility limit for the alloys slowly cooled to room temperature is 0·4 atomic per cent. silver as compared with 0·2 atomic per cent. at 260° C. The solubility limit 0·4 atomic per cent. corresponds to the temperature of 285° C. on our solubility curve.

The process of precipitation is a diffusion process and some time is necessary for its completion. If the time available during cooling is insufficient, precipitation does not occur, and the alloy is left in a state corresponding with equilibrium at a higher temperature.

The solubility curve for the solid solution of silver in magnesium, based on the data given in the Table A and in Fig. B, is given in Fig. C. As will be seen, our X-ray results are closer to the microscopical observation of Payne and Haughton, but all three investigations are in good agreement.

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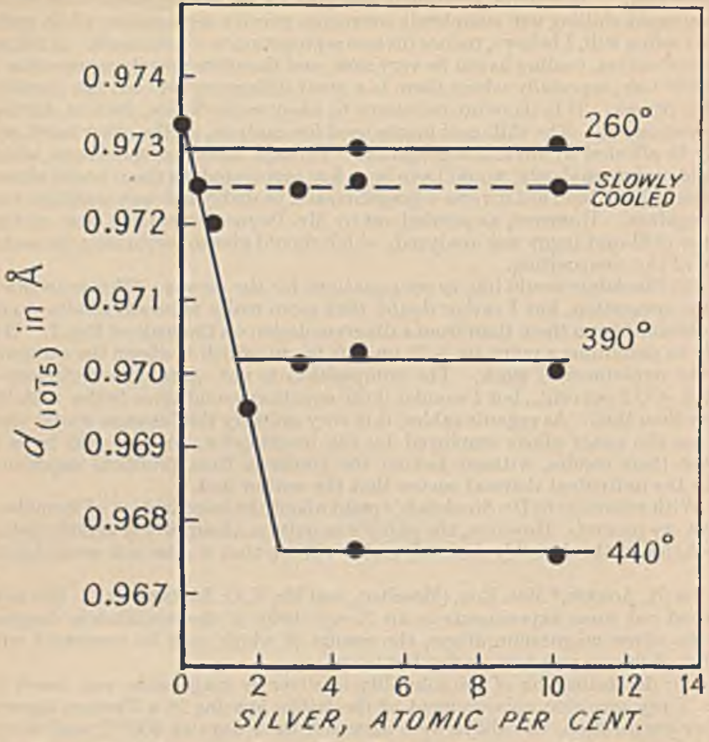

Fig. B.—Lattice Spacings of the Heat-Treated Magnesium-Rich Magnesium-Silver Alloys.

Table A.—*The* $d_{(10\bar{1}5)}$ *of the Magnesium-Rich Silver–Magnesium Solid Solutions and the Solubility Limits.*

Silver, Atomic Per Cent.	Slowly Cooled.	Quenching Temperature.		
		260° C.	390° C.	440° C.
0	0·9734	...	...	...
0·42	...	...	...	0·9725
0·89	...	...	...	0·9720
1·75	...	...	...	0·9695
3·15	0·9725	...	0·9701	...
4·65	0·9726	0·9730	0·9703	0·9676
10·12	0·9725	0·9731	0·9700	0·9675
Solubility limits, silver, atomic per cent.	0·40	0·20	1·40	2·65

The results of the investigation of other parts of the silver-magnesium equilibrium diagram are ready for publication and will be published soon.

Dr. Hume-Rothery and Mr. Butchers (*in reply*): We thank Dr. Ageew and Mr. Kuznezow for their interesting contribution to the discussion. The differences between our own results and those of Dr. Haughton and Mr. Payne may possibly be due to the fact that our alloys were annealed for longer periods. It is satisfactory to note that Dr. Ageew and Mr. Kuznezow's X-ray methods have given results in general agreement with those of the micrographic investigations, but we do not think that a detailed comparison is justified. In Fig. B, the straight line from which Dr. Ageew and Mr. Kuznezow's solubility limits are deduced is obtained from four points, but the point at 0·9720 A. appears to have been almost ignored in drawing the straight line, and we consider this to be somewhat arbitrary; unless there is any reason for doubting the result of the experiment concerned, the point at 0·9720 A. should be taken into account, in which case the best curve will lie slightly to the right of that drawn by Dr. Ageew and Mr. Kuznezow, and the solubilities will be greater. We would refer them to the discussion on our paper on "The Control of Composition in the Application of the Debye–Scherrer Method of X-Ray Crystal Analysis," * where speakers emphasized the dangers of extrapolating lattice spacing–composition curves as has been done in Fig. B. Dr. Ageew and Mr. Kuznezow's solubility values really depend almost entirely on the one point at 0·9695 A., and in view of the inevitable slight experimental errors, this point clearly requires confirmation before an entire solubility curve is deduced. Dr. Ageew and Mr. Kuznezow do

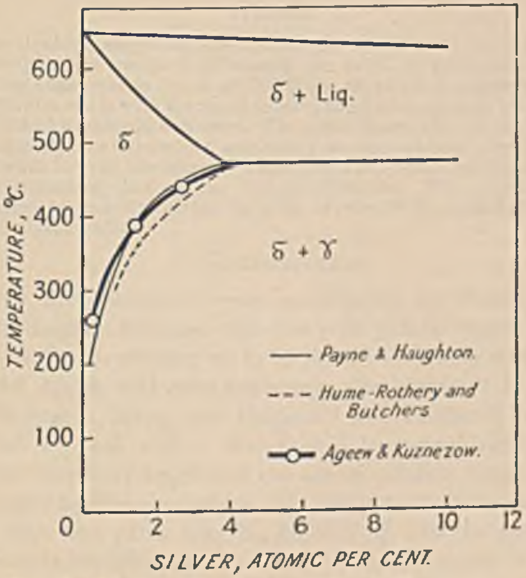

Fig. C.—The Solubility Curve of Silver in Magnesium.

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* This volume, p. 303.

not refer to the analysis of their specimens, and it is to be noted that since magnesium is slightly volatile, results based on the analysis of lump material will tend to give too low values of the solubility limits, so that a complete analysis of the filings for both constituents is highly desirable.

Mr. PAYNE and Dr. HAUGHTON (*in reply*): We are very interested in Dr. Ageew and Mr. Kuznezow's communication. The agreement between their solubility determinations and those of Dr. Hume-Rothery and Mr. Butchers' and ours is very good.

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THE CONSTITUTION OF SILVER-RICH ANTIMONY–SILVER ALLOYS.*

By PETER W. REYNOLDS,† B.A., B.Sc., and WILLIAM HUME-ROTHERY,‡ M.A., D.Sc., MEMBER.

SYNOPSIS.

The liquidus curve of the system silver–antimony is determined accurately in the range 0–25 atomic per cent. of antimony. A new peritectic horizontal is found at 702·5° C., at which temperature the α solid solution reacts with the liquid to form the β solid solution which has a close-packed hexagonal structure. The phase boundaries of the α and β solid solutions are determined accurately at temperatures above 300° C. The general form of the diagram when drawn in terms of electron concentration resembles that of the system silver–tin. The critical points determined are examined from the point of view of Stockdale's theory of integral atomic ratios.

I.—INTRODUCTION.

THE system silver–antimony was investigated by Petrenko[1] whose equilibrium diagram indicates that the solid phases consist of a silver-rich solid solution containing up to 15 per cent. by weight of antimony, a compound Ag_3Sb, and pure antimony. By means of X-ray crystal analysis, Westgren, Hägg, and Eriksson,[2] and Broderick and Ehret[3] showed that a phase with a close-packed hexagonal structure exists between the compound Ag_3Sb and the α-solid solution, a fact which had been indicated by the electrolytic solution potential measurements of Raeder.[4] This new phase may be denoted β§, and the present paper describes a detailed investigation of the phase boundaries in the α and β regions.

II.—EXPERIMENTAL

(a) *Materials Used.*

The silver used was electrolytic silver grain supplied by Messrs. Johnson, Matthey & Co., Ltd., and was of a purity of 99·997 per cent. The antimony was kindly presented by Messrs. The Cookson Lead and

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* Manuscript received September 9, 1936. Presented at the Annual General Meeting, London, March 11, 1937.

† Jesus College, Oxford.

‡ Royal Society Warren Research Fellow, Oxford.

§ The X-ray investigators call this phase ϵ, and use the symbol ϵ' for the Ag_3Sb phase. Apart from the possible confusion between ϵ and ϵ', this nomenclature obscures the close resemblance of the β phases in the systems silver–tin and silver–antimony.

Antimony Co., Ltd., and was of 99·917 per cent. purity, the chief impurities being iron 0·041, lead 0·025, and copper 0·012 per cent.

(b) *Cooling Curve Technique.*

The cooling curves were taken by a method developed for the accurate determination of freezing point depressions. The details of the technique are being published elsewhere.[5] The method consisted essentially in melting 120 grm. of silver under powdered charcoal in a cylindrical graphite crucible provided with a graphite lid in which holes were bored for the admission of a thin silica thermocouple sheath, a silica stirrer, and a thin silica tube by means of which a small sample of the alloy could be removed. After adding the antimony with thorough stirring of the molten alloy, the current through the electrically-heated crucible furnace was adjusted so as to give a rate of cooling of not more than 2° C. per minute at the arrest point. As the temperature approached that of the expected liquidus point, a small sample of the alloy was sucked up the silica tube and removed for analysis; in this way difficulties caused by segregation in the final solid ingot * were avoided, and the composition of the melt a few minutes before the beginning of crystallization was readily determined. The alloy was thoroughly stirred throughout the determinations of the arrest points. It was then reheated, and more antimony was added for the next experiment. Four additional points are included in which the composition was determined from the weights of metals used.

The temperatures were measured by means of a platinum/platinum-rhodium (13%) thermocouple in conjunction with a Carpenter–Stansfield potentiometer of double the usual sensitivity, the coils of which had been accurately calibrated at the National Physical Laboratory. By using strictly standardized conditions, and taking a number of precautions in the potentiometer adjustments, it has been possible to obtain an accuracy of ± 0·3° C. for the freezing points of alloys which show pronounced arrests.

In the present system, a change of 0·1 per cent. in composition is equivalent to roughly 1° C. in the liquidus temperature, so that the accuracy of the liquidus curve is limited more by the precision with which the exact composition of the alloy can be determined, than by the accuracy with which the arrest point can be measured.

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* Experience shows that errors of several per cent. may be introduced if the composition is determined by the analysis of portions of the final ingot, and this error may be accentuated if the alloy is stirred, since the stirring may cause agglomeration of the first portions to solidify.

It has been found that the method of determining the composition of the melt by sampling is liable to give slightly high results for some silver alloys, because the sample is sometimes very slightly richer in the solute element than the melt from which it is taken. For this reason four liquidus points based on synthetic compositions are included in Table I, and marked †. These are very slightly below those obtained by the method of sampling. This discrepancy between the results based on analysis, and on synthetic compositions has been thoroughly investigated, and is fully discussed in the paper referred to above.[5] For the points based on synthetic compositions, the composition is considered exact, and the results accurate to ± 0·3° C. For the remaining points it is considered that the errors do not exceed the limits $\left(\begin{smallmatrix}+\ 0{\cdot}9^\circ\ \text{C.}\\ -\ 0{\cdot}4^\circ\ \text{C.}\end{smallmatrix}\right)$; by this notation it is meant that the values are not more than 0·9° too high, and not more than 0·4° too low. All temperatures were deduced from the measured electromotive force of the thermocouple by means of deviation graphs from the table of Roeser and Wensel,[7] and the *absolute values*, as distinct from the relative accuracy, therefore depend on those of Roeser and Wensel.

(c) *Preparation of Alloys for Annealing and Quenching Experiments.*

The alloys were prepared in quantities of approximately 20 grm. by melting the two metals under charcoal in small Salamander crucibles, and were cast in ¼-in. diameter sand moulds in order to reduce inverse segregation which was then small, and insufficient to interfere with the results.

(d) *Annealing and Quenching Experiments.*

The alloys were annealed in evacuated hard glass tubes, and were quenched in water. For short anneals, the temperature was kept constant within ± 0·3° C. by hand control, whilst for the long anneals use was made of Foster temperature regulators which maintained the furnace temperatures constant to within ± 1·5° C. The general arrangements have already been described.[6]

(e) *Calibration of Thermocouple.*

All temperatures were measured by a platinum/platinum–(13%) rhodium thermocouple standardized against the freezing points of silver (960·5° C.), copper–silver eutectic (778·8° C.), pure aluminium (659° C.), and zinc (419·5° C.). Intermediate temperatures were obtained by means of a deviation graph from the table of Roeser and Wensel.[7]

(f) *Microscopic Examination and Etching Reagents.*

Alloys consisting of the β-phase were very brittle, the individual crystals showing a great tendency to fall apart, but this difficulty was overcome by careful hand sawing and grinding. The twinned crystalline structure of the α-phase was best revealed by etching with a mixture of chromic and sulphuric acids, whilst the presence of chilled liquid in this phase was shown by etching with ammonia and hydrogen peroxide, which revealed the structure of the α-phase only after a long period, but attacked the chilled liquid more rapidly. The latter reagent was also suitable for the determination of the $\alpha/\alpha + \beta$, and $\alpha + \beta/\beta$ boundaries, the β-phase being revealed as a bluish or brownish constituent in contrast to the white α. The structure of the β-phase was best revealed by a mixture of nitric and chromic acids, which was also suitable for the determination of the β solidus, and the $\beta/\beta + \gamma$ solubility curve.

(g) *Analysis.*

All the specimens from the cooling curve experiments, and all the critical specimens near the phase boundaries were analyzed, both silver and antimony being determined. After dissolving the alloy in sulphuric acid, the silver was precipitated as chloride by means of hydrochloric acid. The silver chloride was then filtered off and weighed, and the antimony determined by titration with permanganate after the addition of the required amount of hydrochloric acid. As shown by Pugh,[8] the success of this method depends on the correct adjustment of the relative amounts of sulphuric and hydrochloric acids present. Under the required conditions the standardization of the permanganate by metallic antimony agreed exactly with that by sodium oxalate, and the sums of the percentages of silver and antimony as determined by analysis varied between 99·96 and 100·04.

III.—Experimental Results.

The results of the cooling curve experiments are given in Table I, whilst the critical annealing experiments on either side of the phase boundaries are shown in Table II. The full details of the additional annealing experiments which confirm these results are submitted for deposition in the library of the Institute.* The data included in the Tables, as well as the results of the additional experiments, are shown in Fig. 1,† which is almost self-explanatory.

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* These tables may be consulted in the Institute's library.

† The liquidus points for alloys 9 and 11 are not shown in the figure.

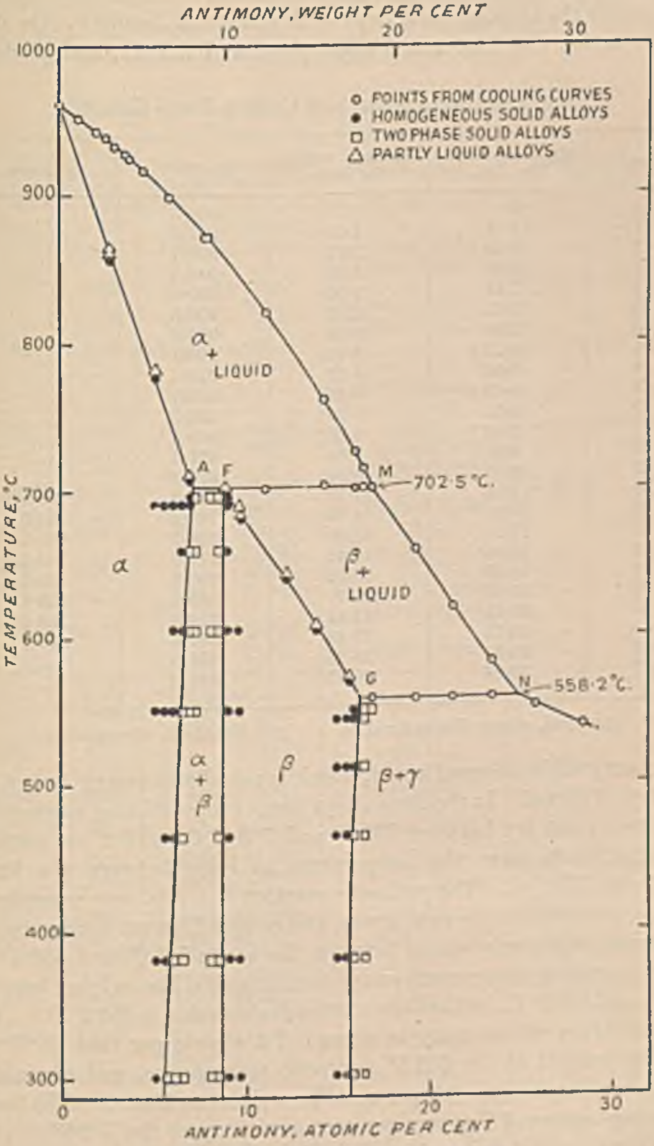

Fig. 1 (see footnote to p. 368).

The liquidus curve for the deposition of the α solid solution agrees closely with the freezing point data of Heycock and Neville.[9] The peritectic reaction $\alpha + \text{Liq.} \rightleftharpoons \beta$ takes place at 702·5° C., and produces only a very slight thermal arrest, which is not shown clearly unless the alloy is well stirred. In the three alloys where proper stirring was possible the arrest point lay between 701·7° and 703·0° C., whilst the quenching experiments gave the temperature as lying between the limits 702·0° and 703·1° C. The peritectic reaction $\beta + \text{Liq.} \rightleftharpoons \gamma$ produced a much more definite thermal arrest, and in four different cooling curves the arrest points only varied between the limits 558·0° and 558·4° C., whilst quenching experiments placed the horizontal line as lying between 557·9° and 558·5° C., so that the most probable value is 558·2° C.* The solid solubility of antimony in silver is 7·2 atomic per cent. (8·05 per cent. by weight) at the 702·5° peritectic temperature, and diminishes to 5·5 atomic per cent. (6·2 per cent. by weight) at 300° C. The limits of the β-phase are 8·8 atomic per cent. antimony at the 702·5° C. peritectic temperature, and 16·3 atomic per cent. antimony at the 558·2° C.

TABLE I.—*The Liquidus and Cooling Curve Results.*

No.	Antimony, Weight Per Cent.	Antimony, Atomic Per Cent.	1st Arrest.	2nd Arrest.
...	0	0	960·5	...
1	1·13	1·00	951·5	...
2	2·16 †	1·92	942·7	...
3	2·24	1·99	942·5	...
4	2·81	2·50	937·1	...
5	3·35	2·98	932·5	...
6	3·94	3·51	927·6	...
7	4·21 †	3·75	924·1	...
8	5·06	4·51	916·4	...
9	6·11 †	5·45	905·1	...
10	6·66	5·95	898·2	...
11	7·40 †	6·62	889·8	...
12	8·80	7·88	871·3	...
13	8·95	8·01	871·5	...
14	12·35	11·10	820·0	700·9 *
15	15·84	14·29	761·2	703·0
16	17·70	16·00	725·7	701·7
17	18·15	16·42	714·8	702·2
18	18·69	16·92	700·9	558·2
19	21·26	19·30	659·4	558·0
20	23·41	21·31	619·9	558·4
21	25·73	23·48	582·4	558·1
22	28·25	25·86	552·9	...
23	30·98	28·45	538·5	...

* Unstirred, stirrer firmly fixed in. † Synthetic compositions.

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* The values given by Petrenko lie between 557° and 562° C.

peritectic horizontal. The range of solubility diminishes slightly as the temperature decreases, and at 300° C. the β solid solubility limits are at 8·6 and 15·6 atomic per cent. of antimony.

TABLE II.—*Annealing and Quenching Experiments.*

Antimony, Weight Per Cent.	Antimony, Atomic Per Cent.	Time and Temperature (° C.) of Final Anneal.	Microstructure.	Previous Annealing Treatment.
3·00	2·67	½ hr. at 856·3°.	α	24 hrs. at 700° C.
„	„	1 hr. at 861·3°.	α + trace of chilled liquid.	„ „
5·71	5·09	¾ hr. at 776·8°.	α	2½ days at 650° C.
„	„	„ 779·9°.	α + trace of chilled liquid.	„ „
7·82	6·99	1 hr. at 707·3°.	α	5½ days at 691° C.
„	„	„ 710·5°.	α + trace of chilled liquid.	„ „
9·98	8·94	1 hr. at 698·0°.	β	5½ days at 691° C.
„	„	„ 700°.	β + minute trace of chilled liquid.	„ „
10·92	9·80	„ 680·8°.	β	13 days at 525° C.
„	„	„ 682·9°.	β + chilled liquid.	„ „
13·57	12·21	„ 640°.	β	„ „
„	„	„ 642·2°.	β + chilled liquid.	„ „
15·39	13·88	„ 605·2°.	β	„ „
„	„	„ 607·4°.	β + minute trace of chilled liquid.	„ „
17·37	15·70	„ 569·6°.	β	„ „
„	„	„ 572·0°.	β + chilled liquid.	„ „
5·71	5·09	21 days at 302°.	α	5½ days at 691° C.
6·27	5·60	„ 302°.	$\alpha + \beta$	„ „
„	„	„ 382°.	α	„ „
6·76	6·04	„ 382°.	α + trace of β.	„ „
„	„	14 days at 465°.	α	„ „
7·38	6·59	10 days at 551°.	α + trace of β.	„ „
„	„	„ 606°.	α	„ „
7·88	7·04	5 days at 659°.	α + trace of β.	„ „
„	„	5½ days at 691°.	α	none.
8·18	7·32	3 days at 696°.	$\alpha + \beta$	10 days at 606° C.
9·55	8·55	21 days at 302°.	$\alpha + \beta$ *	10 days at 606° C.
„	„	3 days at 696°.	$\alpha + \beta$ *	„ „
10·08	9·03	21 days at 302°.	β	5½ days at 691° C.
„	„	3 days at 696°.	β	„ „
17·12	15·47	21 days at 302°.	β	10 days at 544° C.
„	„	10 days at 544°.	β	none.
17·56	15·88	14 days at 465°.	β + trace of γ.	10 days at 544° C.
„	„	10 days at 512°.	β	„ „
18·22	16·48	10 days at 551°.	β + a little γ.	„ „

* In these $\alpha + \beta$ alloys which lie near to the $\alpha + \beta/\beta$ boundary, the relative amount of the β phase increased slightly when the alloys which had previously been annealed at a high temperature were re-annealed at a lower temperature. This indicates that the $\alpha + \beta/\beta$ boundary in Fig. 1 is not vertical, but inclined slightly to the left at lower temperatures.

IV.—Discussion.

In Fig. 2, the equilibrium diagrams of the silver-rich silver–tin and silver–antimony alloys are compared, the diagrams being drawn in terms of electron concentration. The β-phase in the system silver–tin has also a close-packed hexagonal structure,[10] and it is clear that the two equilibrium diagrams resemble one another both as regards the higher peritectic temperatures, and the general form of the diagram. In both systems the composition corresponding with the electron concentration 1·5 lies near the centre of the β-phase area. In other alloy systems it is well known that phases with the body-centred cubic or β-manganese structures tend to occur at this electron concentration. The present work, therefore, confirms that the same electron concentration can also give rise to a group of close-packed hexagonal structures, since this structure at the electron concentration 1·5 is found also in the systems silver–indium,[11] copper–germanium,[12] and copper–gallium.[13] The diagrams in Fig. 2 show that in terms of electron concentration both the $\alpha/\alpha + \beta$ and the $\alpha + \beta/\beta$ boundaries in the system silver–antimony are displaced in the direction of lower antimony content compared with those in the system silver–tin. The $\beta/\beta + \gamma$ boundary is displaced in the same direction at higher temperatures, but at lower temperatures this boundary gives a much narrower range of composition in the system silver–tin.

The phase boundaries in the present work were determined accurately and may be surveyed in the light of Stockdale's hypothesis[14] that critical points occur at integral atomic ratios. The point *A* in Fig. 1 representing the limiting composition of the α-solid solution may be placed at 7·2 ± 0·1 atomic per cent. of antimony. This does not correspond with any simple ratio of numbers up to 12, but if numbers up to 24 are permitted, as in parts of Stockdale's paper, the ratio $\frac{1}{14} = 7{\cdot}14$ per cent. agrees within the limits of experimental error. The point *F* representing the composition of the β-phase at the peritectic temperature lies at 8·8 ± 0·10 atomic per cent. of antimony, the nearest integral ratio being $\frac{2}{23} = 8{\cdot}70$ per cent. The difference between these values is small, but the β solidus curve suggests that the point *F* corresponds with a slightly higher antimony content than that required by the ratio $\frac{2}{23}$. The point *G* representing the composition of the β-phase at the lower peritectic temperature may be placed at 16·3 ± 0·1 atomic per cent. antimony, and definitely differs from the ratio $\frac{1}{6} = 16{\cdot}67$ per cent. which is the nearest ratio involving numbers up to 24. The same ratio appears definitely distinct from the composition of the point *M* on the liquidus which lies at 16·9–17·0 atomic per cent. anti-

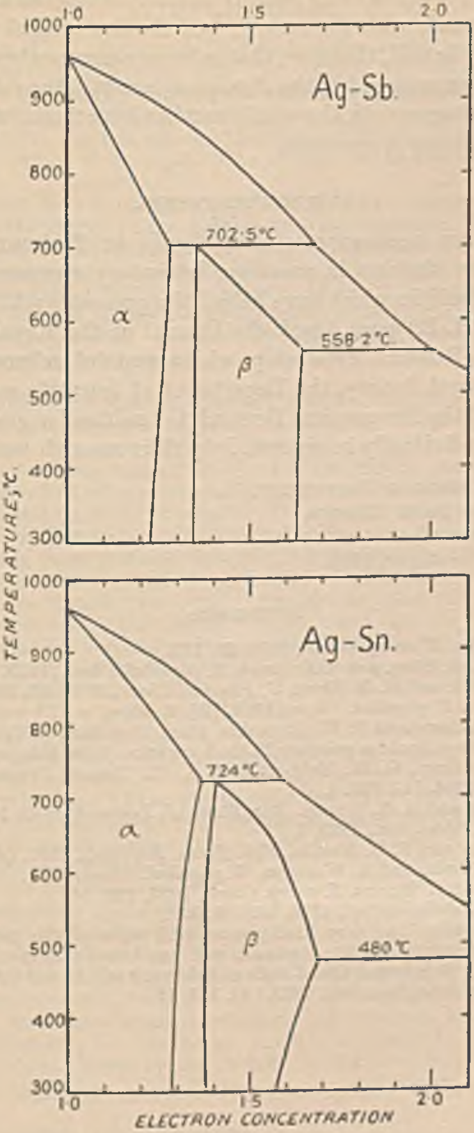
Ag-Sb.
702·5°C
558·2°C
α
β
Ag-Sn.
724°C
480°C
α
β
1·0
1·5
2·0
1000
900
800
700
600
500
400
300
TEMPERATURE, °C.
ELECTRON CONCENTRATION

FIG. 2.

mony, but the lower liquidus point N lies at the composition $25{\cdot}0 \pm 0{\cdot}1$ which corresponds with the ratio $\frac{1}{4}$. Of the five critical points determined, it may be said, therefore, that only one corresponds with the ratio of small whole numbers, but the A point agrees with the ratio $\frac{1}{14}$. Two points do not agree with the whole number hypothesis, whilst for the fifth the conclusion is uncertain.

ACKNOWLEDGMENTS.

The authors must express their thanks to Professor F. Soddy, F.R.S., for his kindness in providing laboratory accommodation, and many other facilities which have helped the present work. One of the authors (W. H.-R.) must thank the Council of the Royal Society for election to a Research Fellowship, whilst grateful acknowledgment is due to the Royal Society, the Department of Scientific and Industrial Research, and the Aeronautical Research Committee for grants made to the authors individually in order to help their research work.

THE OLD CHEMISTRY DEPARTMENT,
THE UNIVERSITY MUSEUM,
OXFORD.
August, 1936.

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[14] D. Stockdale, *Proc. Roy. Soc.*, 1935, [A], **152**, 81.

DISCUSSION.

Dr. Marie L. V. Gayler * (Member): The authors state that they experienced inverse segregation with their alloys; have they any evidence of segregation between the top and the bottom of their castings? I ask this because I made up an alloy containing silver and tin in the proportion of 26·8 per cent. tin, and was amazed to find very different tin contents in the top and the bottom of the ingot. The average of the two gave the desired composition.

The fact that the composition corresponding with the electron concentration 1·5 lies near the centre of the β-phase area is interesting. Does the same hold for β-phase of the silver–mercury system, which has also a close-packed hexagonal structure? What is extraordinary, to my mind, is that the composition corresponding with the electron ratio 1·5 cuts the β-range in half, and that it seems to have no relation to the composition of the phase formed at the peritectic temperature. Is there any fundamental reason why this ratio should divide the β-phase in half?

Dr. D. Stockdale,† M.A. (Member of Council): Some time ago I examined certain of the antimony-rich alloys of this system.‡ Some of my results are shown in Fig. A. The lines *PQS* and *QR* in this figure are from my work, the other lines shown being taken from Fig. 1 of the present paper (p. 369). The point *P* is arrived at after considerable extrapolation. It is near 22·0 atomic per cent., but this value is not reliable. On the other hand, the position of *Q* was examined with some care. It is probably very near 24·9 atomic per cent., this value being more probable than the 25·0 per cent. required by the ratio 1 : 3. I have also determined the solubility of silver in antimony. This is considerably less than 0·1 per cent. The eutectic point was found to be at 41·05 atomic per cent. of antimony. I also found that the boundary *QS* is vertical and that the solubility of silver in antimony is not noticeably affected by temperature. These results substantiate the early work of Petrenko.§

It is suggested that the constitution of this system, save only for the position of the boundary *PT*, is now accurately known.

It is gratifying, though at the same time a little unfortunate, that the authors have raised the question of simple ratios with regard to this particular system. In the first place, except for certain remarks on the cadmium–silver alloys,‖ any rules that I have put forward deal only with eutectic mixtures and simple α-solid solutions. Further, the ranges of solid solution are here limited, with the result that an experimental error of a small fraction of 1 per cent. may become much magnified and obscure the results when ratios are considered. For this reason no great weight can at present be attached to the fact that the position of the point *A*, Fig. 1, is in conformity with the Three Rule.¶ I have examined points similar to *M* and *N* in other systems and have concluded that the bulk of the evidence is against their falling at simple ratios. Hence, the fact that *N* is at a simple ratio may be accidental.

There remain points *F* and *G*. As these are analogous to the "triple" points on α-phase boundaries, these should fall at simple ratios. There are many ways of looking for these ratios, but it is reasonable to suppose that the simplest way, that chosen by the authors, is incorrect, because here we are

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† Fellow of King's College, Cambridge.

‡ D. Stockdale, *J. Inst. Metals*, 1930, **43**, 193; *Proc. Roy. Soc.*, 1935, [A], **152**, 81.

§ G. J. Petrenko, *Z. anorg. Chem.*, 1906, **50**, 139.

‖ P. J. Durrant, *J. Inst. Metals*, 1931, **45**, 116.

¶ D. Stockdale, *Proc. Roy. Soc.*, 1935, [A], **152**, 81.

dealing, not with a primary solid solution, but with a more complicated "compound." A simple ratio superimposed on a "compound" of quite simple formula may lead to extravagant numbers. The problem is to disentangle two simple ratios. We might suppose that the formula of this particular "compound" is Ag_7Sb, in conformity with the Hume-Rothery atom-electron ratio rule. If we assume that the solid solutions are built up by the normal process of substitution on the lattice, it follows that at point *F*, 10

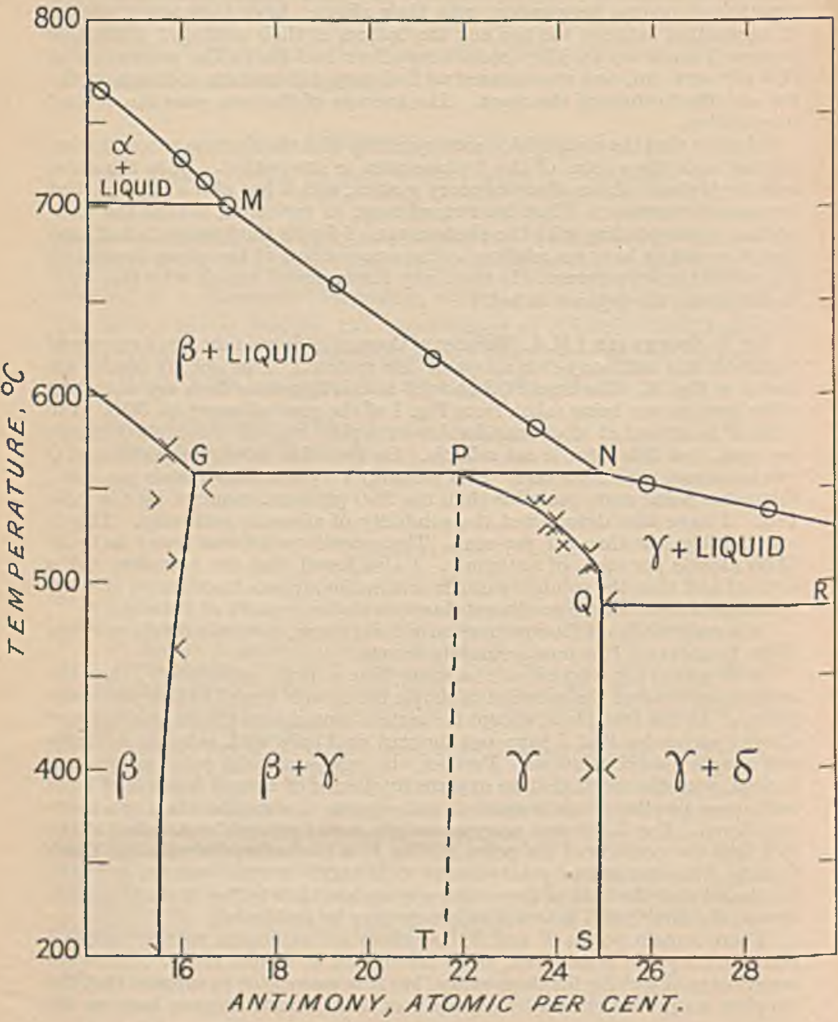

Fig. A.

" molecules " of Ag_7Sb contain 3 atoms of silver acting as antimony atoms (required atomic percentage 8·75; found 8·8±0·10) and at G 10 " molecules " contain 3 atoms of antimony acting as silver atoms (required atomic percentage 16·25; found 16·3 ± 0·1). This is merely an arithmetical exercise to show that ratios can be found if the correct procedure is adopted. This procedure can only be legitimate if it yields results when applied to a large number of systems and in cases where the arrangement of the atoms in the crystal is exactly known. In this particular case there is at least one other formula which gives similar results.

A peritectic reaction in some respects resembles a eutectic reaction, and it might be reasonable to demand that if simple ratio rules apply to the latter they must also apply to the former. Thus F (Fig. 1) and P (Fig. A) should fall at simple ratios. I have shown elsewhere * that there are two different ratios to consider, the constituent and the phase ratios. The simple rules cannot hold for both, but as yet it has been impossible to decide between them. For F, the authors have considered the constituent ratio, a doubtful 2/21. The phase ratio is given by $\frac{FM}{AF}$.

$$\text{Now } \frac{FM}{AF} = \frac{16{\cdot}95 - 8{\cdot}8}{8{\cdot}8 - 7{\cdot}2} = 5{\cdot}09.$$

(Moving F to 8·85 gives 4·91.)

Thus a phase ratio of 1 : 5 is not impossible.

Similarly, taking P at 22·1 atomic per cent.

$$\frac{GP}{PN} = \frac{22{\cdot}1 - 16{\cdot}3}{25{\cdot}0 - 22{\cdot}1} = 2{\cdot}0.$$

As I have pointed out, this system is so cramped that little weight can be given to these figures, but my object now is to show that the authors' work does not put simple ratios out of the question.

Incidentally, the authors use the convention of expressing ratios in terms of number of atoms of the one sort and total number of atoms. I use number of atoms of the one sort and number of atoms of the other. Can a convention now be agreed upon?

The AUTHORS (*in reply*): In reply to Dr. Gayler, we have not experienced much difficulty over vertical segregation in silver–antimony alloys, but we can fully confirm Dr. Gayler's experience with silver–tin alloys, for which we have found marked vertical segregation. Silver alloys appear very puzzling in this respect, and duplicate analyses of different parts of ingots are essential as a safeguard against misleading results. The electron concentration 1·5 does not lie in the centre of the β-phase of the silver–mercury system. The factors affecting the exact compositions of copper and silver " β " phases are very complicated, and we hope to discuss this point fully in the future.

We must thank Dr. Stockdale for his most interesting communication, and are glad to see how his data fit on to our own. We agree that the system is too cramped to allow a critical test of the whole-number laws, but the phase ratios which Dr. Stockdale has calculated are certainly most suggestive, and we hope that we may be able to test more suitable systems in the future. We will also adopt Dr. Stockdale's policy of expressing ratios in terms of the number of atoms of the one sort and the number of atoms of the other.

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* D. Stockdale, *Proc. Roy. Soc.*, 1935, [A], 152, 81.

THE CONSTITUTION OF THE ALLOYS OF SILVER, TIN, AND MERCURY.* 766

By MARIE L. V. GAYLER,† D.Sc. (Mrs. Haughton), Member.

Synopsis.

The constitution of the ternary alloys of silver, tin, and mercury has been determined, except for a small range of composition near the tin corner. Five invariant reactions have been found, while two others have been deduced from experimental and theoretical evidence. Isothermal sections for temperatures of 100°, 84°, and 70° C. have been plotted from experimental data.

The investigation described in the present paper forms part of a research which has been carried out in the Department of Metallurgy of the National Physical Laboratory, on behalf of the Dental Investigation Committee of the Department of Scientific and Industrial Research, and with the aid of funds provided by the Dental Board of the United Kingdom.

(1) Introduction.

Joyner [1] published the results of the first attempt to determine the constitution of silver–tin–mercury alloys by a study of the composition of the liquid phases in contact with solid or solids; this work was amplified later by Knight in conjunction with Joyner.[2] These authors determined the limits of existence of the liquid phase and deduced from the position and shape of these regions, the nature and composition of the solids capable of existing in contact with them. This method was employed at temperatures of 63°, 90°, 166°, and 214° C., and for each temperature an equilibrium diagram was obtained (cf. Figs. 20 and 21). The interpretation of their results, however, was based on the silver–tin, silver–mercury, and tin–mercury binary systems existing at that time. These have since been shown to be incomplete by Murphy [3] and Prytherch,[4] whose results are embodied in Figs. 1, 2, and 3. These diagrams form the basis of the present research.

Murphy identified in the silver–tin system a silver-rich β-phase in addition to the compound Ag_3Sn, while in the case of the silver–mercury

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* Manuscript received July 4, 1936.

† Scientific Officer, Department of Metallurgy, National Physical Laboratory, Teddington.

system he showed that the compound Ag_3Hg_4 does not exist, but that two intermediate phases of restricted compositions were found, *i.e.* a β-phase containing 40 per cent. silver, and a γ-phase containing 29–30 per cent. silver. The composition of the latter phase is close to Ag_3Hg_4, but it is more nearly associated by its lattice structure to the formula Ag_5Hg_8.

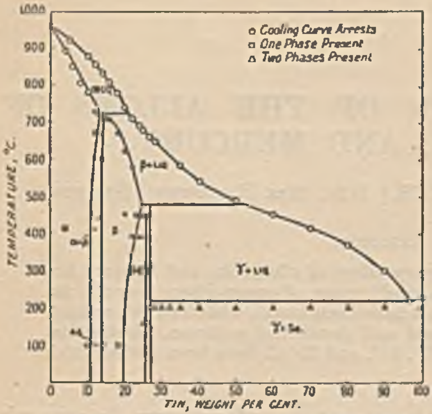

Fig. 1.—Silver–Tin Equilibrium Diagram (Murphy).

With regard to the tin-mercury system, van Heteren [5] concluded that no compound exists between tin and mercury, but Prytherch has proved the existence of three compounds. The γ compound has now been found to react with liquid at 90° C. to form a δ-phase which in turn reacts with liquid, to form $HgSn_3$.*

Tammann and Mansuri [6] determined the hardness of the ternary amalgams of silver, tin, and mercury and, later, Tammann and Dahl [7] studied the constitution at room temperature of silver–tin amalgams over a range of compositions. These authors confirmed the existence of three constituents, Ag_3Sn, a tin–mercury solid solution, and a solid solution of tin in the compound Ag_3Hg_4, respectively.

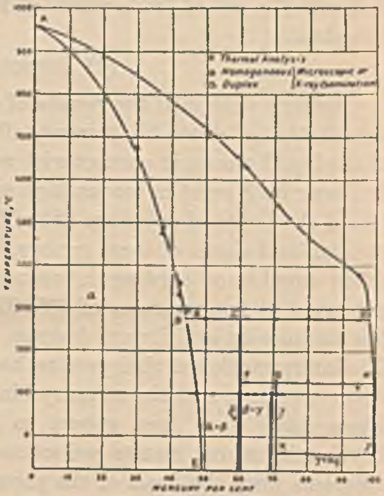

Fig. 2.—Silver–Mercury Equilibrium Diagram (Murphy).

Knight and Joyner concluded from their own researches, that the equilibrium diagram of silver–tin–mercury alloys might be grouped into two classes: those about 70° C. containing a large proportion of solid solution, and those below containing negligible

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* See reply to discussion.

amounts only. These diagrams will be discussed later. These authors summarized amalgamation at room temperature in the equation:

$$Ag_3Sn + 4Hg \longrightarrow Ag_3Hg_4 + Sn$$

The results of the present investigation (apart from the fact that Ag_3Hg_4 does not exist in the binary silver–mercury system) disprove the formation of tin as a product of amalgamation.

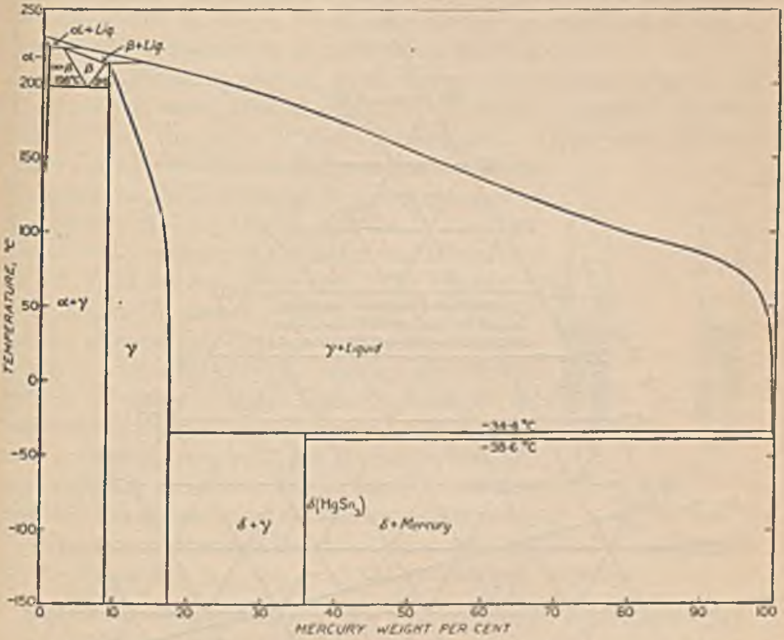

FIG. 3.—Tin–Mercury Equilibrium Diagram (Prytherch, unpublished work).

(2) EXPERIMENTAL DATA.

The determination of the constitution of silver–tin–mercury alloys has been based on (*a*) thermal analysis, (*b*) microscopical analysis, and (*c*) X-ray analysis. The diagrams submitted must be considered as constitutional diagrams, since it has not been possible, in the time during which this investigation has been carried out, to attain equilibrium conditions. Alloys have been annealed, however, at 70° C. and left to "self-anneal" at room temperature before taking low-temperature thermal curves; by these means the limits of existence of free mercury has been ascertained.

The boundaries of the other phase fields have not been fixed other

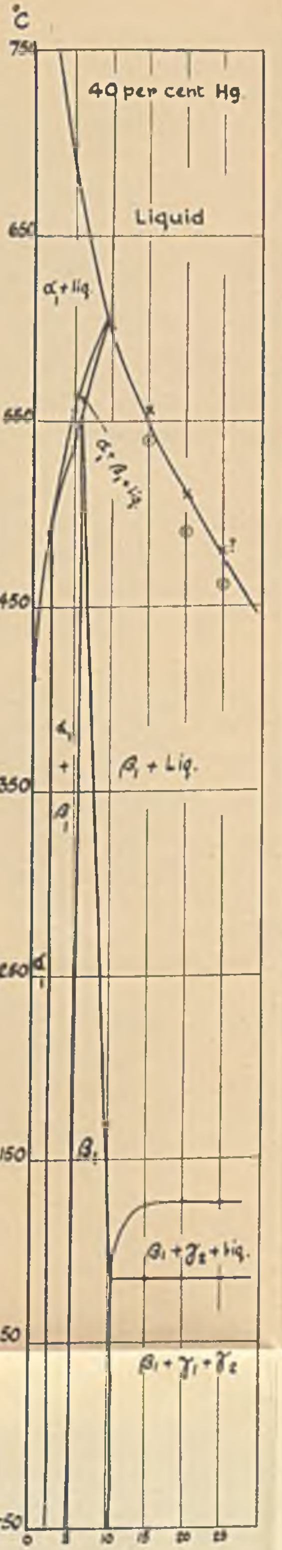

FIG. 7.

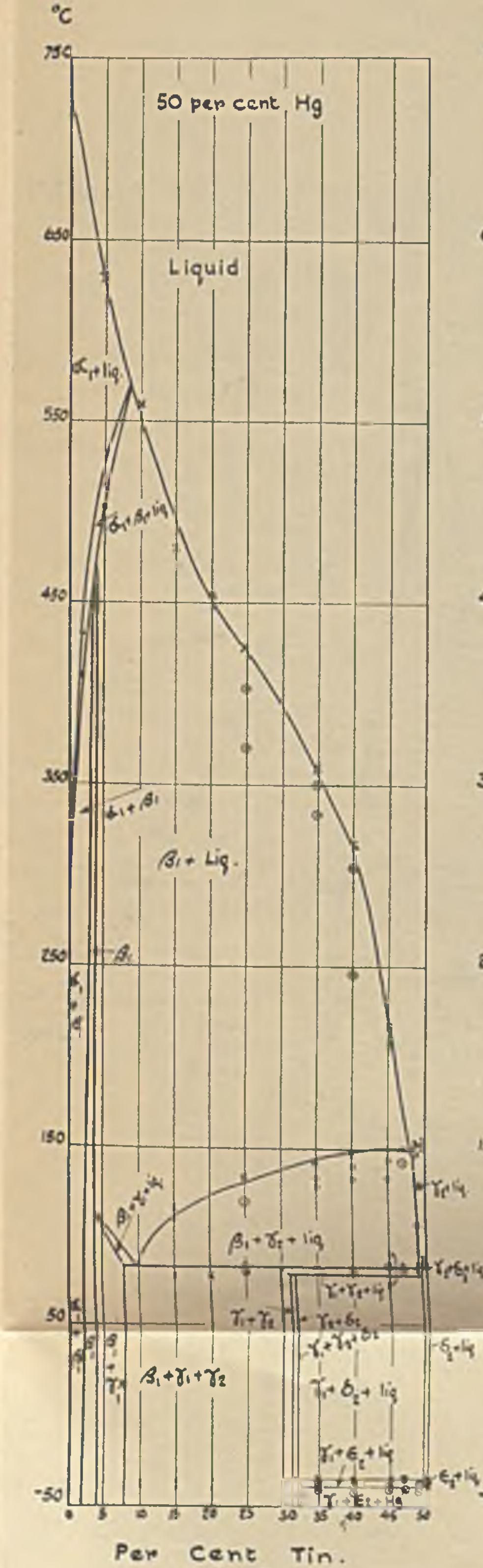

FIG. 8.

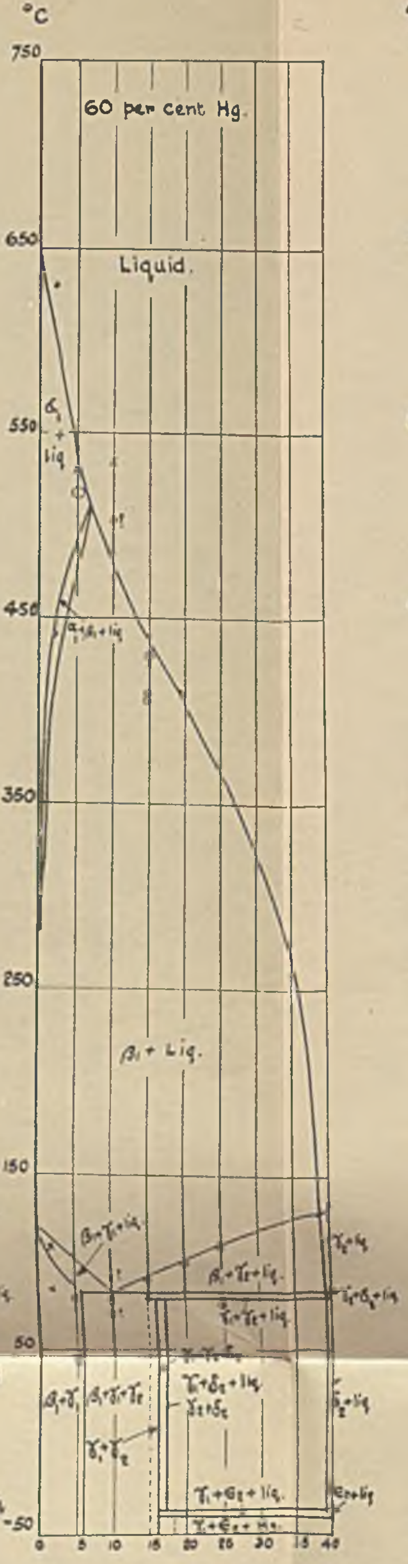

FIG. 9.

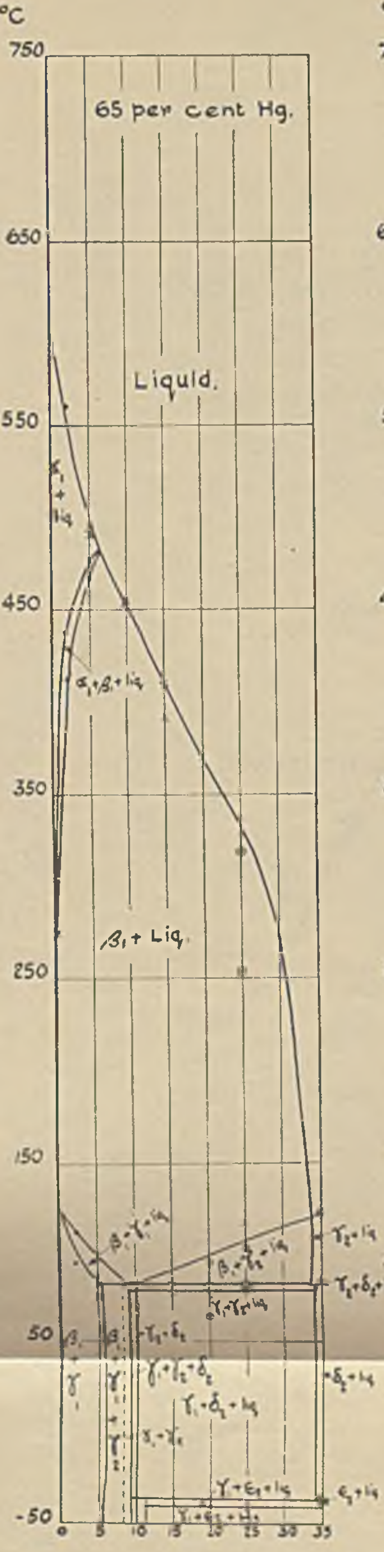

FIG. 10.

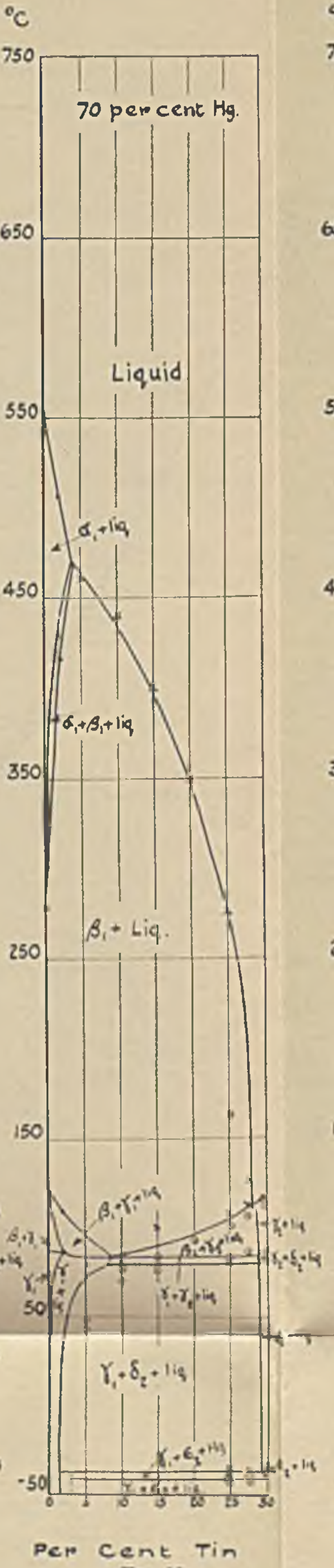

FIG. 11.

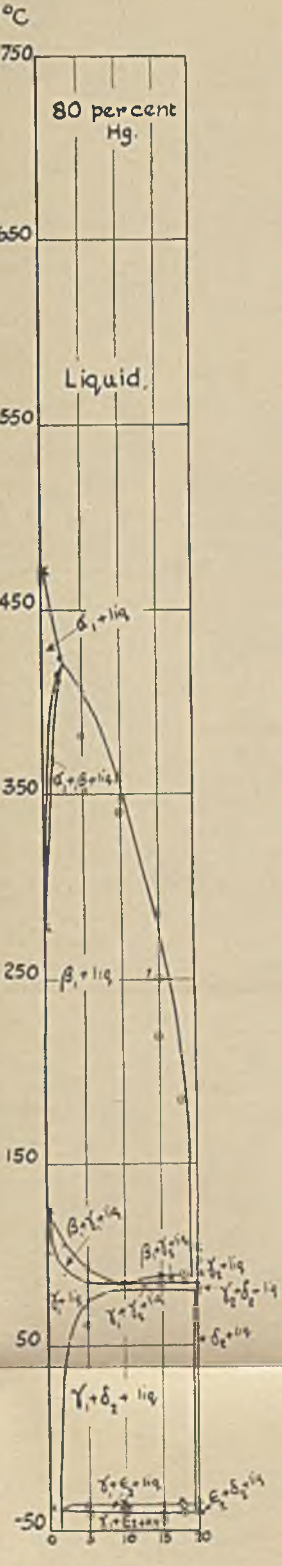

FIG. 12.

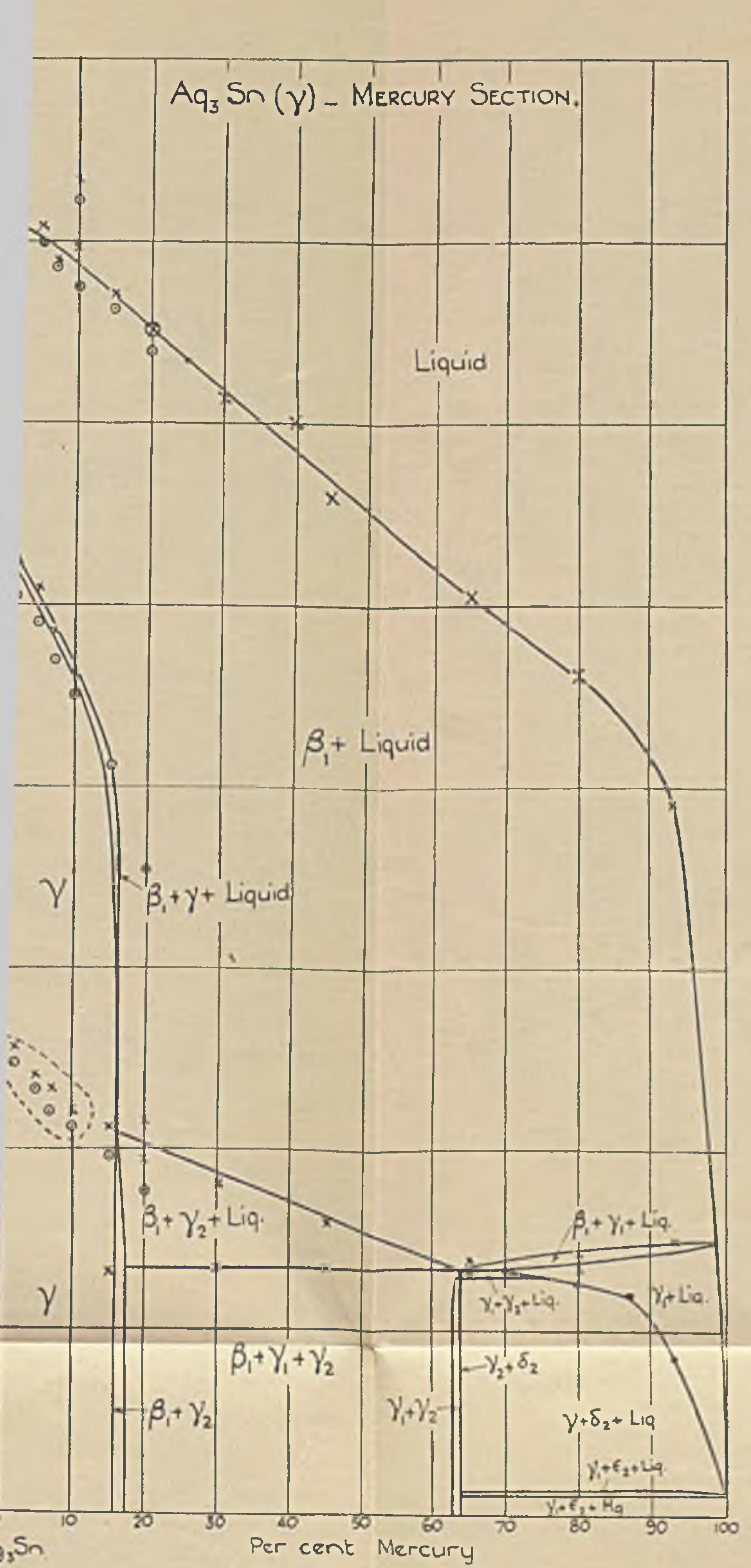

FIG. 13.

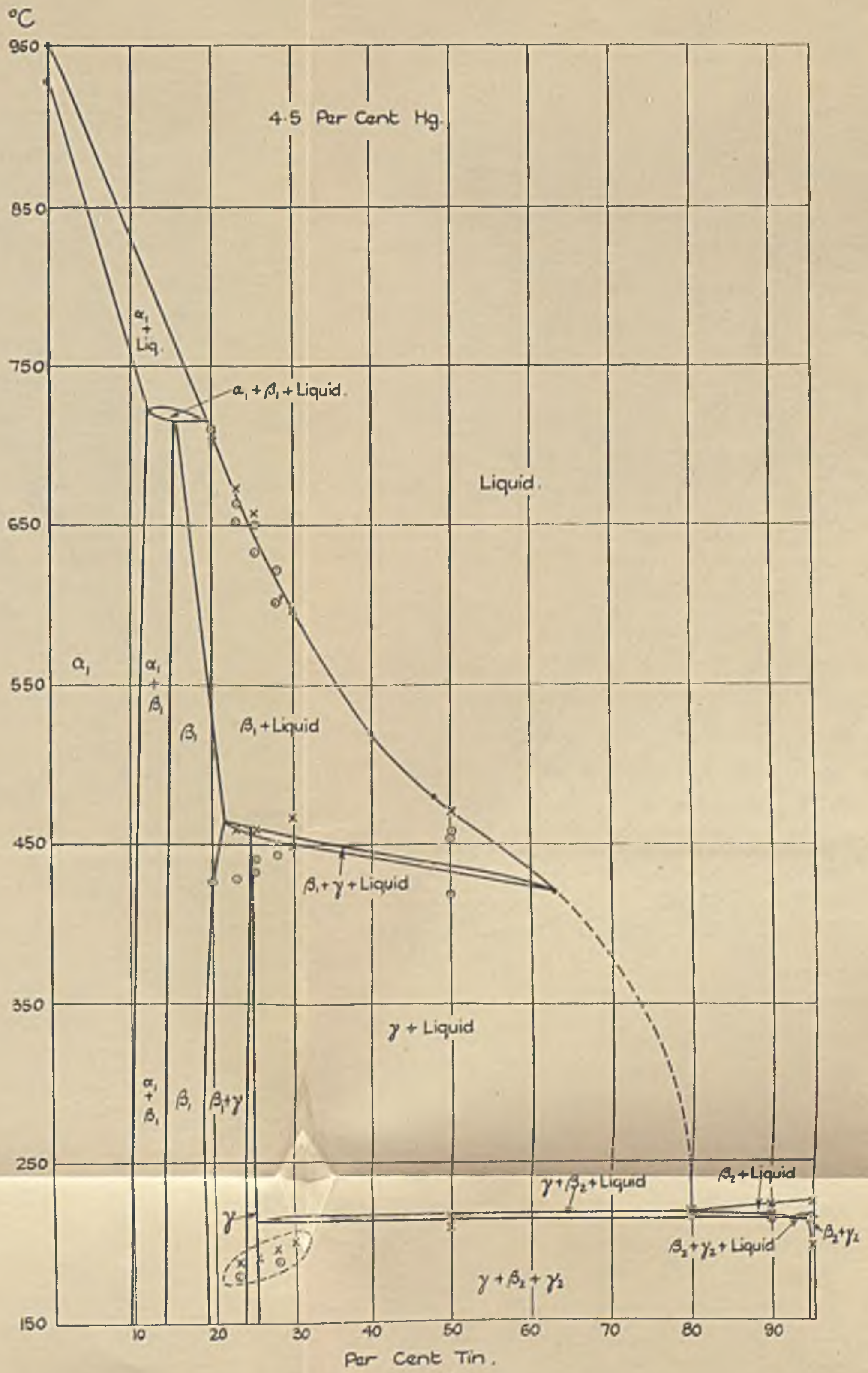

FIG. 14.

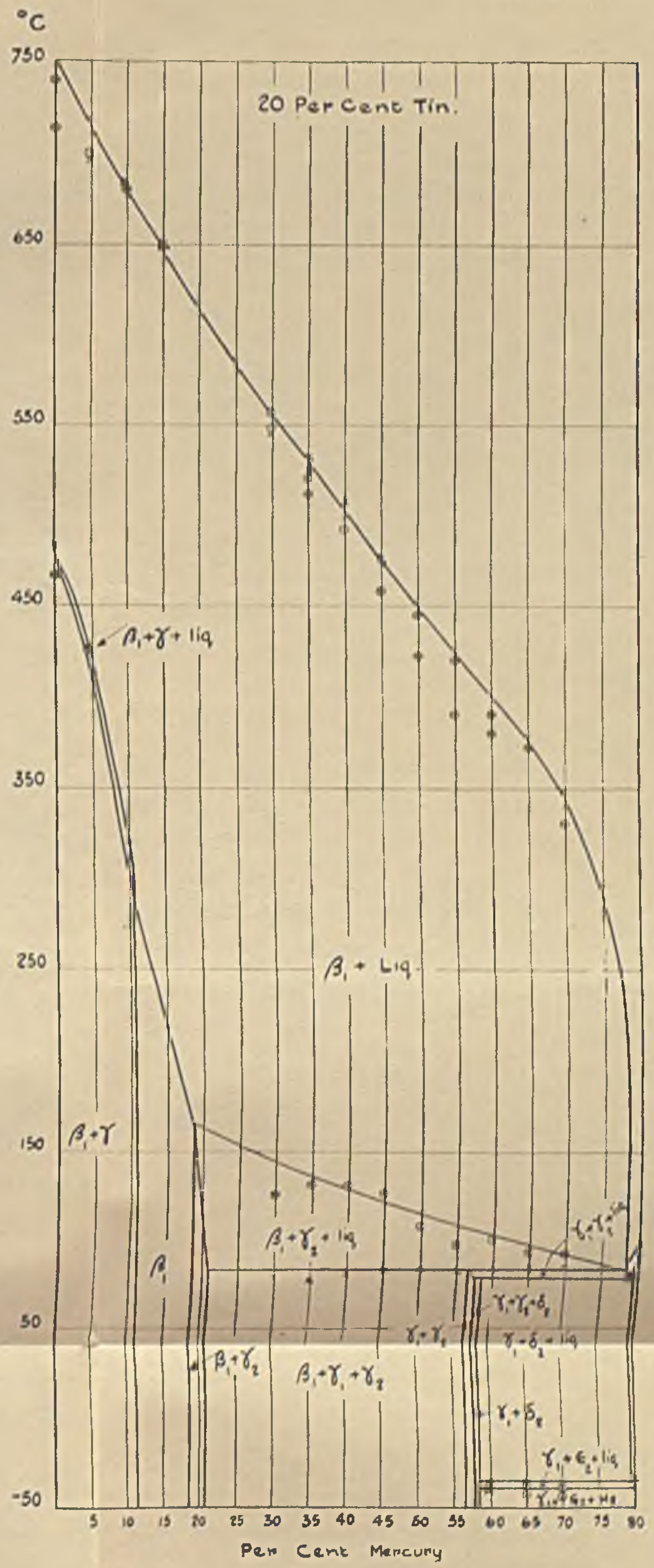

FIG. 15.

[To face p. 384.

An iron–Constantan thermocouple, calibrated against the freezing point of mercury (−38·8° C.), the melting points of tin (232° C.), lead (327° C.), and zinc (419° C.) was used for the low-temperature thermal curves. These were carried out in a small gradient furnace, specially constructed for the purpose. A steel tube 1¼ in. in diameter, and 24 in. long, closed at one end, was wound over a distance of 3 in., at the open end, with Nichrome wire, giving a resistance of 200 Ω; this was surrounded for a length of 15 in. with thermal insulating material, as shown in Fig. 6. About 9 in. of steel tube, extending below the casing, dipped into a quart thermos flask containing a mixture of carbon dioxide snow and acetone. If, however, no thermal arrests were expected at about − 40° C., the freezing mixture was replaced by broken ice, and by its use thermal curves up to temperatures of about 250° C. could be easily obtained. With suitable voltage control of the furnace, a very uniform gradient resulted when the silica container was hauled up or down the furnace at a constant rate.

For thermal analysis at temperatures above 250° C., a 12 per cent. platinum/platinum–rhodium thermocouple was used, calibrated against the standard melting points of gold (1063° C.), zinc (419° C.), and tin (232° C); the general temperature–e.m.f. curve for the batch of wire from which the above was obtained having previously been determined over a wider range of temperature.

The results of thermal analyses are plotted diagrammatically in Figs. 7–15 (Plate LI),* while the heat-treatments at 70° C., together with the subsequent thermal analysis, are given in Appendix II (p. 398).

The liquidus surface, obtained from data given in Figs. 7–15 (Plate LI), is plotted in Fig. 16 (Plate LII), while isothermal sections at 100°, 84°, and 70° C. are given in Figs. 17–19 (Plate LII), respectively.

The addition of tin to silver–mercury alloys causes great changes in the constitution of these alloys. Briefly, the following effects are observed:

(*a*) The temperature of the liquidus is lowered markedly with increasing tin content;

(*b*) The temperature of the α_1 + liquid $\longrightarrow$ β_1 reaction of silver–mercury alloys is raised very steeply with the addition of tin;

(*c*) At temperatures below about 150° C. γ_1(Ag–Hg) or γ_2(Sn–Hg) separate from the β_1 + liquid phase field until at a temperature of 84° C. an invariant reaction occurs and $\gamma_1 + \gamma_2$ separate simultaneously from the liquid. This may be expressed as:

$$\beta_1 + \text{liquid} \longrightarrow \gamma_1 + \gamma_2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

---

* The values obtained are filed in the archives of the Institute of Metals, where they may be consulted on application.

(*d*) This γ_2 phase is unstable in the presence of liquid and, as in the case of the binary tin–mercury alloys, this phase at some lower temperature will react with any liquid above that required for the reaction (1) to form the δ_2 phase of the tin–mercury system. Since γ_1 is present, this reaction must be invariant; it takes place at 80° C. according to the equation:

$$\gamma_1 + \gamma_2 + \text{liquid} \longrightarrow \gamma_1 + \delta_2 \quad . \quad . \quad . \quad . \quad (2)$$

(*e*) Similarly, at a still lower temperature the δ_2 phase is unstable in the presence of liquid and at about 3° above the freezing point of mercury (— 38·8° C.), *i.e.* — 36° C. approximately, this phase reacts with excess liquid to form the ϵ_2 phase of the tin–mercury system. This reaction again is an invariant one owing to the presence of γ_1.

$$\gamma_1 + \delta_2 + \text{liquid} \longrightarrow \gamma_1 + \epsilon_2 \quad . \quad . \quad . \quad . \quad (3)$$

(*f*) With further lowering of temperature to that of the freezing point of mercury (— 38·8° C.), the residual liquid solidifies at constant temperature.

$$\gamma_1 + \epsilon_2 + \text{liquid} \longrightarrow \gamma_1 + \epsilon_2 + \text{Hg} \quad . \quad . \quad . \quad (4)$$

Thus, four invariant reactions take place at temperatures between the liquidus and the solidus of the ternary alloys of silver, tin, and mercury, over a wide range of composition as seen in Figs. 7–15, respectively. Of these invariant reactions those expressed by equations (1) and (2) are of fundamental importance for the setting of dental amalgams.

(*g*) Further, analysis shows that the β_1 phase is isomorphous with the β phase of the silver–tin system (cf. Figs. 17–19); in other words, the β (Ag–Sn) phase will hold a large amount of mercury in solid solution and the β_1 (Ag–Hg) phase will hold an appreciable amount of tin in solid solution. This fact, again, is of fundamental importance, since a dental filling, made under " ideal " conditions and whose final composition corresponds with the maximum amount of tin and mercury simultaneously held in solid solution in the β_1 phase should show little or no dimensional changes during setting. An explanation of this fact is given in a separate paper [12] which deals with the setting of dental amalgams.

(*h*) The effect of the addition of mercury to the silver–tin γ-phase Ag_3Sn has been studied in some detail. The results are summed up in Fig. 13 and show how extremely complex are the changes that take place.

From thermal analysis the boundary between the $\beta_1 + \gamma_2$ and the $\beta_1 + \gamma_1 + \gamma_2$ phase fields (Fig. 13) is about 18 per cent. mercury (on the Ag_3Sn–Hg section); and this, together with other results, would place the above whole boundary in the position shown by the line *PM*, in Fig. 19. This result is obviously incorrect and must represent a metastable condition since, from theoretical reasoning, the ternary phase field $\beta_1 + \gamma_1 + \gamma_2$ must be bounded by straight lines joining the points representing the compositions of the phases β_1, γ_1, and γ_2, respectively. It is probable, therefore, that ML (Fig. 19) would represent more closely the position of the boundary under equilibrium conditions.

(*i*) The presence of other phases in the 4·5 per cent. mercury section, and the general character of the Ag_3Sn–Hg section, and that of alloys containing 20 per cent. tin, indicate that the following invariant reactions must take place in the ternary system:

$$\gamma(Ag_3Sn) + \alpha_2 + \text{liquid} \longrightarrow \gamma + \beta_2 \quad . \quad . \quad . \quad (5)$$

$$\gamma + \beta_2 + \text{liquid} \longrightarrow \gamma + \gamma_2 \quad . \quad . \quad . \quad (6)$$

$$\gamma + \text{liquid} \longrightarrow \beta_1 + \gamma_2 \quad . \quad . \quad . \quad (7)$$

Time has not permitted a closer investigation of these reactions, but the temperature of the invariant reaction

$$\gamma + \beta_2 + \text{liquid} \longrightarrow \gamma + \gamma_2 \quad . \quad . \quad . \quad . \quad (6)$$

has been found by thermal analysis to be 217° C. (see Fig. 14). Since the Ag_3Sn–tin binary eutectic separation takes place at 221° C., and the peritectic reaction $Sn_{\alpha_1} + \text{liquid} \longrightarrow \beta_2$ of the tin–mercury system takes place at 226° C., it follows that the invariant reaction

$$\gamma + \alpha_2 + \text{liquid} \longrightarrow \gamma + \beta_2 \quad . \quad . \quad . \quad . \quad (5)$$

must take place at some temperature below 221° C. but above 217° C. Further, from an examination of the liquidus surface, Fig. 16, and from the fact that the binary reaction of the tin–mercury system $\beta_2 + \text{liquid} \longrightarrow \gamma_2$ occurs at 216° C., it may be deduced that the temperature of the invariant reaction

$$\gamma + \text{liquid} \longrightarrow \beta_1 + \gamma_2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

must take place at some temperature below 216° C. and probably above 210° C.

(b) *Microscopic Analysis.*

The microscopic examination of specimens specially prepared and annealed for several months at 70° C., which in these cases is below their solidus, together with their X-ray analysis, has been carried out over a very limited range of composition. The examination is admittedly incomplete, owing to the lack of time, but it is sufficient to confirm the conclusions of thermal analysis regarding the existence of the various phase fields. The limits, however, of these constituents under equilibrium conditions have not been determined, but the results obtained, as shown in Figs. 7–19, show the constitution of the alloys under the conditions of thermal analysis and certain heat-treatments. The boundaries shown may probably be shifted somewhat by subsequent work; but apart from the limit of the $\beta_1 + \gamma_2$ and the $\beta_1 + \gamma_1 + \gamma_2$ phase fields, the constitution shown will probably not be far from equilibrium conditions. Examination of sections of the constitutional model plotted with constant tin contents, parallel to the silver–mercury side of the base of the model shows, in the case of silver–rich alloys, that over a wide range of composition the limits of the solidus can only be determined, if at all, with great experimental difficulty; while from sections, shown in Figs. 7–12, which are parallel to the silver–tin side, and which are constant mercury sections, it will be seen that prolonged low-temperature annealing of these mercury-rich alloys is essential, if their solidus is to be determined. For various reasons, it is probable that the limits inserted in Figs. 7–19 are substantially correct, but the limits of the $\beta_1 + \gamma_1 + \gamma_2$ phase field have, as yet, not been determined.

The alloys examined were made up in a manner similar to that used for thermal analysis, slowly heated to about 400° C. and then slowly cooled to room temperature, in order to ensure complete amalgamation before subsequent annealing. The annealings were carried out in a thermostatically controlled water-bath at 70° C. for weeks or months, details being given in Appendix III (p. 399).

Typical microstructures are given in Figs. 22–30 (Plates LIII–LV), inclusive. The polishing and etching of the alloys were very difficult owing to the ease with which the alloys tarnished during polishing or, in those in which the γ_2 phase was present, the relative difference in hardness of the constituents made it impossible to obtain a surface without the compound γ_2 in relief. The alloys were etched by means of a polish attack on the pad with a dilute solution of ammonium persulphate to which a few drops of ammonia had been added.

Figs. 22, 23, and 24 show the microstructures of the ternary alloys containing 5 per cent. tin with 45, 50, and 55 per cent. mercury. Fig. 22

shows homogeneous β_1; the round dots are probably due to cavities left by the absorption on annealing at 70° C. of residual mercury. The addition of more mercury results in the formation of the γ_1 phase of the silver–mercury system (see Figs. 23 and 24). This phase persists in increasing quantity in the alloy containing 60 per cent. mercury.

A series containing 10 per cent. tin was next examined. In the unetched state, a very hard white constituent identified as γ_2 appeared during polishing on the pad which increased with increasing mercury content. On etching, a third phase was detected in the matrix in the ternary alloy containing 40 per cent. mercury; these phases have been identified as the γ_2 and γ_1 phases, respectively. Fig. 25 shows the microstructure of this alloy in the unetched state. Unetched, the alloy containing 45 per cent. showed the two phases β_1 and γ_2 (cf. Fig. 26) while more of the γ_2 phase appeared in the alloy containing 55 per cent. mercury. Fig. 27 shows the microstructure of this alloy etched by means of the polish attack; the background was etched, showing two distinct phases (as in the case of the alloy containing 10 per cent. tin and 40 per cent. mercury), which are probably β_1, γ_1, and γ_2. There is little doubt, on etching alloys containing 10 per cent. tin, 45–55 per cent. mercury, that a third phase appears, though photographically it is difficult to distinguish the two. There is, however, an apparent difference in hardness.

Of alloys containing 15 per cent. tin, that containing 35 per cent. mercury showed unetched the presence of the hard, white γ_2 phase in an amount appreciably less than that in the alloy containing 10 per cent. tin, 50 per cent. mercury, and probably more than that in the alloy containing 10 per cent. tin, 40 per cent. mercury. A polish attack, however, etches the γ_2 phase, and, as before, shows the presence of a phase surrounding it. This phase is apparently harder than the matrix, *i.e.* β_1 and its association with the γ_2 compound would suggest its formation either simultaneously with γ_2, or else as a product of some reaction between γ_2 and β_1. From Fig. 19 this phase is probably γ_1. Fig. 28 shows the etched alloy containing 15 per cent. tin, 35 per cent. mercury. The alloy containing 40 per cent. mercury contains more of this third phase surrounding γ_2: further increase of the mercury content results in more γ_2 and γ_1 and less β_1. Fig. 29 is of the alloy containing 15 per cent. tin, 50 per cent. mercury in the unetched state. This, compared with Fig. 25, demonstrates the relative increase of the γ_2 phase with increasing tin and mercury contents.

A similar section of an alloy containing 40 per cent. tin 30 per cent. mercury, unetched, is shown in Fig. 30; the substance in relief is γ_2. A polish attack etches up another phase which surrounds this γ_2 phase, in a manner similar to that shown in Fig. 27. X-ray analysis confirmed that these three phases must be γ_2, γ_1, and β_1.

It is seen, therefore, that the hard white phase increases in amount (*a*) with the tin content, (*b*) with mercury content, and more rapidly when both constituents are increased simultaneously. This fact, apart from other evidence, supports the conclusion that this phase is associated with a tin–mercury phase. X-ray analysis identifies the actual presence of such a phase in these alloys.

(c) *X-Ray Analysis.*

The X-ray analysis of annealed specimens has been carried out by the author's colleague, Mr. C. Wainwright, to whom she is much indebted for his valuable contribution.

The results have not been used to determine phase limits, but only as an independent means to identify or corroborate the nature of the constituents found by microscopic examination. In this connection the occurrence of a new phase is usually plainly observable under the microscope before its quantity is sufficient to give positive evidence by the X-ray method.

The specimens, which previously had been heat-treated as shown in Appendix III (p. 399), were examined microscopically and then the surface was filed and the filings submitted to X-ray analysis. The results obtained are given in Table I, together with those observed from microscopic examination.

TABLE I.

	Mercury, Per Cent.	Silver, Per Cent.	X-Ray Analysis.	Microscopic Analysis.
5 per cent. Tin Series	45	50	β_1	β_1
	50	45	β_1	$\beta_1 + \gamma_1$
	55	40	$\beta_1 + \gamma_1$	$\beta_1 + \gamma_1$
	60	35	γ + tr. β	$\beta_1 + \gamma_1$
10 per cent. Tin Series	40	50	β_1	
	45	45	β_1 + little γ_1	
	50	40	$\beta_1 + \gamma_1$ + tr. γ_2	
	Tin, Per Cent.			
50 per cent. Mercury Series	5	45	β_1	$\beta_1 + \gamma_1$
	10	40	$\gamma_1 + \beta_1$	$\gamma_1 + \gamma_2 + \beta_1$
	15	35	γ_1 + tr. β_1 + tr. γ_2	$\gamma_1 + \gamma_2 + \beta_1$
	25 *	25	$\gamma_1 + \gamma_2$ + tr. β_1 ?	$\gamma_1 + \gamma_2$ + possibly a third phase

* Thermal curve ingot, annealed 3 weeks at 70° C.

In order to confirm the identification of the phase termed γ_2, the thermal ingot of an alloy containing 40 per cent. tin, 30 per cent. mercury and 30 per cent. silver after being annealed for 6 days at 70° C. was examined microscopically and by X-ray analysis. Fig. 30 (Plate LV) shows the microstructure; the hard phase standing in relief was identified as the γ_2 phase, while the background consists mainly of β_1 or γ_1. Visually it seemed as if twice as much γ_1 (or β_1) than γ_2 was present and yet only γ_2 was found with difficulty by X-ray analysis. There were indications that a reaction ring surrounded the γ_1 phase; this, however, does not appear in the photomicrograph. It will be seen from these few results that both X-ray and microscopic analysis support those obtained from thermal analysis.

Results have been obtained, however, which do not, on the surface, appear to be consistent with thermal analysis. Three specimens were made up, by the method already described, annealed for 28 days at 490° C. and then quenched in water. The composition of the alloys were:

(i) Tin 2, mercury 50, silver 48 per cent.
(ii) „ 4, „ 50, „ 46 „
(iii) „ 6, „ 50, „ 44 „

Microscopic examination showed the presence of quenched liquid in all three specimens, a small amount in (i) and an appreciable amount in (iii). The first alloy consisted definitely of two constituents, one of which was in the crystal boundaries and was very brittle: this was presumably quenched liquid. The other phase was slightly twinned and was definitely ductile. On grinding the sample for X-ray analysis, the brittle phase powdered easily, but the other phase was hammered into ductile plates. An X-ray analysis of each constituent, independently, gave the same lattice structure in each case, *i.e.* γ_1 (silver–mercury compound).

The other two alloys, containing 4 and 6 per cent. tin, respectively, consisted of three phases:

(*a*) the ductile matrix;
(*b*) the brittle quenched liquid in the crystal boundaries; and
(*c*) a white phase which pitted easily during polishing.

X-ray analysis of the alloy containing 4 per cent. tin, again showed the lattice structure of one phase only, *viz.* γ_1 (Ag–Hg).

From the constitutional diagram of alloys containing 50 per cent. mercury (Fig. 8), it is seen that the alloys containing 2 per cent. tin consist of α_1 + liquid at the temperature of quenching, *i.e.* 490° C., while both of the two alloys containing 4 and 6 per cent. tin consist of the phases $\alpha_1 + \beta_1$ + liquid, the latter of these two alloys being near to the β_1 + liquid phase field. That these alloys, though three phases are visible on microscopic examination, should only show the presence of

γ_1 (Ag–Hg) on X-ray analysis is remarkable and cannot be explained satisfactorily, except by the fact that it may be impossible to retain the β_1 phase in the quenched state and that the separation of the γ_1 phase takes place in spite of quenching (see Fig. 8).

(3) THE CONSTITUTIONAL DIAGRAM.

The constitution of ternary alloys of silver, tin, and mercury at temperatures of 100°, 84°, and 70° C. are shown in Figs. 17, 18, and 19 (Plate LII). With temperatures above 100° C., the β_1 + liquid phase field enlarges at the expense of the adjoining phase fields, until the liquidus, as shown in Fig. 16, is reached.

The constitution of the ternary alloys containing 0–50 per cent. silver, 0–25 per cent. tin has been fairly well established. It is probable, as previously explained, that the position of the junction of the β_1 phase field with the three phase fields may be displaced owing to non-equilibrium conditions. The evidence available suggests that the α and β phases of the binary silver–tin and silver–mercury systems form continuous series of solid solutions, as shown in the diagrams, and, further, that the silver–tin–mercury ternary system is divided into the ternary fields: (*a*) γ–α_2–β_2, (*b*) γ–β_2–γ_2, (*c*) γ–β_1–γ_2, (*d*) β_1–γ_1–γ_2, (*e*) γ_1–γ_2–δ_2, (*f*) γ_1–γ_2–ϵ_2, (*g*) γ_1–ϵ_2–Hg.

Of vital importance to dental amalgams is the constitution of alloys (amalgams) containing about 40–50 per cent. mercury, and about 13–16 per cent. tin. It has been shown [8] that the composition of dental amalgams which will expand on setting not more than 4 μ on 3–4 mm., should lie within the above-mentioned range of composition, and that the composition of dental fillings which contract on setting contain less than 40 per cent. mercury and more than 15 per cent. tin, and those which show marked expansion more than 50 per cent. mercury and less than 13 per cent. tin. From a study of the constitution, it is seen that (with a small displacement, see paper on Dental Amalgams [12], Fig. 4, *PQR*) these dimensional changes may be associated with the simultaneous disappearance or reappearance of the γ_1 and γ_2 phases; and that the boundaries *LM*, *MS* of the ternary phase field $\beta_1 + \gamma_1 + \gamma_2$ mark the limits of the compositions of those amalgams which contract or expand, respectively, on setting. Furthermore, it has been noted that the compositions of amalgams showing little or no dimensional changes on setting, lie close to *M*, *i.e.* the junction of the β_1 phase field with the ternary phase field, $\beta_1 + \gamma_1 + \gamma_2$. Hence the disappearance of γ_1 and the presence of γ_2 in the dental amalgam may be associated with contraction while the re-appearance of γ_1 and disappearance of γ_2, with expansion. The disappearance of both phases is associated with little or no dimensional change.

The setting of dental amalgams is described fully in another paper on Dental Amalgams [12] and, therefore, only brief mention of it is made here. The composition of silver–tin dental alloys has been found to be extremely critical [8] and the best compositions are those which contain not less than 25 or more than 27 per cent. tin (copper may replace silver up to 5 per cent.). This composition practically corresponds with that of the γ compound of the silver–tin system, *i.e.* Ag_3Sn, and, therefore, the section showing the effect of the addition of mercury (Fig. 13) to this compound is of the utmost importance.

It is noticed that in Fig. 13 a series of thermal arrests at a temperature of 200° C. and lower are marked. These are associated with those seen in the section Fig. 14, which cuts across the above section at 4·5 per cent. mercury; as has been already pointed out these thermal arrests are indicative of non-equilibrium conditions. This section (Fig. 13) is of the utmost importance, since the changes which take place during the setting of dental amalgams made from alloys consisting of silver and tin in the ratio of that in the compound Ag_3Sn, must be associated with their constitution.

The addition of small amounts of mercury to Ag_3Sn, results in the formation of the β_1 phase at the expense of γ (*i.e.* Ag_3Sn). Increasing amounts of mercury result in the formation of γ_2, and then γ_1, the relative proportions depending on the amount of mercury. It is seen, therefore, that under equilibrium conditions a dental amalgam should finally consist of $\beta_1 + \gamma_2$ or $\beta_1 + \gamma_1 + \gamma_2$, depending on the mercury content. It is likely, however, that the changes taking place in a dental filling during setting are an indication of an unstable state, which is unlikely ever to reach equilibrium, though the rate of change may approach zero asymptotically.

From the liquidus surface, given in Fig. 16, it is seen that the β + liquid phase field extends over the major part of the ternary system and that at the tin and mercury ends, respectively, it must meet two other liquidus surfaces to form an invariant point in each corner. The invariant reactions are:

$$(a)\quad \gamma + \text{liq.} \longrightarrow \beta_1 + \gamma_2$$
$$(b)\quad \beta_1 + \text{liq.} \longrightarrow \gamma_1 + \gamma_2$$

The 100° C. isotherm (Fig. 17) shows that under this β_1 + liquid surface, the $\beta_1 + \gamma_2$ + liquid binary complex surface extends over very nearly the same range of composition, while that of the $\beta_1 + \gamma_1$ + liquid is small. The $\beta_1 + \gamma$ + liquid phase region exists at much higher temperatures, but not at this temperature 100° C.

At a temperature of 84° C., the invariant reaction

$$\beta_1 + \text{liq.} \longrightarrow \gamma_1 + \gamma_2$$

occurs; Fig. 18 shows the constitution of the alloys as existing just a fraction above the invariant reaction temperature, while Fig. 19 shows that at 70° C., where the composition of the alloys which are still liquid down to the temperature of the freezing of mercury, lie to the right of the line joining the $\gamma_1 + \gamma_2$ phase fields.

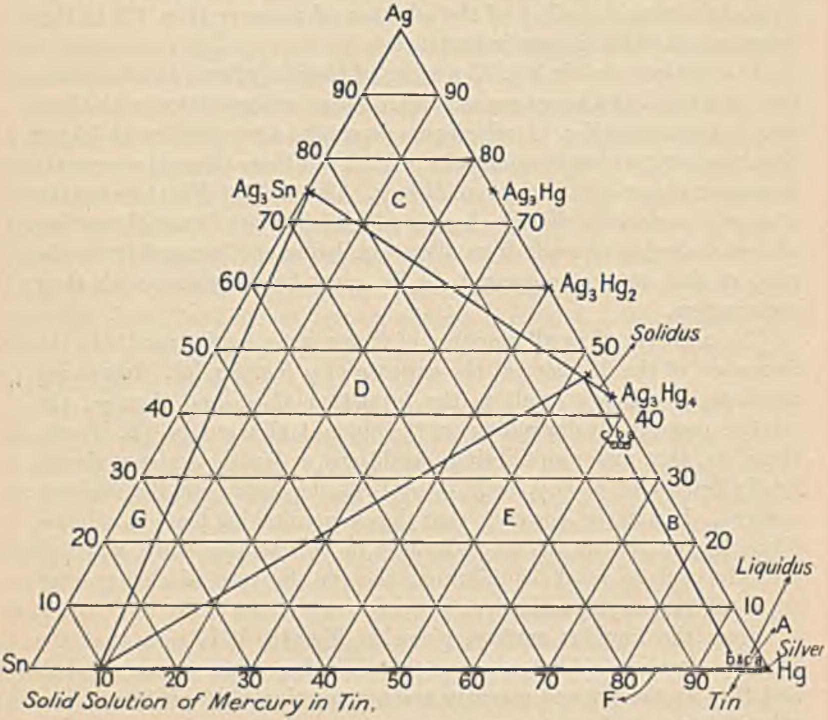

FIG. 20.—63° C. Isotherm.

The boundaries of the $\beta_1 + \gamma_2 +$ liquid phase field (Fig. 18) towards the tin end of the diagram have not been drawn, since the data at hand are insufficient to establish its limits. In Fig. 19, however, the dotted lines indicate the probable limits of the $\beta_1 + \gamma$ and $\beta_1 + \gamma_2$ phase fields. The limit of the $\beta_1 + \gamma_1 + \gamma_2$ phase field has not been established. The dotted line *PM* (from thermal analysis alone) cannot possibly be the boundary of this field under equilibrium conditions.

From these diagrams it is also seen that the β phases of the silver–tin and silver–mercury systems form a wide range of solid solutions.

Knight and Joyner [2] found that the compositions of the point *M* at 63° and at 90° C. were

	Atomic Per Cent.			Weight Per Cent.		
	Ag	Sn	Hg	Ag	Sn	Hg
90° C. . . .	57	11	32	44·2	9·35	46·45
63° C. . . .	46	2	52	31·78	1·52	66·7

Their results shown in Figs. 20 and 21 were obtained by the analysis of the liquid phase determined by sealing weighed amounts of the three constituents, silver, tin, and mercury, in reaction tubes in an atmosphere of coal gas. . . . "Care was taken that all the solid had really come into contact with all the liquid. . . ." "After the reaction tubes had remained in the thermostat for a sufficiently long time to ensure the attainment of equilibrium—this time varied from 4 days at the low temperatures to as many hours at the high temperatures—part of the liquid phase was removed and analyzed. . . ."

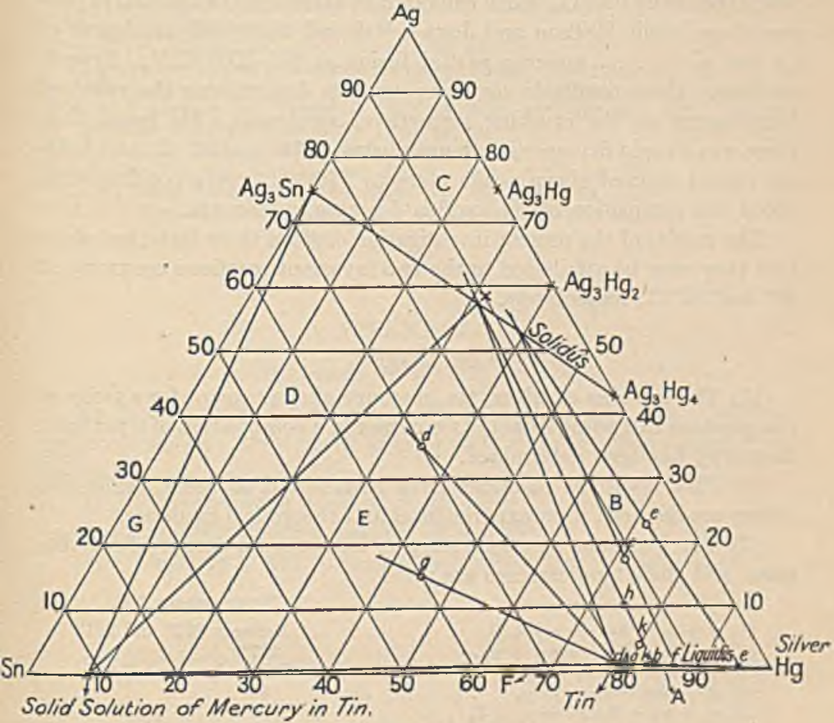

Fig. 21.—90° C. Isotherm.

The results from the present research indicate that the composition of *M* at 100° C. is little, if at all, different from that at 70° C. This composition is found to be approximately

Silver . . .	50 per cent.
Tin	10 ,, ,,
Mercury . . .	40 ,, ,,

and is of the same order as that found by the above authors at 90° C.

Black [9] observed that a permanent change occurred in an amalgam heated to about 100° C., which could not be attributed to thermal expansion alone, while McBain and Joyner [10] found that "all amalgams of tin and silver . . . undergo partial fusion at 65°–100° C."; Gray [11] confirmed these results in some experiments determining the effect of temperature on the crushing strength of amalgams. He found that there was a rapid decrease in strength between 70° and 80° C., and heating curves showed sharp peaks close to 77·3° C., corresponding with about the completion of the sudden decrease in strength.

The results of the present investigation confirm these facts, but show that they may be attributed to the two invariant reactions occurring at 80° and 84° C., respectively.

CONCLUSIONS.

(1) The liquidus of silver, tin, mercury alloys (except for a range of composition extending from the tin corner to a composition of 6 per cent. mercury), has been determined.

(2) Five invariant reactions have been found to occur, while two others are deduced from experimental and theoretical evidence.

(3) The invariant reactions starting from the tin corner of the diagram and their temperatures are:

	Temperature, ° C.
(1) $\gamma + \alpha_2 + \text{liq.} \longrightarrow \gamma + \beta_2$ . . .	Between 217° and 221°
(2) $\gamma + \beta_2 + \text{liq.} \longrightarrow \gamma + \gamma_2$	217°
(3) $\gamma + \text{liq.} \longrightarrow \beta_1 + \gamma_2$	Probably about 210° C.
(4) $\beta_1 + \text{liq.} \longrightarrow \gamma_1 + \gamma_2$	84°
(5) $\gamma_1 + \gamma_2 + \text{liq.} \longrightarrow \gamma_1 + \delta_2$ . . .	80°
(6) $\gamma_1 + \delta_2 + \text{liq.} \longrightarrow \gamma_1 + \epsilon_2$ . . .	−36°
(7) $\gamma_1 + \epsilon_2 + \text{liq.} \longrightarrow \gamma_1 + \epsilon_2 + \text{Hg}$ . .	−38·8°

(4) Isothermal sections for temperatures of 100°, 84°, and 70° C. have been plotted from the experimental data obtained.

ACKNOWLEDGMENTS.

The author wishes to express her thanks to the Dental Investigation Committee of the Department of Scientific and Industrial Research, on whose recommendation this paper is published, and to Dr. C. H. Desch, F.R.S., Superintendent of the Metallurgy Department, for his continued interest and encouragement.

Mr. E. G. Sutherland, B.Sc., throughout, has assisted in the experimental part of this research; the author would express her appreciation of his very careful and accurate work.

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APPENDIX I.

ANALYSES OF MATERIALS USED.

(1) Silver obtained from the Sheffield Smelting Co., Ltd. Spectrographic analysis: total metallic impurities not exceeding one part per million.

(2) Silver containing 0·066 per cent. copper by analysis.

(3) Chemically purified, re-distilled mercury.

(4) "Chempur" tin. Chemical analysis: trace of iron only.

APPENDIX II.

The Numeral before "T" Denotes Per Cent. Tin. The Numeral after "T" Denotes Per Cent. Mercury.	Temperature of Arrests on Cooling, ° C.		
	Number of Weeks at 70° C.	Before Annealing at 70° C.	After Annealing at 70° C.
2T63		−40 −42	No arrest at either temperature.
2T68		−42 −39	One very small arrest at −41°.
2T73		Not done	Arrest at −40°. Arrest at −42°.
5T55	39	−41	No arrest at either temperature.
5T60	39	−40 −38	" " " "
5T65	39	−44 −40	" " " "
5T70	40	−44 −40	Arrests at both temperatures.
5T75	40	−49 −39	" " "
10T50	32	−39 −37	No arrest at either temperature.
10T65	12		Arrests at both temperatures.
15T50	32	−40	No arrest at either temperature.
15T55	3	−41 −39	" " " "
15T60	14	−42 −41	Arrests at both temperatures.
15T70	14	−43 −40	" " "
20T55	19	−42	No arrest at either temperature.
20T60	19	−41 −39	Arrests at both temperatures.
20T65	19	−41 −39	" " "
25T50	19	−40 −38	No arrest at either temperature.
25T55	12	−40 −38	Arrests at both temperatures.

APPENDIX III.

MICROSCOPIC ANALYSIS.

The specimens were sealed in an atmosphere of dry hydrogen, in transparent quartz tubes, provided with closed stuffer tubes to reduce the available gas space.

MICROSCOPIC ANALYSIS.

Alloy.	Composition, Per Cent.			Number of Weeks at 70° C.	Number of Phases Present.	X-Ray Structure.
	Tin.	Silver.	Mercury.			
5T45	4·99	49·71	45·05	40	Homogeneous	β_1
5T50	4·96	45·08	49·9	36	Two. Small amount of a second phase	β_1
5T55	4·98	39·46	55·54	36	Two. A deal more of the second phase	$\beta_1 + \gamma_1$
5T60	5·12	33·98	60·86	40	Two. Still more of the second phase	$\beta_1 + \gamma_1$
10T40	9·85	48·56	41·5	44	Two. A small amount of a hard white phase. Possibly a third phase	β_1
10T45	10·14	44·41	45·4	44	Two	β_1 + little γ_1
10T50	10·03	39·37	50·46	40	Possibly three phases. A greater amount of the hard white phase.	$\beta_1 + \gamma_1$ + tr. γ_2
10T55	9·99	34·13	55·76	44	Possibly three phases. A great deal more of the hard phase	Not done
15T35	15·11	50·21	34·6	44	Possibly four. Appreciably less of the hard white phase than in 10T50, but more than in 10T40.	Not done
15T40	15·14	45·14	39·72	44	Possibly four. One of which is the hard phase	Not done
15T45	15·21	39·06	45·72	44	Possibly four. More of the hard phase	Not done
15T50	14·97	35·03	49·96	40	Possibly four. Still more of the hard phase	γ_1 + tr. β_1 + tr. γ_2
2T50				Quenched in water after 28 days at 490° C.	Possibly three, including small amount of quenched liquid	γ_1 only
4T50				"	Three. A greater amount of quenched liquid	γ_1 only.
6T50				"	Three. Still greater amount of quenched liquid	Not done
25T50 Cooling Curve Ingot				3	Possibly four. A large amount of the hard phase.	$\gamma_1 + \gamma_2$ + tr. β_1

HEAT-TREATMENT FOR COMPLETE AMALGAMATION.

The tube containing the specimen was encased in an iron tube, which was placed in an electric furnace, the temperature of which was slowly increased to about 400° C. The furnace was maintained at this temperature for 12 hrs. then increased to about 30° C. above the liquidus of the specimen, and held there for 1 hr. to ensure complete fusion. The current of the furnace was then switched off, and the specimen allowed to cool in the furnace.

The position of the specimen tube was so arranged that the upper portion was in the hottest part of the furnace, thus making a temperature gradient from top to bottom. This was found to prevent condensation of mercury on the sides of the specimen tube.

The specimens were then annealed at 70° C. in a thermostatically controlled water-bath from 9 to 11 months.

CORRESPONDENCE.

Mr. E. H. Bucknall,[*] M.Sc. (Member): Dr. Gayler's paper describes the almost complete elucidation of a hitherto practically unexplored ternary system of unusual complexity in a very restricted compass. Readers are likely to be puzzled by differences between the binary mercury–tin system as presented in Fig. 3 and that deducible from Figs. 7–19 as the limit of the ternary system when the silver content becomes zero. In the ternary diagrams a binary constituent referred to as δ_2 is represented as occurring in a wide range of alloys at temperatures between 90° and — 34° C., below which temperature an ϵ_2 constituent is shown (apparently Prytherch's δ). The isothermal section at 100° C. also indicates the existence of a β_2 constituent, although in Fig. 3 β is shown to decompose at 198° C. into $(\alpha + \gamma)$. From the foregoing it would appear that the binary diagram for tin and mercury accepted by Dr. Gayler differs markedly from that suggested by Prytherch, although the highly condensed text of the paper does nothing to suggest this.

Two small points in connection with the presentation of the ternary system, which seem to me to call for further attention are the unusual shape of the $(\beta_1 + \gamma_2 + \text{liquid})$ fields at 100° and 84° C. and the equations (2), (3), (4), (5), and (6) used in the text to denote some of the invariant reactions. In true equilibrium all three-phase fields in ternary systems must, of course, be triangular in isothermal section and one wonders whether the dotted extension of these fields to the left of the point *M*, in Figs. 17 and 18, is really caused by the non-attainment of equilibrium during the thermal curves, as is suggested by Dr. Gayler, or whether it represents an additional three-phase field formed by a reaction at a temperature indistinguishably close to that forming $(\beta_1 + \gamma_2 + \text{liquid})$. To turn to the second point, the equations referred to appear unnecessarily complex. Invariant reactions in ternary systems involve in general four constituents, of which two may be found on each side of the reaction plane, or alternatively three on the one side and one on the other. The two kinds of reaction are adequately represented by equations of the form:

$$\alpha + \beta \rightleftharpoons \gamma + \delta$$
$$\alpha + \beta + \gamma \rightleftharpoons \delta$$

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FIG. 22.—Sn 5, Hg 45, Ag 50%. Polish Attack with Ammonium Persulphate and Ammonia. × 150.

FIG. 23.—Sn 5, Hg 50, Ag 45%. Polish Attack with Ammonium Persulphate and Ammonia. × 150.

FIG. 24.—Sn 5, Hg 55, Ag 40%. Polish Attack with Ammonium Persulphate and Ammonia × 150.

FIG. 25.—Sn 10, Hg 40, Ag 50%. Unetched. × 150.

All Annealed at 70° C. for 9–11 Months.

[*To face p.* 400.

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Fig. 26.—Sn 10, Hg 45, Ag 45%. Polish Attack with Ammonium Persulphate and Ammonia. × 150.
Fig. 27.—Sn 10, Hg 55, Ag 35%. Polish Attack with Ammonium Persulphate and Ammonia. × 150.
Fig. 28.—Sn 15, Hg 35, Ag 50%. Polish Attack with Ammonium Persulphate and Ammonia. × 150.
Fig. 29.—Sn 15, Hg 50, Ag 35%. Unetched. × 150.

All Annealed at 70° C. for 9–11 Months.

Fig. 30.—Sn 40, Hg 30, Ag 30%. Unetched. × 150.

Cooling Curve Ingot.

To use more than four items in such equations particularizes the reaction to a part of the total area of the reaction plane and the advantages of generalization are lost.

Dr. ARTHUR W. GRAY,* A.B. (Member): I should be glad if Dr. Gayler would describe in detail the exact nature of the evidence and the reasoning that led her to important conclusions, especially when her conclusions differ from those of other investigators. What are the particular characteristics of each phase that enabled her to identify it? Neither X-ray nor microscopic evidence seems to be very definite, and Dr. Gayler herself points out inconsistencies.

What is the proof that the β_1 and the γ_1 phases do not contain intermetallic compounds, but are solid solutions of narrowly limited ranges of composition? Does evidence now available definitely exclude the possibility of such compounds, with or without accompanying solid solution in them or of them in solid solutions? or, does the evidence merely suggest the interpretations given by Dr. Gayler? On p. 380 she states that Murphy "showed that the compound Ag_3Hg_4 does not exist"; but Murphy † writes: "In the absence of accurate values for the specific gravity the X-ray observations throw no light on the atomic ratios in the compounds which might be considered to be the bases of these phases: formulæ of the type Ag_4Hg_3 or Ag_5Hg_4 would satisfy the thermal and microscopic observations relating to the composition of the β phase, and in the same way Ag_3Hg_4, Ag_4Hg_5, &c., could be suggested for the γ phase." How were the doubts about these hypothetical compounds and about Ag_5Hg_8 finally cleared up? Also, on p. 380 Dr. Gayler states that "Prytherch has found evidence for the existence of three" between tin and mercury; but she shows only one ($HgSn_3$) in either the Sn–Hg diagram (Fig. 3), which she reproduces from Prytherch's unpublished work, or in her own diagrams of the Ag–Sn–Hg system, and she does not mention the nature of the evidence.

How was the "very hard white constituent identified as γ_2," as mentioned on p. 389 and indicated in Figs. 25–30? The solid solution of mercury in tin is not ordinarily regarded as very hard. Tammann and Mansuri (Dr. Gayler's reference 6) found the maximum hardness obtained by dissolving mercury in tin to be about the same as that of cadmium. This maximum was very sharp at about 5 per cent. mercury. According to the tin–mercury diagram of Prytherch, this amalgam would consist of α_2 and γ_2; but Tammann and Mansuri (p. 66) report only one constituent visible through the microscope up to 18 per cent. mercury. Did Dr. Gayler compare the hardness of the pure Sn–Hg phase designated γ_2 on the diagram of Prytherch with the hard constituent that she has designated as γ_2 in her Figs. 25–30? A comparison could be made easily by means of Bierbaum's micro-character. Of course, solution of silver in γ_2 might cause additional hardening, but no evidence on this point is submitted.

There seems to be uncertainty in the identification of the phases marked β_1 and γ_1 in Figs. 22–30. On p. 391 the description of Fig. 30 indicates that β_1 could not be distinguished from γ_1 and that "only γ_2 was found with difficulty by X-ray analysis." On p. 389 it is stated that the constituents shown in Fig. 27 are "*probably* β_1, γ_1, and γ_2." Farther down on the same page, after describing a constituent of the amalgam composed of silver 50, tin 15, and mercury 35 per cent. it is concluded: "From Fig. 19 this phase is *probably* γ_1." However, Fig. 19 shows no γ_1, but only β_1 and γ_2 for this composition.

Fig. 25 indicates that the amalgam composed of silver 50, tin 10, and mercury 40 per cent. is mainly β_1 with some γ_2; but Fig. 7 indicates that it consists entirely of β_1. In all the amalgams illustrated in Figs. 22–30, and also in amalgams of Ag_3Sn containing 40–50 per cent. mercury, the mercury content ranges from about 41 to about 61 per cent. of the total of mercury plus silver in the amalgam.

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† *J. Inst. Metals*, 1931, 46, 513.

According to Murphy's silver–mercury diagram, amalgams of silver only that contain from 41 to 61 per cent. mercury consist of α_1, β_1, or a mixture of the two; according to Dr. Gayler, the addition of tin changes the constituents to β_1, or β_1 and γ_1, with γ_2 appearing when the concentration of tin and mercury becomes high enough. According to Table I, p. 390, microscopic analysis showed that the amalgam composed of silver 35, tin 15, and mercury 50 per cent. consisted of γ_1 and γ_2; but Fig. 29 represents it as consisting of γ_2 surrounded by very much more β_1; the table reports X-ray analysis as indicating γ_1 with a trace of β_1 and a trace of γ_2. The amalgam composed of silver 35, tin 5, and mercury 60 per cent. is reported to show γ plus a trace of β by X-ray analysis, but β_1 plus γ_1 by microscopic analysis. Incidently, the table represents all three amalgams of the 10 per cent. tin series as composed of 105 per cent.

An error similar to the one just mentioned occurs in line 6 from the top of p. 395, which interchanges the atomic percentages of silver and mercury derived from Knight and Joyner's 63° isotherm (Fig. 20). As a consequence of this slip the weight percentages calculated are likewise incorrect.

How were the boundary lines of the several fields represented in the diagrams determined where no points indicating observations are shown? In some cases the widths of the fields seem less than the uncertainties of observations. Some points on these boundaries are plotted that do not correspond to alloys shown in Fig. 4, which p. 383 represents as showing all the alloys examined. For example, how was Fig. 7 drawn for less than 10 per cent. tin? and Fig. 14 for less than 20 per cent. tin?

The tin–mercury diagram of Prytherch (Fig. 3) shows no β_2 below 200° C.; but Dr. Gayler's 100° isotherm (Fig. 17) shows fields marked β_2, $\alpha_2 + \beta_2$, $\beta_2 + \gamma_2$, $\gamma + \alpha_2 + \beta_2$, $\beta_2 + \gamma$, and $\beta_2 + \gamma + \gamma_2$; also, Fig. 14 shows $\gamma + \beta_2 + \gamma_2$ below 200°. How were these fields determined?

Fig. 14 indicates that amalgams containing 4·5 per cent. mercury consist of γ plus liquid immediately under the liquidus when the tin content is from about 63 to 80 per cent., and of β_2 plus liquid when it is from 80 to 96 per cent. Murphy's silver–tin diagram shows that with 0 per cent. mercury there is γ plus liquid under the liquidus from about 52 per cent. tin to 96·5 per cent. Fig. 16 shows under the liquidus a field marked γ plus liquid extending right up to the Sn–Hg side of the triangle at both 0 and 4·5 per cent. mercury. Also, on the Ag–Sn side of the triangle in Fig. 16, α plus liquid is represented adjacent to both the silver and the tin corners. Are these representations consistent with one another? Again, is Fig. 7 consistent with Figs. 8, 9, 10, 13, and 15? Apparently the field in Fig. 7 marked $\beta_1 + \gamma_2 + \delta_2$ should have been marked $\beta_1 + \gamma_1 + \gamma_2$.

In describing the occurrence of the γ_1 phase of the silver–mercury system (p. 389) it is stated that " this phase persists in increasing quantity up to 60 per cent. mercury "; but Fig. 19 indicates up to 70 per cent.

Professor E. W. SKINNER,* Ph.D.: I have no criticism to make concerning the data given in this paper nor the accuracy with which they were determined. However, from the point of view of dental interpretation of the results, it is not clear why a temperature of 70° C. was selected for the annealing of the specimens for microscopic examination. This temperature is very close to the transition temperatures found by Gray in some of his specimens, and a lower annealing temperature, if only 5°–10° C. might be more convincing as a basis for the comparison with dental amalgam restorations. However, on the basis of her own data, the author is justified in this respect.

One cannot help but be impressed with the complex structures involved, and also by the fact that the author does not claim to have reached equilibrium conditions even after the rather extensive homogenization carried out. It is little wonder that dimensional change and plastic flow measurements show a

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slow but continuous change taking place in these materials for as long a time as the tests have been continued.

It is of interest to note the difference in hardness between the various phases as demonstrated by the polishing technique. These observations may eventually be of value in explaining the plastic flow which occurs in these amalgams.

The Author (*in reply*): Mr. Bucknall has observed differences between Prytherch's tin–mercury diagram (Fig. 3) and that which can be deduced from the end points of Figs. 7–9 when the silver content is nil. The text has been very briefly amended to explain this divergence and the following will amplify that explanation.

In a private communication, Prytherch has said that he observed some slight arrests in thermal curves of some alloys at a temperature of about 100° C., but a very limited examination in the solid state showed no evidence of a new phase. Thermal curves of the ternary alloys, however, indicated the evidence of a reaction which could be associated definitely with the tin–mercury system, and thermal curves of the binary alloys taken under the same experimental conditions as those used for the ternary alloys also showed the existence of thermal arrests at about 90° C. on both heating and cooling curves. Fig. A shows the liquidus of the binary system based on van Heteren's and Prytherch's data, indicated by small circles and crosses, respectively; while the results obtained during the present investigation from thermal curves on three alloys

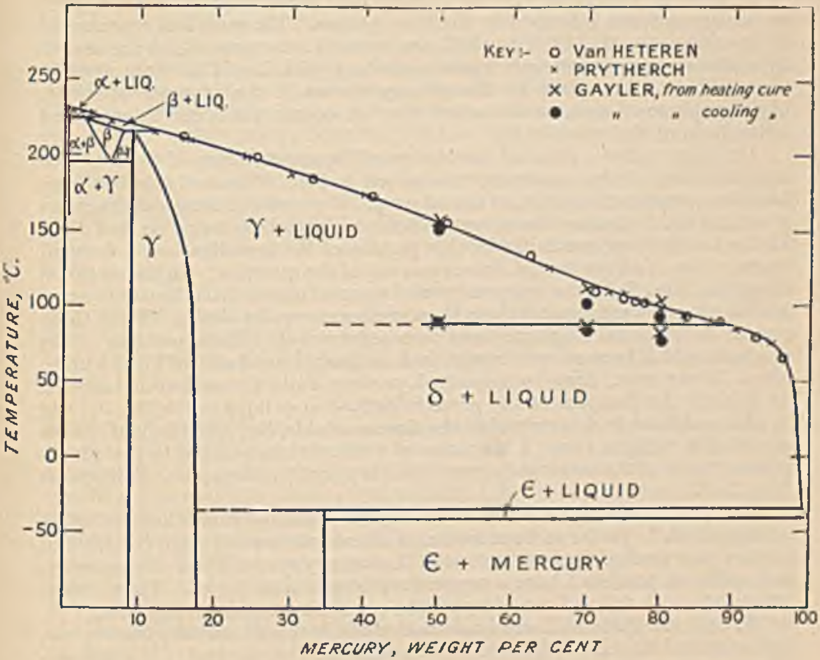

Fig. A.

forming the end-points of the 80, 70, and 50 per cent. mercury sections of the ternary system, are shown by large crosses (heating) and full circles (cooling). These results point to the existence of a new δ phase formed by a peritectic reaction between the γ phase and liquid.

The ($\beta_1 + \gamma_2 +$ liquid) field at 100° and 84° C. is unusual in shape and theoretically impossible. The experimental data available, however, indicated limits as shown in Figs. 17 and 18. The investigation over this region was necessarily incomplete, and further work will be required to elucidate this region. The dotted lines in the isothermal sections are only put forward as possible boundaries; their existence was necessary to explain phases present in the Ag_3Sn–Hg and the 4·5 per cent. mercury sections (Figs. 13 and 14).

Invariant ternary reactions, Mr. Bucknall suggests, must be of the form either $\alpha + \beta \rightleftarrows \gamma + \delta$ or $\alpha + \beta + \gamma \rightleftarrows \delta$. Equation (2) may be written as (*a*) $\text{liq} \rightleftarrows \gamma_1 + \gamma_2 + \delta_2$ or (*b*) $\gamma_2 + \text{liq} \rightleftarrows \gamma_1 + \delta_2$. The first does not hold, since no ternary eutectic is formed by the three phases. The reactions represented by equations (2), (3), (4), (5), and (6) are peritectic reactions which are caused by a phase in the tin–mercury system reacting with liquid to form another phase. This takes place in the ternary system in the presence of the γ_1 (Ag–Hg) phase; hence, an invariant reaction occurs which can be expressed in the form of the equation (*b*).

Dr. Gray wishes a detailed description of the exact nature of the evidence and reasoning of the conclusion reached on p. 396. The evidence has been based on experimental data, as stated on p. 381; and the sectional diagrams given in Figs. 7–15 show the interpretation which has been based on that data. In the limited time available for this portion of the investigation, a detailed examination of alloys in equilibrium was out of the question. In the sectional diagrams, Figs. 7–15, the temperatures of thermal arrests from heating curves are indicated by crosses and those from cooling curves by circles. From these results the sectional diagrams have been constructed. Those portions of the diagrams which have no such marks, such as the left-hand side of Fig. 14 up to about 20 per cent., have been inserted, perforce, from theoretical deductions. In Fig. 15 the junction of the phase fields $\beta_1 + \gamma + \text{liq}$, $\beta_1 + \text{liq}$, $\beta + \gamma$, and β_1 also could not be determined in the time available, but again lack of crosses and circles indicate this. I have also plotted sections parallel to the silver–mercury side of the ternary diagram and they confirm the sectional diagrams Figs. 7–15.

Dr. Gray comments on my "conclusions differing from those of other investigators." So far as I am aware no investigators other than Knight and Joyner have studied the constitution of the ternary system silver–tin–mercury, and so far as possible I have compared my results with theirs. There are no other data with which I can compare the conclusions reached on p. 396.

The microscopic and X-ray examination of alloys is admittedly incomplete, but, as stated, that is owing to circumstances beyond my control. It is impossible to solve the constitution of amalgams from an examination of alloys of restricted composition and I found it necessary to extend the field of my investigation far beyond that which covers the range of composition of dental amalgams. The sectional diagrams put forward represent the constitution of the ternary alloys and indicate the reactions which take place in alloys at temperatures below the liquidus.

With regard to Dr. Gray's remarks about the β_1 and γ_1 phases, the old metallurgical conception of intermetallic compounds has been replaced by that formulated by X-ray investigators, who regard such phases as crystal structures existing over a wide range of composition; whether these are compounds or not is of no importance. In discussing Murphy's paper on silver–mercury alloys, Westgren has pointed out that the γ_1 phase has the structure of γ brass and hence, according to the Hume-Rothery rule, must be assigned the formula Ag_5Hg_8.

My reason for amending Prytherch's tin–mercury diagram has been given in my reply to Mr. Bucknall. The four compounds β, γ, δ, and ε in Fig. A appear in Figs. 7–15.

The hard white constituent (p. 389) identified as "γ_2," increased in amount as (*a*) the tin content increased, (*b*) the mercury content increased: it must, therefore, be associated with a tin–mercury phase. The ternary diagrams which have been based on the results of thermal analysis indicated that this hard phase must be the "γ_2" phase of the binary system (Fig. A).

Dr. Gray's suggestion of analysis by hardness measurements is interesting. I have made no hardness measurements of the pure tin–mercury phase; time has not permitted any physical properties of the alloys to be investigated, other than those reported in the paper.

The very limited microscopical analysis carried out has been used "to confirm the conclusions of thermal analysis regarding the *existence* of the various phase fields" (p. 388). It has been stated definitely that the alloys examined may not be in equilibrium and therefore the microstructures Figs. 22–30 must not be interpreted as "equilibrium" structures and used to define the limits of phase fields: they simply show that such phase fields exist in the neighbourhood of their composition.

The effect of the addition of tin to silver–mercury alloys is very marked: 2 per cent. tin increases the temperature of the peritectic reaction $\alpha + \text{liq} \rightarrow \beta$ from 278° to above 400° C. Thermal arrests indicating the formation o the $\beta + \gamma_1 +$ liquid phase field appear in alloys containing 56 per cent. and more mercury.

I thank Dr. Gray for pointing out the error in the composition of the 10 per cent. tin series and in Knight and Joyner's results; both have been corrected; also in the microscopic analysis of alloys containing 50 per cent. mercury and 10 and 15 per cent. tin, a third phase, β_1, had been observed, though it was unfortunately omitted from Table I. It has now been inserted.

Dr. Gray refers to the difference between the results of X-ray and microscopic analysis, *viz.* phases are seen in appreciable amounts in the photomicrographs and yet only traces are observed on X-ray analysis. The X-ray spectra of the γ_1 phase is composed of a very great number of lines, and it is consequently extremely difficult to identify other phases present in the alloy except when they are present in appreciable amount. Hence, X-ray analysis alone should not be used as a means of indicating the number of phases present in these alloys. The micro-examination of dental fillings showed three distinct constituents under the microscope, but here again X-ray analysis failed to detect any phase other than the γ_1 (Ag–Hg) phase.

The position of the boundaries in the diagrams has been discussed earlier. In Fig. 17 $\alpha_2 + \gamma_2$ should have been written instead of β_2: this has since been corrected.

The thermal analysis of alloys containing 4·5 per cent. mercury gave thermal arrests indicated in Fig. 14: these values linked up at the end-points with the silver–mercury and the tin–mercury systems, respectively. There was no experimental evidence against the diagram being drawn other than as in Fig. 14. It has been deduced, as stated on p. 392, that there is evidence for the existence of the ternary fields as shown in Fig. 17 at the tin corner. No claim has been made that these fields have been determined.

With regard to Fig. 16 no attempt has been made to determine the liquidus beyond the line forming the boundary of the $\beta +$ liquid and the $\gamma +$ liquid surfaces. The positions of the $\alpha + \text{liq}$ and the $\alpha_2 + \text{liq.}$ phase field are indicated so that their existence in that corner is realized.

Fig. 7 is consistent with the other diagrams. I regret that δ_2 has been inserted for γ_2; this has been altered. The sentence on p. 389 to which Dr. Gray refers, applies only to the composition of the alloy whose microstructure was examined and for "up to" read "in the alloy containing."

I thank Dr. Gray for pointing out that Fig. 19 differs from the isotherm in the paper on Dental Amalgams. This has now been corrected.

In reply to Professor Skinner the temperature of 70° C. was selected for the annealing of microscopic specimens for the following reasons:

(*a*) Thermal analysis showed that no transformation occurs in these alloys between the temperatures of − 36° and 80° C.

(*b*) Amalgams at mouth temperature, *i.e.* 37° C., tend to attain a condition associated with the reaction which takes place at 80° C. Such low-temperature reactions only proceed very slowly, so that if the alloys are annealed at a temperature close to the transformation temperature, *i.e.* at 70° C., there is more likelihood that equilibrium conditions may be approached more nearly in a comparatively reasonable time. The transition temperature found by Gray took place on heating at about 77° C.; no corresponding evolution of heat was observed on cooling. The conditions under which his thermal analysis were carried out differed from those of the present investigation in that in the latter case the alloys were amalgamated thoroughly before the thermal analysis. Gray, on the other hand, relied on the absorption of mercury under pressure. The composition of the amalgams which he used is not stated in his paper, and it is probable that the small difference in temperature of the transformation found by him (77° C.) and by me (80° C.) may be accounted for by the compositions of the alloys which were used in both cases; added elements would tend to lower the temperature of the transformation. There is no reason, however, to doubt that within certain limits the additions of small amounts of added elements will have little effect on the interpretation of the results.

The complexity of the constitution of these alloys emphasizes more strongly the need for further investigation of the changes taking place in amalgams made under different conditions.

DENTAL AMALGAMS.* 7

By MARIE L. V. GAYLER,† D.Sc. (Mrs. Haughton), Member.

Synopsis.

A theory of the setting of dental amalgams is submitted which is based on a study of the constitution of the ternary alloys of silver, tin, and mercury, together with the results of published data on the correlation between the dimensional changes occurring during the setting of these amalgams with (*a*) the composition of the dental alloys from which they are made; (*b*) the composition of the dental filling itself; and (*c*) the disappearance and appearance of the γ_2(Sn–Hg) phase in the amalgam or, *vice versa*, the appearance and disappearance of the γ_1(Ag–Hg) phase.

The changes taking place on setting are attributed to complex reactions which probably do not proceed to completion. These may be summed up briefly as:

$$(1)\ Ag_3Sn + Hg \longrightarrow \beta_1 + \gamma_2$$
$$(2)\ \beta_1 + \gamma_2 \longrightarrow \beta_1 + \gamma_1 + \gamma_2$$

No explanation for the marked contraction or expansion can be obtained from X-ray analysis, but the former is attributed to the formation of a solid solution of mercury in Ag_3Sn.

The investigation described in the present paper forms part of a research which has been carried out in the Department of Metallurgy of the National Physical Laboratory, on behalf of the Dental Investigation Committee of the Department of Scientific and Industrial Research, and with the aid of funds provided by the Dental Board of the United Kingdom.

(1) The Setting of Amalgams.

It has long been known that if mercury be mixed with filings of silver–tin alloys, which have or have not been previously aged at 100° C., dimensional changes occur during the setting of the resultant amalgam. G. V. Black [1–3] (*circa* 1896) was the first to carry out researches on this problem, and it is only comparatively recently that attention has once more been directed to the control of these dimensional changes.

Space does not permit more than reference to the work of those who, within the last few years, have supplemented Black's pioneer work.

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* Manuscript received July 4, 1936.

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Of these investigators, however, Gray,[4-10] Souder and Peters,[11,12] Taylor,[13-15] Ward and Scott,[16] Rothen,[17] McBain and Knight,[18] Loebich [19,20] and Nowach,[21] Sterner-Rainer [22] have contributed largely to the knowledge of amalgams. Apart from the researches of Joyner,[23] and later of Knight and Joyner,[24] the constitution of the silver–tin–mercury alloys has not been studied and, therefore, explanations of this problem of the setting of amalgams have not been based on fundamental knowledge.

Fenchel [25] photographed the structure of an amalgam at intervals up to 24 hrs. after mixing and thereby demonstrated the growth of crystals in an amalgam. He was not able to identify the constituents which were formed.

The constitution of the silver–tin–mercury system was determined, therefore, in order to elucidate, if possible, the problems connected with amalgams. The present paper represents the correlation of results obtained during researches on the setting of amalgams (made from alloys of definite composition and under standardized conditions) with their constitution, as deduced from an examination of the silver–tin–mercury ternary system.

It has been shown [26] that dimensional changes during setting bear a definite relation to the composition of the dental alloys from which they are made. The microscopical examination of binary silver–tin alloys containing less than 25 per cent. tin, in the cast state, shows the presence of the β silver–tin phase embedded in a matrix of Ag_3Sn in an amount proportional to the percentage of tin present in the alloy, while that of alloys with 27 or more per cent. tin shows free tin and Ag_3Sn. If filings of such alloys are mixed with mercury under the conditions laid down and packed in a dental cavity, then amalgams made from alloys containing the lesser amount of tin will expand, while those with the greater amount will contract on setting, the degree of expansion or contraction depending on the amount of β or free tin, respectively, in the alloys.

If up to 5 per cent. copper be added, replacing silver in Ag_3Sn, a general stiffening of the amalgam takes place, together with an increase in expansion (contraction being considered as negative expansion). As before, alloys giving amalgams which expand on setting contain less than 25 per cent. tin, and those which contract, more than 27 per cent. tin.

The compositions of the alloys investigated are plotted in Fig. 2, and the boundaries between the $\beta + \gamma$, γ, and $\gamma + \mathrm{Sn}$ phase fields, appear to coincide with those drawn distinguishing amalgams which expand or contract on setting. It is seen that the addition of copper

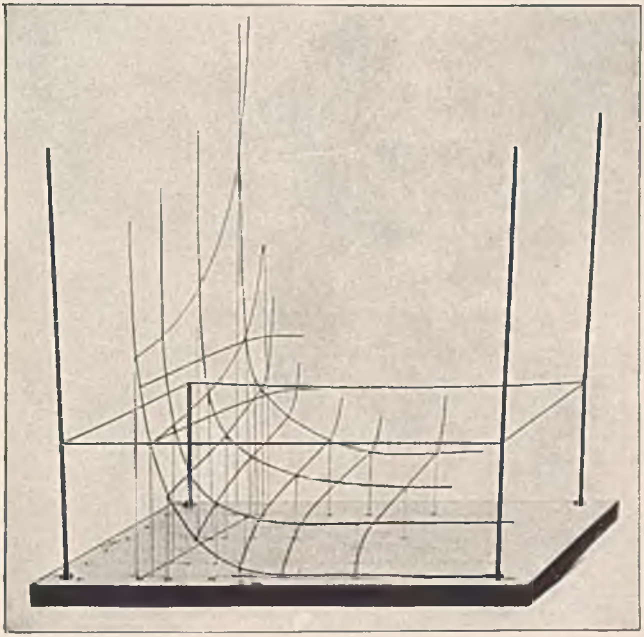

FIG. 1.

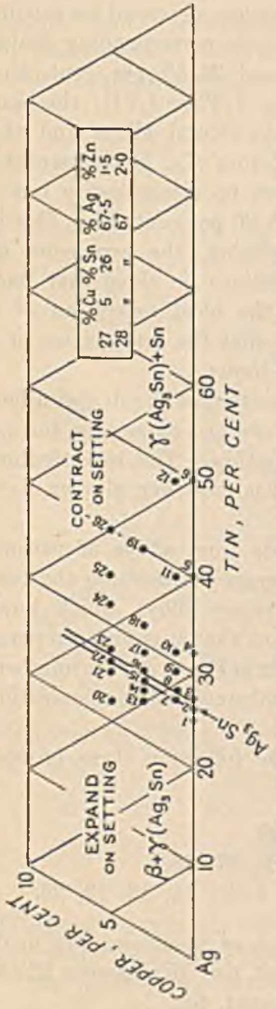

FIG. 2.—Constitution of Dental Alloys "As Cast." Silver–Tin–Copper Alloys. Amalgams Made from Alloys of Composition Indicated.

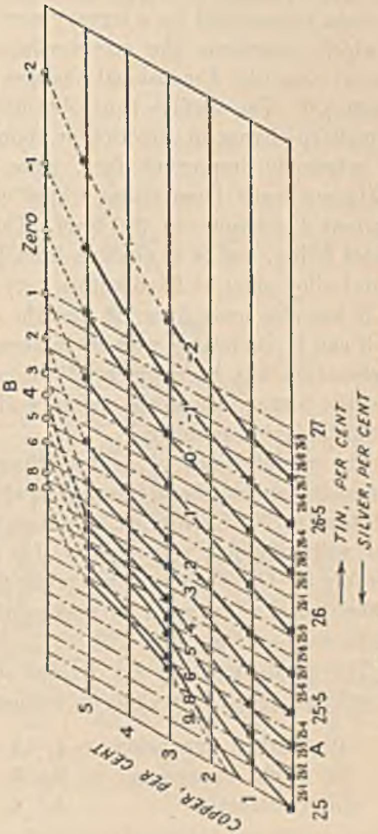

FIG. 3.—Contours of Dilatation 10 Hrs. after Mixing.

does not appear to alter the constitution of the Ag_3Sn phase; a solution of copper in Ag_3Sn is apparently formed, the copper atoms replacing an equivalent number of silver atoms.

The relation between the dimensional changes observed on setting 10 hrs. after mixing, and the compositions of the corresponding dental alloys, containing 0–5 per cent. copper and 22–50 per cent. tin, has been represented by a ternary model (Fig. 1, Plate LVI); the base of which represents the compositions of the dental alloys and the vertical axis, the dimensional changes in microns (*i.e.* in thousandths of mm.).[27] The surface thus obtained shows no discontinuity but a very sharp change in direction at about 25·5–26 per cent. tin. This is an extremely important fact, since on setting, the expansion of amalgams made from alloys whose compositions lie along that line, is about 4 microns on 3–4 mm. This is the ideal expansion of a dental filling, and it is obvious from Fig. 3 that the composition of a dental alloy must be fixed within very close limits.

It has also been shown [28] that the composition of the dental filling itself can be correlated with its dimensional changes on setting, but no explanation has been given of this relationship. The investigation into the ternary silver–tin–mercury alloys has, however, thrown light on this complex problem.

The compositions of dental fillings made from alloys of various compositions have been inserted in the diagram representing the constitution at 70° C. (Fig. 4), of silver–tin–mercury alloys, which, however, will differ only very slightly, if at all, from that at mouth temperature, *viz.* 37° C. The numbers against the dots in Fig. 4, are the numbers of the dental alloys used for making the amalgams; their composition can be read off from Fig. 2.

The amalgams may be divided into the following three groups, according to their behaviour on setting.

(i)	Marked expansion .	1, 13, 14, 20.
(ii)	Slight expansion .	2, 7, 15, 22, 27, 28.
(iii)	Contraction . .	5, 6, 8, 9, 10, 11, 12, 19, 26.

The dental alloys from which these groups of amalgams are made contain, respectively: (i) less than 25 per cent. tin; (ii) between 25 and 27 per cent. tin; and (iii) more than 27 per cent. tin.

From Fig. 4 it will be seen that the alloys of the third group lie above the line Hg–*A* joining the mercury corner with the boundary between Ag_3Sn and the $Ag_3Sn + Sn$ phase field; the first group below the line Hg–*B* joining the mercury corner with the boundary between Ag_3Sn and the $Ag_3Sn + \beta$ (Ag–Sn) phase field, while the compositions of amalgams belonging to the intermediate group lie in the area between these two lines. Fig. 4 probably approximates equilibrium conditions, as already explained in the paper on the constitution of these ternary alloys,[29] and therefore the boundary *LMS*, Fig. 4, may indicate the limit of existence of the $\beta_1 + \gamma_1 + \gamma_2$ phase field. A dental amalgam, however, probably approaches the ideal state more nearly than those of thermal curve ingots ; therefore *PQR* rather than *LMS* will represent more truly the limit of the $\beta_1 + \gamma_1 + \gamma_2$ phase field.

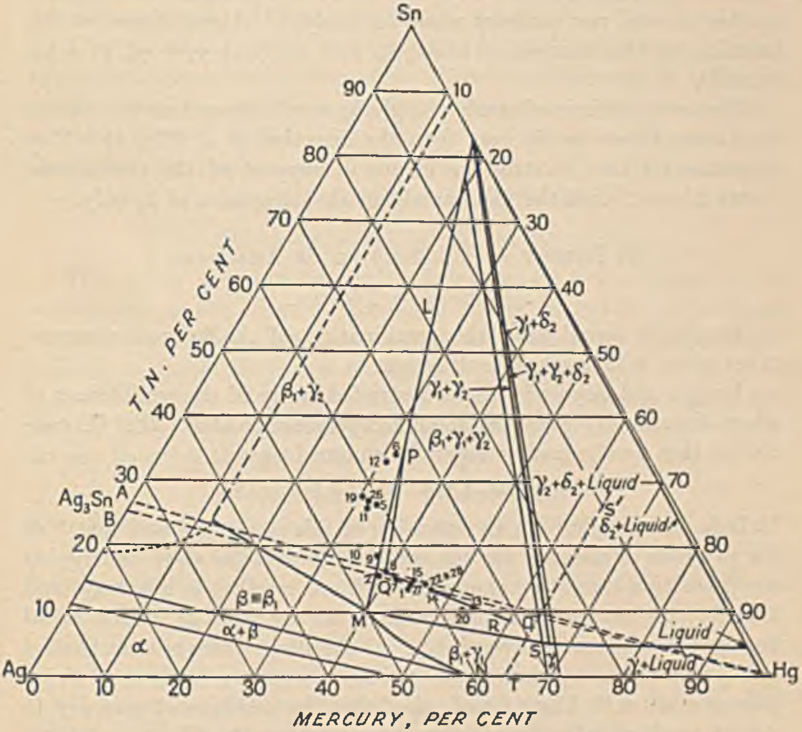

Fig. 4.—70° C. Isotherm.

The point *Q* (or *M*) represents the junction of the β_1, $\beta_1 + \gamma_1$, $\beta_1 + \gamma_1 + \gamma_2$, $\beta_1 + \gamma_2$ phase fields; amalgams whose compositions lie to the left of *PQ*, contract on setting, those below *QR* expand, while those whose compositions are close to *Q*, in the direction *QR*, show slight expansion. The compositions of such amalgams lie within the limits tin 13·5–16, and mercury 47–40 per cent. To sum up, expansion and contraction of amalgams, may be associated with the disappearance and appearance, respectively, of the γ_2 phase of the tin–mercury system or conversely, with the appearance and disappearance of γ_1 of the silver–mercury system. Hence, excess of tin in the dental alloy is to be condemned, since it causes the formation of the γ_2 constituent; on the other hand, an insufficient amount of tin in the alloy increases the amount of the γ_1 silver–mercury compound formed, which results in expansion. Therefore the composition of an amalgam which shall neither expand nor contract must lie, under ideal conditions, at the junction of the four phase fields, β_1, $\beta_1 + \gamma_1$, $\beta_1 + \gamma_1 + \gamma_2$, $\beta_1 + \gamma_2$, *i.e.* at *Q*.

The compositions of amalgams giving small expansions on setting have been shown to lie near *Q* in the direction of *R* (Fig. 4). This experimental fact is strong evidence in support of the conclusions drawn above : that the ideal amalgam should consist of β_1 only.

(2) THEORY OF THE SETTING OF AMALGAMS.

(A) *Existing Theories.*

Fenchel[30] found that the combination of Ag_3Sn and mercury takes place with marked contraction.

Knight and Joyner[24] from a restricted study of the equilibrium of silver–tin–mercury alloys at room temperature to about 214° C., concluded that amalgamation might be summed up as :

$$Ag_3Sn + 4\,Hg \longrightarrow Ag_3Hg_4 + Sn$$

McBain and Knight[31] in an extension of this research found that " in the presence of mercury the tin and the silver in the alloy undergoing amalgamation cannot be combined with one another in any way, and therefore the products of amalgamation are the same as if each metal had been amalgamated separately . . . the alloy, which is a mechanical mixture of the compound Ag_3Sn and tin, becomes a mixture of *Arbor Dianæ* and tin." They found, also, that the addition of mercury to Ag_3Sn resulted in marked contraction whether the filings were previously aged at 100° C. or not; they remark that " every case occurring in dental practice must be intermediate between no volume change and the extreme changes mentioned above. This will depend on how nearly the amalgamation is complete before insertion."

Gray,[8, 10] explained the peculiar alternation of contractions and expansions which take place in amalgams (when made in a specified manner) by a theory based on the work of McBain, Joyner, and Knight, supplemented by his own observations and general physico-chemical facts :

" (*a*) The rapid drop to a minimum that forms the first part of the typical curve of reaction expansion evidently represents the end of the stage dominated by contraction accompanying solution of the alloy in mercury and formation of compounds with silver and copper.

"(*b*) Crystallization of these mercury compounds quickly follows their formation, and is accompanied by expansion. The first minimum in the curve marks the time when the rapidity of this expansion just equals the rapidity of the contraction caused by the simultaneous formation of more of these same compounds.

"(*c*) As the solution and reaction diminish, the crystallization expansion comes to predominate. This predominance is indicated by the rise of the curve from the first minimum to the first maximum."

Gray accepts McBain's and Joyner's conclusions with regard to the process of amalgamation, *viz.*

$$Ag_3Sn + 4\,Hg \longrightarrow Ag_3Hg_4 + Sn$$

(B) *Theory Submitted by the Present Author.*

The theory now put forward is based on (1) a knowledge of the constitution of the alloys of silver, tin, and mercury; (2) observations on the behaviour of alloys and mercury during mixing; and (3) X-ray analysis of dental alloys and amalgams.

It has already been shown in the paper on the constitution of the ternary alloys [29] that the effect of the additions of mercury to Ag_3Sn cannot be summed up by the simple equation

$$Ag_3Sn + 4\,Hg \longrightarrow Ag_3Hg_4 + Sn$$

A very much more complex reaction takes place.

The addition of up to 64 per cent. mercury to Ag_3Sn results in the formation of three phases in proportions depending on the constitution of the alloy :

(*a*) The β phase of the silver–tin system, in which mercury is held in solid solution, forms a continuous series of solid solutions with the β_1 phase of the silver–mercury system in which tin is held in solid solution. These two phases are therefore isomorphous and form a series of solid solutions (which have been designated β_1), which stretch right across the ternary diagram.

(*b*) The γ_1 phase of the silver–mercury system which contains a small amount of tin in solid solution.

(*c*) The γ_2 phase of the tin–mercury system.

If Ag_3Sn and not more than 64 per cent. mercury are mixed together at some temperature above 150° C., and then cooled to mouth temperature, the following reactions take place (cf. Fig. 13, of the paper on the constitution of the alloys of silver, tin, and mercury).[29]

(i) $Ag_3Sn + \text{liq. } Hg \longrightarrow \beta_1 + \text{liquid (at } 150^\circ\text{ C.)}$;

(ii) As the temperature falls the γ_2 phase separates from the mixture, β_1 + liquid, until the temperature of 84° C. is reached. Here, from the residual β_1 and liquid, the $\gamma_1 + \gamma_2$ phases separate according to the following equation

$$\beta_1 + \text{liq.} \longrightarrow \gamma_1 + \gamma_2$$

Alloys in equilibrium containing less than 65 per cent. mercury will, therefore, be completely solid below 84° C. and will consist of $\beta_1 + \gamma_2$ from 15 to 18 per cent. mercury, and of $\beta_1 + \gamma_1 + \gamma_2$ from 18 to 65 per cent. mercury. Excess mercury, above 65 per cent., results in additional complex reactions as shown on examining the diagram mentioned above.

The changes taking place when mercury is mixed with Ag_3Sn cannot, therefore, be summed up by a simple equation; under equilibrium conditions, the resulting product of amalgamation at temperatures below 70° C. consists of a mixture of the β_1 and γ_2 phases with or without the γ_1 phase, depending on the amount of mercury used.

In the case of dental amalgams, the degree of amalgamation varies with the method of mixing and therefore the final constitution of the resulting amalgam will depend on factors connected with mixing and subsequent manipulation.

It has been found [28] that an alloy of satisfactory composition should be mixed with mercury in the ratio 1 : 1·75 which corresponds with 63·6 per cent. mercury and is represented by some point on $S'T$ (Fig. 4) according to the composition of the alloy. In the case of alloys in which copper replaces up to 5 per cent. of silver in the compound Ag_3Sn, this particular ratio will give an alloy of composition O (Fig. 4) which is identical with that of the invariant point, at 84° C., given by the equation

$$\beta_1 + \text{liq.} \longrightarrow \gamma_1 + \gamma_2$$

Therefore, the transformation of Ag_3Sn into, ultimately, $\gamma_1 + \gamma_2$, should proceed at a maximum rate at room temperature when the amount of mercury used is 64 per cent.

It is highly probable that the first step in the transformation of Ag_3Sn, will be the formation of a solid solution of mercury in Ag_3Sn and then the formation of $\beta_1 + \gamma_2$ on the outside of the particles; the amount formed will depend on the rate of the diffusion of mercury through the layer of $\beta_1 + \gamma_2$ which will decrease as the amount of these phases increases. If the particle size be large, or the amount of mercury insufficient, a core of Ag_3Sn may be left surrounded with $\beta_1 + \gamma_2$. These constituents will react with the adjoining mercury as soon as they are formed to give $\gamma_1 + \gamma_2$, thereby inhibiting the diffusion of mercury and preventing further transformation of Ag_3Sn. The quantity of γ_2 formed simultaneously with γ_1 is necessarily relatively very little, as can be seen from the constitution of the alloys (Fig. 4).

The proportions of the different phases which finally are formed in the amalgam will depend on:

(i) The composition of the dental alloy;
(ii) The method of mixing and manipulation.

X-ray analyses have been carried out on amalgams made from Ag_3Sn with and without copper in solid solution and varying percentages of mercury. The author is indebted to her colleague Mr. C. Wainwright, for carrying out these analyses. The results are summed up in Table I.

TABLE I.

	Alloy.	Photographed.	
		During ¾–1½ Hrs. after Mixing.	20 Hrs. after Mixing.
1	Ag_3Sn + 30% Hg	γ_1 (Ag–Hg)	γ_1 (Ag–Hg)
2	„ 20 „	$\gamma_1 + Ag_3Sn$?	γ_1
3	„ 10 „	$\gamma_1 + Ag_3Sn$ (equal quantities)	$\gamma_1 + Ag_3Sn$ (equal quantities)
4	„ 5 „	...	*After 2 days* Ag_3Sn
5	26·4% Sn 4·8% Cu 2·0% Zn 66·9% Ag + 64% Hg	γ_1	γ_1
6	34·8% Sn 4·85% Cu 60·35% Ag + 64% Hg	γ_1	γ_1

These alloys were mixed with mercury in a rubber thumbstall for 1 minute and then any excess mercury was expressed by squeezing through linen. No mercury was expressed in the case of alloys Nos. 1–4. Amalgams 3 and 4 were very crumbly.

X-ray analysis gives positive evidence of the formation of the γ_1 (Ag–Hg) phase and shows that the transformation of Ag_3Sn has proceeded to a large extent within 1½ hrs. No other constituent could be detected by these means, even though the microscopic examination of amalgam No. 5, showed that two, possibly three, phases were present. The X-ray method of analysis employed is therefore unable to detect small quantities of other constituents formed during the process of the setting of amalgams. This fact demonstrates the danger of assuming from X-ray analysis that the amalgam consists of one phase only.

The fact that γ_1 and a proportionally small amount of γ_2 are formed so rapidly when filings of Ag_3Sn are mixed with mercury, does not necessarily indicate that the amalgam soon reaches a stable state. Further reactions take place when the amalgam is packed in a tooth.

It has been shown, using particles of alloy of definite size and mixing under standardized conditions, that the mercury content of the amalgam is finally reduced from the original 64 per cent. to 40–47 per cent. Reference to Fig. 4 shows that the composition of such an alloy lies near Q and that its constitution, in a condition approaching equilibrium, should consist of β_1 with a little γ_1 and very little γ_2.

It is obvious that particle size, as well as the composition of the dental alloy and the method of mixing, will have a marked effect on the setting of the resultant amalgam. If the particle size is very fine, the transformation of Ag_3Sn + mercury into $\gamma_1 + \gamma_2$ should proceed more nearly to completion, since diffusion will take place comparatively rapidly. If coarser particles of the same alloy are mixed with the same percentage of mercury, the reactions taking place on mixing will not proceed as far as in the above case. Most probably after mixing, the amalgam will consist of small amounts of Ag_3Sn, β_1, γ_1, and γ_2, depending on the particular size. Expressing mercury reduces the content from 64 to 40–47 per cent. mercury, hence the subsequent reactions taking place will be different from those occurring when very fine particles of alloy are mixed.

The changes taking place in a dental filling made under standardized conditions, *viz.* mixing in a rubber thumb-stall for 1 minute, letting the amalgam stand for 2 minutes, during the first of which it is squeezed in linen; packing the amalgam in a cavity in 3 minutes, will probably be as follows according to the size of particles used (ratio of alloy to mercury being 1 : 1·75):

(1) Very fine particles of alloy: after mixing, the amalgam will consist of a little unchanged Ag_3Sn, possibly β_1, but mainly of $\gamma_1 + \gamma_2$. After expressing mercury and packing in the dental cavity, further reaction will take place with the ultimate formation of $\gamma_1 + \gamma_2$ and possibly a very little β_1. The amount of γ_2 should be very small, in comparison with that of γ_1.

(2) Coarse particles of alloy: after mixing, the amalgam will consist of a comparatively large amount of unchanged Ag_3Sn; β_1 and possibly a little γ_1 and a very little γ_2. Mercury is next expressed, reducing the content to about 40–47 per cent., and therefore, the changes during setting will consist mainly of β_1 to $\gamma_1 + \gamma_2$, the amounts of $\gamma_1 + \gamma_2$ depending on the mercury content, *viz.* the less mercury, the greater the amount of γ_2 formed.

It would be expected that an examination of the known lattice parameters of the phases taking part in these reactions would throw light on the dimensional changes involved. In Table II are given the parameters and calculated volume per atom of each constituent formed.

TABLE II.

	Phase.	Lattice Parameter, A.	Vol. per Atom, A.^{3}.	Observer.
1	Ag_3Sn	$a_1 = 2{\cdot}953$ $a_3 = 4{\cdot}771$ } o. rhombic	18·405	Nial [32]
2	β_1 (AgHg)	$a = 2{\cdot}98$ $c = 1{\cdot}60$ } c.p. hexag.	18·4	Stenbeck [33]
3	γ_1 (AgHg)	$a = 9{\cdot}98$ cubic	19·1	,,
4	γ_2 (Sn–Hg)	$a = 3{\cdot}198$ $ac = 2{\cdot}980$ } c.p. hexag.	26·3	,,
5	Sn	$a = 5{\cdot}818$ $c = 3{\cdot}174$ } tetragonal	26·85	Neuburger [34]

If mercury is mixed with Ag_3Sn a marked contraction occurs; from the constitution of these alloys the first effect of the addition of mercury is the absorption of mercury and, possibly, the formation of the β_1 phase, from which $\beta_1 + \gamma_2 + \gamma_1$ are ultimately formed. From an examination of Table II, it is difficult to account for the marked contraction other than by the removal of mercury by its absorption by the dental alloy filings to form a solid solution of mercury in Ag_3Sn *i.e.* γ, and subsequently $\beta_1 + \gamma_2$ (cf. Fig. 13 [29]). If the dental alloy consists of Ag_3Sn + tin, the addition of mercury results in most complex changes taking place accompanied by a very rapid absorption of mercury. Dental alloys, containing less than 25 per cent. tin, when mixed with mercury, exhibit very marked expansion, which again is difficult to explain in the light of Table II.

One is therefore forced back to the possible cause of expansion being due, as originally suggested by Gray, to the mechanical thrust due to crystal growth. He considers, however, that contraction accompanies the solution of the alloy in mercury, but in the light of the present knowledge of the constitution of the ternary alloys of silver, tin, and mercury, the contraction observed in the amalgam during the initial stages of the setting may be attributed to the formation of a solid solution of mercury in Ag_3Sn. From the Ag_3Sn–mercury section given in Fig. 13, of the paper on the constitution of these alloys,[29] it is seen that at mouth temperature about 15 per cent. of mercury is capable of being held in solid solution in Ag_3Sn (γ), while the β_1, γ_1, and γ_2 phases appear to possess little or no solubility in each other or in mercury.

SUMMARY.

(1) Dimensional changes occurring during the setting of amalgams may be correlated with the compositions of the dental alloys from which they are made. These results have been represented graphically by means of a ternary model, in the case of silver–tin alloys containing 0–5 per cent. copper.

(2) Expansion during setting can be correlated with the presence of the β silver–tin compound with Ag_3Sn in the dental alloy, and contraction, with the presence of free tin with Ag_3Sn. The first two phases exist in alloys containing less than 25 per cent. tin, the latter in those containing more than 27 per cent.

(3) Dimensional changes during setting may also be correlated with the composition of the dental filling itself and consequently with the constitution of the ternary silver–tin–mercury alloys.

(4) Expansion and contraction may be attributed to the disappearance and appearance of the γ_2 (Sn–Hg) phase in the amalgam or *vice versa*, the appearance and disappearance of the γ_1 (Ag–Hg) phase.

(5) The changes occurring in amalgams may be said to be due to complex reactions which probably do not proceed to completion. These reactions depend on: (i) the composition of the dental alloy; (ii) the method of mixing and manipulation; and (iii) particle size.

(6) In the case of dental alloys whose composition consists of Ag_3Sn, these reactions, if allowed to proceed to equilibrium conditions, may be summed up briefly as follows:

$$\text{(i)}\ Ag_3Sn + Hg \longrightarrow \beta_1 + \gamma_2$$
$$\text{(ii)}\ \beta_1 + \gamma_2 \longrightarrow \beta_1 + \gamma_1 + \gamma_2$$

(7) No explanation for the marked contraction or expansion on setting can be obtained from X-ray data.

(8) It is concluded that Gray's theory that expansion may be attributed to crystal growth is probably the true explanation, but that the cause of contraction, from a study of the constitution, is now attributed to the absorption of mercury by the dental alloy filings resulting in the formation of a solid solution of mercury in Ag_3Sn, and not to the solution of the dental alloy in mercury as put forward by Gray.

ACKNOWLEDGMENTS.

In conclusion, the author would express her thanks to the Dental Investigation Committee of the Department of Scientific and Industrial Research on whose recommendation this paper is published, and to

Dr. C. H. Desch, F.R.S., Superintendent of the Metallurgy Department, for his continued interest. She is indebted also to Mr. W. E. Carrington for the construction and photograph of the ternary model.

Figs. 1 and 3 are reproduced by kind permission of the *British Dental Journal.*

September, 1935.

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CORRESPONDENCE.

MR. E. H. BUCKNALL,* M.Sc. (Member): The experimental study of dental amalgams described in the present paper comprises, in addition to purely constitutional work, a detailed investigation of the compositions and the dimensional changes in setting amalgams. Within this field the investigation was carried out in a most thorough and detailed manner (as may perhaps better be seen from the reports published in the *British Dental Journal* than the summary here given), but it is doubtful whether such work alone is sufficient to support a theoretical consideration of the process of setting. In this

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connection the papers of Tammann with Dahl and with Mansuri appear important. These authors traced the hardness changes during the setting of amalgams and found the hardening to be greater for Hg–Ag_3Sn mixtures than for other compositions.

The effect of additions of copper on the dilatation is extremely interesting as the contours of equal dimensional change run so nearly parallel to an Ag_3Sn–Cu_3Sn line, commencing at 26·8 per cent. tin and passing through the point 5 per cent. copper, 27·8 per cent. tin. It is noteworthy that alloys on this line are not, however, those which produce fillings with either zero or the desired small positive change. It is presumed that copper finds its way into commercial dental alloys primarily as a hardener.

Attention is directed by Dr. Gayler to the fact that the mixture of dental alloy with mercury at the stage before it has been "condensed" into a cavity, with the expression of mercury slightly contaminated by silver and tin, approximates in composition to an invariant point at 84° C. in the neighbourhood of point *O* on Fig. 4; it is then inferred that in this mixture the rate of transformation is a maximum. One is doubtful whether it is ever possible to argue from an equilibrium diagram with regard to rates of reaction and wonders whether this is a conclusion from practical results. The isothermal section at 84° C., given as Fig. 18 of the constitutional paper, does not seem to reveal this invariant point although it is shown on vertical sections. As Dr. Gayler goes on to observe, the alloy does not have time closely to approach equilibrium at this stage, as is of course indicated by the fact that liquid mercury is expressible leaving an alloy containing only about 40 instead of 64 per cent. mercury. The new composition clearly represents the average composition of the solid phases present at this stage, a composition which could not be reached by mixtures of the γ_1 and γ_2 phases.

Dr. A. J. Rothen *: From the theoretical point of view, this study is important in so far as it means a contribution to the knowledge of the physico-chemical composition of ternary alloys of silver–tin–mercury.

From the practical point of view of dental alloys, Dr. Gayler arrives at precise conclusions fixing the limits of the composition within which the alloy has the necessary stability of volume. Here, it must be pointed out that, if these conclusions are valid for the conditions of the experiments made by the author, they should, however, not be generalized, *i.e.* extended to all alloys. Dr. Gayler has worked on filings of a determined size, with an exact quantity of mercury, and applying a standardized mixing technique. The conclusions at which the author arrived, in these conditions, are not necessarily valid for filings of another size, nor for other proportions of mercury; besides, Dr. Gayler rightly says in her paper: "These reactions depend on the composition of the dental alloy, the method of mixing and manipulation, and particle size."

So long as the part played by each of these different elements is not exactly determined, the practical problem to be solved is, in my opinion, not to manufacture an alloy having the desired stability in certain precise manipulating conditions, but rather to find an alloy presenting a maximum of stability and leaving, at the same time, as large a scope as possible to the variations of manipulation.

The working conditions in dental practice are considerably different from those of a physical laboratory; as standardized as it may be, the manipulation of the products by the dentist is inevitably subject to variations. Therefore, the composition of an alloy should be such as to protect the product, as much as possible, against such variations.

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If, in her paper, the author has explained certain properties of the alloys, some other characteristics have been neglected. Admitting that the expansion is due to the appearance of phase γ_1, resulting from γ_2, the conclusion is that, the more mercury is left in a filling, the more expansion there will be. For the same reason, a fine-grained alloy should show more expansion than the same product cut in coarser grains; now, experience shows that just the contrary is the case.

In the domain of dental amalgams, the junction between practice and theory has not been realized as yet; this is the reason why caution is advisable in accepting new standardizations.

Professor E. W. SKINNER,* Ph.D.: Any theory for the dimensional changes which occur during the hardening of amalgams must of necessity be rather involved in order to account for the many variables to which this phenomenon is subject. Such a theory should explain all the effects observed with change of composition, particle size, and manipulation. The theory presented by the author meets these requirements. Furthermore it is a theory based on sound constitutional data.

However, in America, amalgam workers are apt to criticize the method by which the author obtained the dilatation data on which the present theory is based. Dr. Gayler condensed the amalgam into a cavity with four walls and a floor, thus obtaining a preparation similar to that employed by the dentist in certain cases. In America, the general custom is to use specimens which are free to change dimension unrestricted by enclosures. The method employed by Dr. Gayler may be of greater value than the second method in interpreting the changes which might occur in a dental restoration (although this point is debatable), but it is not clear how the results of such measurements can be reliable as metallographic data, because of added disturbances brought about by the restraining forces of the cavity walls. Black † who used the Wedelstaedt test tube for this purpose, notes that an expansion occurring under these conditions is more nearly a cubical expansion than a linear change. Gray ‡ does not credit the method with measuring either linear or volumetric expansion, but rather a "heaped measure expansion." He further states that a linear contraction cannot occur under these conditions "until the amalgam has become completely free from the constraints imposed upon it by the walls of the cavity."

In order to test this point, I recently attempted to reproduce some of Dr. Gayler's results in my own laboratory by means of the dental interferometer. A commercial amalgam alloy was selected with composition by weight silver 68·8, tin 26·4, and copper 4·4 per cent. As may be observed from Fig. 1, this alloy should exhibit neither expansion nor contraction. When all conditions were controlled as nearly as possible to conform with those described by Dr. Gayler § an average expansion of 9·8 microns/cm. was obtained at the end of a period of 24 hrs.

It should be emphasized further that the alloys of composition plotted in Figs. 1 and 4 of the present paper reacted as stated by the author only when a very exact manipulation was employed. For example, by the use of a special technique of manipulation which is not far removed from that employed by dentists, I have obtained expansions in excess of 200 microns/cm. from an

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* Northwestern University Dental School, Chicago, Illinois, U.S.A.

† G. V. Black, "Operative Dentistry," Vol. II, p. 307, 6th Edition (Medico-Dental Publishing Co.).

‡ A. W. Gray, "Metallographic Phenomena Observed in Amalgam," *J. Nat. Dental Assoc.*, 1919, 5, 909–910.

§ M. L. V. Gayler, "The Setting of Dental Amalgams," *Brit. Dental J.*, 1935, 58, 143–160.

amalgam whose alloy composition was: silver 55, tin 41, copper 3, and zinc 1 per cent. The alloy is a commercial product; it was mixed with mercury in the ratio 1 : 1·6, little or no mercury being expressed during the condensation. These results are difficult to explain by Dr. Gayler's theory, unless it is assumed that the phase boundary line in Fig. 4 is changed by the zinc content so as to allow the ultimate formation of γ_1 + liquid.

Dr. WILMER SOUDER *: So far as I am competent to express an opinion, this paper is sound in its metallurgical interpretations. Should not the copper percentages at the left of Fig. 1 be doubled?

Our dental researches at the Bureau of Standards have not been prosecuted along these lines. We have taken the experience of large numbers of dentists and from these reports selected the alloys named as most satisfactory. Chemical and physical tests of these alloys were made and a performance specification set up which is now used in the purchase of dental alloys. Full responsibility for the production of an alloy and instructions for mixing and packing the alloy so that it will meet the performance specification is placed on the manufacturer.

There are difficulties in setting up a narrow limit on chemical compositions for an alloy as the performance in a filling is dependent on so many additional items. The size and shape of cut, the annealing, the trituration time, the trituration pressures, the packing time, the packing pressures and mercury content of the finished filling have each an individual effect on the finished restoration.

We have perhaps avoided these variations by demanding that the manufacturer produce the alloy, test it and furnish a technique for its use, so that the resulting restoration will meet the performance demand of the specification.

The AUTHOR (*in reply*): Rates of reaction, as Mr. Bucknall suggests, cannot be determined from equilibrium diagrams. The statement that the transformation of Ag_3Sn into $\gamma_1 + \gamma_2$ should proceed at a maximum rate when the amount of mercury used is 64 per cent. is intended to emphasize the practical value of using excess mercury during amalgamation rather than to refer to the actual rates at which the reactions proceed. From Table I it is seen that lesser amounts of mercury result in a more or less proportionate amount of unattacked Ag_3Sn; and if the amount of mercury used is that which is required to be left in a dental filling, *i.e.* 40–47 per cent., then it appears that the changes in the amalgam will take place at a slower rate than if excess mercury is first used and then expressed.

For simplicity, the isothermal section given in Fig. 18 (see this vol., Plate LII) has been drawn to represent the conditions existing immediately before the invariant plane is reached.

It is quite clear from Fig. 13 (Plate LI) of this same paper, No. 766 (see this vol., facing p. 384), that the final composition of the dental filling containing about 40 per cent. mercury could not possibly be reached by mixtures of the γ_1 and γ_2 phases; if, however, no mercury were expressed from an amalgam containing 64 per cent. mercury, then ultimately it should consist of the γ_1 and γ_2 phases.

The presence of liquid mercury in a dental filling may be due to incomplete expression of mercury; in such cases absorption of mercury in the dental filling would be likely to take place very slowly. As stated, a dental filling should ultimately consist of a mixture of the β_1, γ_1, and γ_2 phases.

I am glad that Dr. Rothen has emphasized that my conclusions are valid for the conditions of experiments cited by me, and that these conclusions

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should not be generalized. It is a point which I have stressed in the more practical papers on dental amalgams which have been published in the *British Dental Journal*; these publications show that if any one factor in the experiments is altered, quite unexpected results may be obtained.

I agree with Dr. Rothen that the search for an alloy which will permit wide variation in manipulation is a practical problem; but before such a problem can be solved, it is essential that a knowledge of the effect of variation of any one factor in the trituration and manipulation of the amalgam should be known and, if possible, the effect caused by varying two or more factors simultaneously. The investigations that I have carried out have been directed towards the latter problem with a view to their forming a basis for the more practical problem to which Dr. Rothen has referred.

It is not to be expected that theory and practice can be united until a great deal more fundamental research on amalgams has been carried out. New standardizations based on known facts are preferable, however, to a great deal of present-day practice, which has little or no scientific justification.

The method of obtaining the dilatation data, by filling Ivorine teeth, used during the investigation on amalgams, was considered to approach more closely that found in dental practice than that to which Professor Skinner refers. I appreciate his remarks on the value of such a method in contrast to that in which specimens are free to change unrestrictedly, but, so far as I can judge from the results of experiments carried out during the earlier stages of this investigation, results obtained from both methods were comparable (making allowances for difference in the height of the specimens). For really practical results I think that a great deal more research should be carried out using both methods, standardizing exactly the conditions of the experiments.

One of the most important factors which I have not yet been able to study, is the size of particle, and I think that it is highly probable that this is the cause of the difference in results obtained by Professor Skinner using the high silver alloy. In the second case, the fact that he obtained expansion from an alloy containing 41 per cent. tin where a contraction would be expected, would suggest that the manipulation of the amalgam is the cause. I have found, using a commercial alloy, that marked expansion in the amalgam could be induced by (*a*) light mixing pressure, (*b*) light packing pressure, (*c*) decrease in the time of mixing, (*d*) decrease in the amount of mercury used for amalgamation, (*e*) decrease in the time of kneading.*

If trituration be carried out in a mortar, little or no control of the pressure of the pestle can be maintained, and pressure during mixing is a most important factor, together with time of mixing and kneading. It is for these reasons that I decided that another method of mixing was essential if similar results were to be obtained by all using the same amalgam: experiments showed that the thumbstall method of mixing gave repeatedly consistent results.

I would suggest that the amalgam mixed in a mortar under the conditions referred to, is in a highly metastable state of equilibrium, owing to the fact that actual amalgamation of the filings is probably extremely superficial. It is impossible in these circumstances to offer an explanation of the characteristics of such an amalgam without carrying out further investigations.

In reply to Dr. Souder, the scale of the tin percentages in Fig. 1 was halved in order to reduce the size of diagram.

The dental researches carried out at the Bureau of Standards are extremely important, and I hope that the results of the present investigation

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* See *Brit. Dental J.*, 1933, 54, 269.

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MAY LECTURE, 1937

THE FLOW OF METALS.

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By Professor E. N. da C. ANDRADE,* D.Sc., Ph.D., F.R.S.

TWENTY-SEVENTH MAY LECTURE TO THE INSTITUTE OF METALS, DELIVERED MAY 5, 1937.

Synopsis.

Flow is most easily observed in the liquid state, but the structure of the liquid state is still obscure. Nevertheless it is possible on simple lines to formulate a theory of liquid viscosity, which both gives the observed viscosity of simple liquids and accounts for the temperature variation. In this connection viscosity of liquid metals is important, on account of the simplicity of the molecular state.

The flow of solids is best observed in single crystals of metals. Certain general laws have been formulated, from which it is clear that the velocity of flow is of fundamental significance. The perfect crystal lattice does not offer a basis for any theory of the flow of solids: the only successful attempts to construct a mechanism to explain plastic behaviour are based on the assumption of flaws, or dislocations, in the lattice, which are propagated along preferential directions when external stresses are applied. Thermal fluctuations must also be invoked. Further investigation of the nature of the inherent flaws is of importance, not only for physical theory but also for metallurgical practice.

Matter can exist in three states: the solid, the liquid, and the gaseous. During the past two generations the interest of most physicists was concentrated on the gaseous state, and for this there were very good reasons. On the one hand the pioneers of electronic physics, men like J. J. Thomson, P. Lenard, and W. Wien, carried out their work in tubes containing gases at extremely low pressures, and their astounding successes, and the beauty and novelty of their results, directed attention to discharges in gases; on the other hand the kinetic theory of gases, as elaborated by Clerk Maxwell and Clausius, proved to be capable not only of giving a general account of the known properties of gases, but also of predicting apparently paradoxical results, such as the independence of viscosity of pressure.

From the point of view of theoretical physics gases are, of course, much simpler than solids or liquids: the molecules are, relatively speaking, so far apart that, for the most part of the time, they can be

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* Quain Professor of Physics in the University of London.

considered as isolated from the effects of their neighbours, as behaving in a manner unembarrassed, as it were, by the elbowing of their fellows. For instance, all the simple results of the kinetic theory of gases can be obtained by considering that each molecule travels in a straight line, uninfluenced by all the others, except for the comparatively rare occasions when it comes into close contact with another atom. Along these lines the general mechanical properties of gases can be calculated, and the size of the molecules worked out, and, while there are, of course, many remote provinces left to be explored, we can say that gases, except at very high pressures or very low temperatures, behave in a manner that seems reasonable to the theoretical physicist.

Of recent years, due to the work of the Braggs, and their collaborators and followers in many lands, the structure of crystalline solids has been worked out in great detail, so that we now know the pattern according to which atoms are built up in a great variety of compounds. This is not to say, however, that we can calculate the forces acting on the individual atoms, which would give their heat movements about their equilibrium positions, but that we can find out experimentally, for any particular structure, what the average positions of the atoms are.

We know, then, a good deal about gases, which flow freely, and a great deal about the structure of ideal solids, *i.e.* crystals, which should not flow at all. When, however, we turn to the liquid state, we meet with great difficulties, and it is scarcely too much to say, as Bernal does, that the wider problem of why the liquid state should exist at all has as yet only been touched. There is no clear knowledge as to what happens when a solid melts. The chief physical sign of melting is that the substance suddenly begins to flow freely: the solid just below the melting point will, it is true, flow if forces sufficiently large are applied, but there is an enormous change of viscosity on melting, much greater than that in any other property. The change of volume is comparatively small: in general a pure metal expands on melting, but in the case of a few elements of complicated crystal structure, such as gallium, it actually contracts. The distances apart of the atoms in the solid and the liquid are, then, much the same, but we have this great difference of mechanical properties, entirely due to differences in the arrangement of the atoms. The molecules are not arranged as in the crystal, nor are they absolutely at random, but rather they have an intermediate arrangement, something like the crystal pattern with a relaxed discipline, smeared out, as it were, by the heat agitation. On the whole a liquid molecule will have a certain average number of nearest neighbours, with centres near a sphere surrounding it, and there will be a certain departure from lying exactly on the sphere, but the tendency to regular arrangement will be there. What we require is a precise measure of the departure of the liquid arrangement from the crystalline arrangement, and Prins, Bernal, and others are now working on these lines. All that I want at the moment is to show you what the problem is.

Let us now return to the crystal, and see how we should expect it to behave under stress. For simplicity we will first of all consider not a metal crystal, but one composed of positive and negative ions, like sodium chloride, since the mathematics of such a crystal have been worked out by Born and others. When at a distance such ions attract one another according to an inverse square law, but when close together they must repel one another, or they would approach indefinitely. Such a repulsion, varying inversely as a higher power of the distance, can be explained by the fact that the ions are themselves made up of positive and negative charges, in a way that need not be considered here. Normally, then, these ions will be in a position of equilibrium where the positive and negative forces just balance, or where the potential is a minimum. Suppose that we apply a force tending to pull them apart, they will move to a position where the attractive force is greater than the repulsive, and just balances the external force. As we increase the external force the molecules will move further apart until a certain distance is reached where the total intermolecular force reaches a maximum. Near this point it is clear that any increase in external force should produce a very large movement, or the Young's modulus for the crystal should approach zero. Any further increase in force should produce rupture. We have, then, on this simple physical picture of a crystal, elastic yield, with continually decreasing Young's modulus, until at a certain point rupture ensues. This is, of course, nothing at all like what occurs. In practice we have either elastic yield, at constant Young's modulus, followed by brittle rupture, generally with permanent yield in between; or else plastic yield, that is, flow.

I do not want to discuss brittle rupture this evening, but I should like, in passing, to point out that very simple considerations suffice to show that even here the simple crystal model is quite unsatisfactory. We can work out from considerations of surface tension what the strength of a crystal should be, and it comes out to be very high, about a thousand to ten thousand times as great as it actually is. These considerations apply to metal crystals as well as ionic crystals; in the latter case the behaviour can be worked out by a more precise method, the agreement of which confirms the correctness of the more general treatment.

We have now to consider the general problem of explaining how it is that a crystal can be plastically deformed. If a perfect crystal (and for simplicity we consider again a cubic ionic crystal, like rock-salt) is subjected to a shearing stress parallel to a simple crystal plane, and in a simple crystal direction, we should expect that the displacement would increase smoothly with the stress until it reached a maximum at the point when any one plane had been displaced by half the crystal spacing with respect to the other, and that then the force would be sufficient to displace the plane indefinitely, so that, after an initial elastic displacement, the crystal would shear into two. Actually it is well known that nothing of the kind takes place, and we have the fundamental difficulties: (1) that permanent displacement begins at a force which is smaller, by some thousands of times, than that theoretically predicted; and (2) that the crystal becomes harder as deformation proceeds, so that, with a given stress, a certain permanent set is produced. The latter phenomenon, that of work-hardening, is one that recurs as one of the major problems of polycrystalline metals.

The flow of liquids and of solids presents, then, grave problems which demand, perhaps, further systematic experiment rather than elaborate mathematical theories. For these experiments metals seem particularly suited. A simple metal contains atoms of only one kind: it can, in many cases, be obtained of exceptional purity, and single crystals can be prepared in forms convenient for experiment, either wires for extension or cylinders for compression. It is true that the structure of a metal is still something of a mystery. In an ionic crystal the cohesion can clearly be explained as due to the attraction existing between the positive and negative ions: in a homopolar crystal, such as, say, diamond, it is attributed to the sharing of electrons, which has been so successful in explaining certain classes of chemical compounds: the cohesion of the rare gases in the solid state is attributed to the so-called van der Waals forces, due to electric polarizations set up by one atom acting on the other. In metals there is no doubt a lattice of positive metal ions, and a cloud of valency electrons, distributed and moving through it. Hume-Rothery has pointed out that the different types of crystal structure exhibited by the metals in different columns of the periodic table can be explained on a conception of electron sharing by the atoms, which involves something corresponding to the covalent bonds in chemistry. The binding energy and the compressibility have been worked out by a complicated application of the method of wave mechanics in certain simple cases, with fair success. Nothing, however, has been done as regards mechanical strength.

Having formulated the general problems, let us return to a consideration of the liquid state. For the problem of liquid viscosity, the electrons can, it is suggested, be neglected, since viscosity is a question of the transfer of momentum, and the electrons have negligible mass. Certain theories were at one time put forward which treated a liquid as a kind of gas, but they had little success, which is not, perhaps, remarkable, since, as we have seen, a liquid is really a kind of solid with a relaxed discipline, of density very like that of the solid, but with a greater power of diffusion, *i.e.* a single atom can work its way through the others much more easily than can an atom of a solid. I have calculated, for instance, that one atom of liquid lead will move through a distance equal to the atomic diameter in $1{\cdot}89 \times 10^{-11}$ seconds, which is the time of about 38 complete vibrations. This calculation depends only upon the self-diffusion of liquid lead, measured experimentally with a radioactive isotope, and makes no assumption about liquid structure. The simple theory which I have suggested for liquid viscosity is on the following lines.

Whereas in gases momentum is transferred from one layer to another by a molecule crossing an imaginary dividing plane, and making a collision after travelling a distance very many times its diameter, which involves the conception of a mean free path, I suppose that, in liquids, momentum is transferred by molecules vibrating about a mean position, and sharing momentum when they approach at the extremities of the vibration, if conditions are favourable. The distance over which momentum is transmitted is thus σ, the mean distance between molecules, and the frequency with which it is transmitted is found, not, as with gases, by consideration of a mean free path and a molecular velocity, but by the frequency of vibration, which, it is considered, must be much the same as in the solid state. If it is supposed that at the melting point momentum is shared at every extreme libration, then the liquid viscosity can be calculated in terms of the fundamental frequency. It is

$$\eta = \frac{4}{3}\frac{\nu m}{\sigma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ν is the fundamental frequency of vibration of the molecule and m is its mass. The constant 4/3 is only an approximate value: the important point is the general form of the expression. Since Lindemann has given an expression for the fundamental frequency in terms of the temperature of melting, the atomic weight, and the atomic volume, we can find the viscosity at melting point in terms of these quantities, without any arbitrary constant. It comes out to be

$$\eta = 5{\cdot}1 \times 10^{-4}\frac{(A T_m)^{\frac{1}{2}}}{V_A^{\frac{2}{3}}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where T_m is the absolute melting point, A is the molecular weight, and V_A the volume of the grm.-molecule at T_m. The values calculated from this expression (2) agree well with the experimental values found for metals, especially for the metals of close-packed structure, as shown in the following table, which comprises all the metals for which reliable experimental values are to hand. The first group of metals are of closely packed, or approximately closely packed, structure: the last three are of more complicated crystal structure, and belong to Hume-Rothery's Group III. The simple consideration of the theory cannot be expected to apply to such metals.

TABLE I.

Metal.	Viscosity of Liquid at Melting Point.	
	Calculated.	Experimental.
Potassium . . .	0·0045	0·0054
Sodium . . .	0·0050	0·0069
Tin	0·019	0·020
Mercury . . .	0·021	0·021
Lead	0·025	0·028
Copper . . .	0·038	0·038
Bismuth . . .	0·018	0·023
Antimony . . .	0·015	0·024
Gallium . . .	0·015	0·020

The agreement can also be expressed by comparing the fundamental frequency, found by putting the experimental value of the viscosity at melting point in (1), with that given by Lindemann's formula, as is done in Table II. What it is desired to emphasize is not so much the

TABLE II.

Metal.	Fundamental Frequency.	
	Calculated from Liquid Viscosity.	Calculated from Melting Point (Lindemann).
Lithium . . .	$1{\cdot}38\times 10^{12}$	$1{\cdot}4\times 10^{12}$
Potassium . . .	2·66	2·6
Sodium . . .	4·62	4·3
Tin	2·33	2·5
Lead	1·96	2·0
Copper . . .	6·37	7·4
Mercury . . .	1·34	1·3
Bismuth . . .	1·63	1·8
Antimony . . .	2·80	3·2
Gallium . . .	3·54	2·8

closeness of the agreement (this depends to some extent upon the exact value of the constant, given above as 4/3, which is very difficult to calculate, but cannot be far from 1) but, firstly, that the expression gives the right order for the coefficient of viscosity, and, secondly, that it arranges the metals in correct order as regards their viscosity.

To obtain the variation of viscosity with temperature we can adapt ideas which have already been applied to association in the kinetic theory of gases. The sharing of momentum which I postulate is a kind of instantaneous association. Whether atoms combine or not has been held to be determined by whether the atoms, at their closest approach, are favourably disposed in respect of their relative position, or inner state. The easiest picture to form is to suppose that there are, in the liquid molecules, axes, certain relative orientations of which are favourable for instantaneous combination, or sharing of momentum. There will be a local electrostatic field tending to orient the molecules, but the temperature agitation will interfere with this orientation. So precise a picture is not, however, necessary: all that we need assume is that positions marked by a certain potential energy are favourable for transfer of momentum. An application of the Boltzmann distribution formula then gives

$$\eta = Ae^{\frac{b}{kT}}$$

where b is a constant measuring the potential energy concerned. This formula should express the variation of viscosity with temperature, as a first approximation. If we allow for the effect of expansion in separating the molecules, and further suppose that the potential energy varies inversely as the volume, this becomes

$$\eta v^{\frac{1}{3}} = Ae^{\frac{c}{vT}}$$

This formula expresses the results obtained with liquid metals very closely*: as an example we may take the viscosity of liquid sodium and potassium, as found by Dr. Chiong in my laboratory, where the departures nowhere exceed 0·5 per cent., as will be seen from Table III.

To check this theory, and, in particular, to find how the energy c/v is connected with other properties, it seems desirable to measure systematically the viscosities of the liquid metals, and a beginning on this task has been made in my laboratory. For instance, if the theory is correct, then at very high temperatures, sufficient to produce a nearly random arrangement of the molecules, in spite of the orienting effect of the local forces, the viscosity should be independent of the

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* It also applies to a very wide selection of organic liquids, but that need not detain us here.

temperature. Dr. Spells has measured the viscosity of liquid gallium up to 1100° C., and has found that in the neighbourhood of 1100° the viscosity varies only by 2 per cent. per 100°. The viscosities of the liquid alkali metals are also being measured.*

TABLE III.

Temperature ° C.	η Experimental (c.g.s. units).	η Calculated.	η Exp.−η Cal.
	Sodium.		
			Per Cent.
120·4	0·006170	0·006188	−0·29
154·5	0·005314	0·005336	−0·41
155·0	0·005322	0·005308	+0·26
159·1	0·005225	0·005221	+0·07
173·7	0·004942	0·004933	+0·19
183·4	0·004760	0·004761	−0·02
206·7	0·004431	0·004399	+0·72
218·0	0·004239	0·004240	−0·02
289·0	0·003506	0·003495	+0·31
355·0	0·003015	0·003035	−0·66
	Potassium.		
67·0	0·005256	0·005242	+0·27
67·9	0·005230	0·005216	+0·26
79·4	0·004930	0·004945	−0·31
99·5	0·004540	0·004539	+0·02
119·6	0·004188	0·004203	−0·36
155·5	0·003707	0·003729	−0·59
175·5	0·003530	0·003515	+0·43
207·7	0·003249	0·003231	+0·56
282·5	0·002750	0·002756	−0·22
352·5	0·002457	0·002458	−0·04

The method which we have worked out has proved very suitable for liquid metals, especially those which are rare or oxidize easily. The liquid is enclosed in a sphere, which is hung by a bifilar suspension and set in torsional oscillation about a vertical axis. The whole is enclosed in a high vacuum, as shown in Fig. 1. The damping of the oscillation allows the viscosity to be calculated. Considerable care in design is needed to avoid any swinging motion, and the calculations are somewhat complicated, but the method has the great advantage that the liquid is sealed up from any possibility of contamination, that the measurements may be repeated any number of times without adjustment of the apparatus, and that possible specks of oxide, which would ruin any capillary tube determination, have no effect. The main part of the damping takes place in the neighbourhood of the equator, so

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* Sodium and potassium, quoted above, have already been done. See Y. S. Chiong, *Proc. Roy. Soc.*, 1936, [A], 157, 264.

that the neck of the sphere does not introduce any error. Further, the sphere containing the liquid is small, and does not need to be

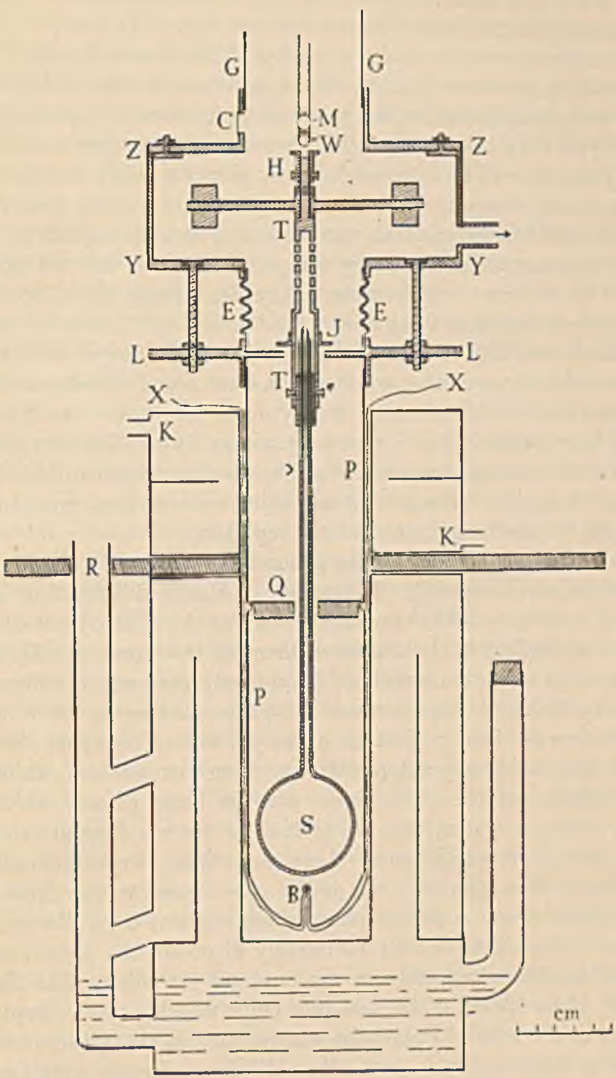

FIG. 1.

observed, so that it can easily be enclosed in a furnace. In another form of the method a magnet is attached to the neck of the sphere, and subjected to an impulsive couple once every oscillation, by means of a discharge sent through a pair of Helmholtz coils. The oscillation settles down to a fixed amplitude, at which the energy thus supplied just compensates for that dissipated by the viscous forces.

These measurements of the viscosity of liquid metals will, I hope, do something to throw light on the liquid state, but have they or the theory any significance for the practical man, some of you may ask? I think you may take it that the viscosity of all molten metals with which you deal will be (*a*) small, that is, even for heavy metals of high melting point, where the viscosity is highest, not greater than that of a 40 per cent. sugar solution, say 10 lumps to a teacupfull of water, and (*b*) not much influenced by temperature. You are not going to get metals to pour much more easily by taking them to higher temperatures, as far as I can see.

I should now like to turn to the question of the flow of solid metals. We have already seen that we have the questions: (1) why do metals hold together at all? (2) why, if they do so, don't they do it better? and (3) how comes it that a metal crystal can flow? The first question is one for the dealers in wave-mechanics, who have decided that a metal does hold together. The second and third are ones that must to some extent, as we shall see, be considered together.

First of all, let us look at the general behaviour of a single crystal of a metal when stressed. The region of elastic deformation is very small, if it exists at all*: the shear strain at the elastic limit certainly does not exceed 10^{-4}. In whatever direction the stress, usually a pure tension or a pure compression, is applied, permanent deformation begins by relative displacement on planes belonging to a certain crystallographic family, and in a certain crystallographic direction. In the case of hexagonal metals, at room temperature, things are fairly simple, for the glide planes are the basic planes, which constitute a unique system, and the glide direction is a digonal axis in the glide plane, of which axes there are three, crystallographically equivalent. The operative one is the one nearest to the direction of the applied force. A pretty phenomenon occurs, if by chance, there are two digonal axes equally favourably disposed, the crystal slipping in short lengths alternately in the one and the other glide direction (Fig. 2, Plate LVII). The case of a cubic metal is more complicated, because in the case of important planes, such as (111), there are other crystallographically equivalent sets, *e.g.* $(1\bar{1}1)$, each containing a possible direction of flow. Which plane is operative is then determined by

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* B. Chalmers (*Proc. Roy. Soc.*, 1936, [A], 156, 427), employing a very delicate extensometer, found that with single crystals of tin creep occurred under the smallest stresses.

geometrical conditions. It may happen that two different planes, with their glide directions, are equally favourably disposed: then we get slip on both sets, *i.e.* the phenomenon of double glide, illustrated in Fig. 3, Plate LVII, by a crystal of solid mercury, photographed by Dr. Greenland in my laboratory.*

The particular plane which is the glide plane may vary with the temperature; thus with magnesium Schmid says that, at higher temperatures, glide can take place on $(10\bar{1}1)$ planes in a $[11\bar{2}0]$ direction, as well as on the hexagonal basal plane in the direction of a digonal axis.†

A great deal of work has been done on metals of different crystal structure, to determine the glide plane and glide direction, from which one general rule emerges, that the glide direction is that direction in the crystal along which the atoms are most closely packed. The only doubt that has ever been thrown on this rule is by Elam, in the case of α-iron and the alloy β-brass, but other workers, *e.g.* Gough and G. I. Taylor, have found it to hold for both these metals. Both the crystals on which Elam worked were of the body-centred cubic type, which is the most troublesome type so far investigated in detail. Mr. Tsien and I have recently worked on single crystals of sodium and potassium, both of which have this structure, and have found the most closely-packed direction, *i.e.* the [111] direction, to be the glide direction, a result which Mr. Tsien and Miss Chow have also found to be true for the body-centred cubic metal molybdenum.

As regards the glide plane, this is generally the most closely-packed plane, except in the case of body-centred cubic crystals, where generalization is difficult. In the case of α-iron, G. I. Taylor has found that no particular crystallographic plane is operative, the metal slipping as a bundle of hexagonal rods might do: on the other hand Fahrenhorst and Schmid find that a single slip plane best explains their results, while Gough's alternating torsion tests suggests a simultaneous slipping on pairs of planes. With sodium and potassium we find a fixed crystallographic family, {123}, as the slip planes, but for molybdenum Mr. Tsien and Miss Chow find that, while the slip takes place on a simple family of planes, the particular family which acts changes with the temperature, being {112} at room temperature, and {110} in the neighbourhood of 1500° C. It is clear, then, that the body-centred cubic crystal offers particular difficulties.

In general, it may be said that the glide direction is more definite than the glide plane. Even in the case of metals of other systems than

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* The crystal structure of mercury is rhombohedral.

† See also the case of molybdenum, quoted later.

the body-centred cubic the glide planes show irregularities, which manifest themselves as small departures from the perfect curve in the neighbourhood of the head of the elliptic trace of the glide plane, in the case of cylindrical wires. Dr. Greenland in my laboratory has found, however, that perfect or irregular glide planes can be produced at will with the same metal, namely very pure mercury. If the soft crystals are handled with the greatest care, irregular bands occur: if the slightest bending takes place before the crystals are stressed, perfect elliptic traces are produced. It would appear, therefore, that any slight distortion produces some kind of a disturbance along crystallographic planes which makes them more fit to act as glide planes. Attempts to produce good elliptic traces with single crystal wires of α-iron were not, however, successful.

One essential fact about the glide which is the mechanism by which metals flow is, then, that it takes place in a preferred crystallographic direction, and, in general, on a preferred crystallographic plane. We now turn to the question of the stress required to produce glide. The work of Polanyi, Schmid, G. I. Taylor, and others led to the conclusion that what determines the initiation of glide is the resolved shear stress (per unit area of glide plane of course) in the glide direction, and that the tension normal to the plane is without effect. This is expressed in the formula $\frac{F}{A}\sin\chi_0\cos\lambda_0 = S_0$, where F is the load, A the area of normal cross-section, χ_0 the angle between the glide plane and the direction of the applied force, and λ_0 the angle between the glide direction and the applied force, while S_0 is a constant. The least resolved shear stress S_0 that produces glide is, then, a constant for a given metal, and is called the critical shear stress. Probably some recent experiments of Dr. Roscoe and myself give the most accurate confirmation of this law. The results, which were obtained with cadmium, a metal of hexagonal structure, are expressed in Fig. 4, where $\frac{F}{A}\cos\alpha$ is plotted against χ_0. Here α is the angle between the glide direction and the projection of the wire axes on the glide plane, so that $\cos\lambda_0 = \cos\chi_0\cos\alpha$. The law is then $\frac{F}{A}\cos\alpha = \frac{2S_0}{\sin 2\chi_0}$. The line shown in the figure is $y = \frac{111}{\sin 2\chi_0}$ or is the line given by the formula with $S_0 = 55{\cdot}5$ grm.wt./mm.^{2} and it will be observed that the points lie very close to it. It follows from these results that variation of the normal tension from 215 to 10 grm.wt./mm.^{2} does not affect the critical shear stress by as much as 2 per cent., which is well within experimental error, that is, a normal tension up to four times the critical shear stress does not affect the flow appreciably. This does not necessarily imply that a very much greater normal tension would have no effect, but it is difficult geometrically to produce such a tension. It does, however, mean that a crystal is so strong for tension normal to the glide direction that there is no appreciable yield for such forces as can be applied in practice. The way in which the glide takes place preferentially on the basal planes, even when they are nearly normal to the direction of pull, is well illustrated by the cadmium crystal shown in Fig. 5, Plate LVII (Andrade and Roscoe).

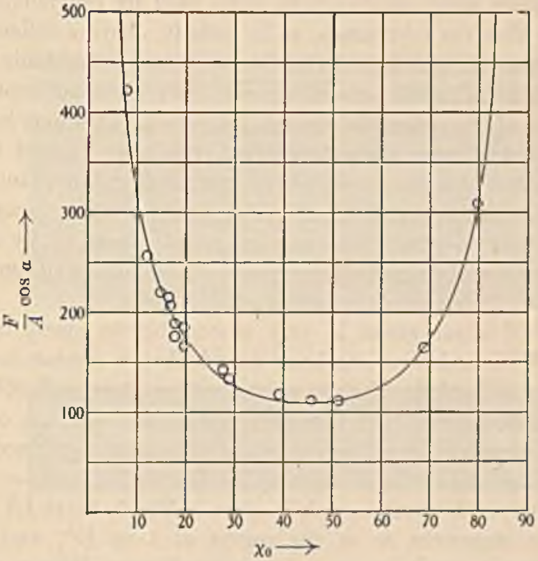

Fig. 4.

The critical shear stress is not such a definite constant as the earlier workers thought. We have found that, if the crystals are prepared so as to be strain-free, their behaviour is very constant, but even with extremely small stresses a very slow rate of glide takes place, so that it is necessary to fix some arbitrary small rate as the beginning of glide, which was, *e.g.*, taken as 1 per cent. per second for the results in Fig. 3. The variation of rate u with stress, which has been studied by Dr. Roscoe and myself, is an exponential one of the type $u = Ae^{-b(S_0' - S_0)^2}$, where S_0 is the applied shear stress, so that the variation of rate for a small change of S_0 is extremely large. With the purest cadmium,* for instance, $S_0 = 17$, 15, and 13 give, respectively,

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* The cadmium used for the results of Fig. 3 contained 0·11 per cent. lead and 0·03 per cent. zinc, and is much harder than the pure metal.

1 per cent. glide per 4 minutes, per 15 minutes, and per hour. It may be objected that the formula gives a flow for no stress, but the rate is only 1 per cent. in about 3 years, and the theoretical arguments underlying the formula, which will be mentioned later, do not contemplate absolute correctness in this extreme case. If this view is correct, then, single crystals will flow even under the smallest force, but the rate of flow varies so rapidly with the stress that there is a limited range of stress within which it first becomes appreciable. We may note that Chalmers, working with tin, has experimentally found creep down to stresses much smaller than those used by previous workers, but he finds that the microcreep, as he calls it, obeys a different law, so that the point at which the rate of creep increases suddenly is more definite than is indicated by our formula. We have not studied the slowest rates, of the order 10^{-7} cm./cm./minute, as Chalmers has done, but taking an arbitrary rate of 1 per cent. per hour we find for pure cadmium a critical shear stress of 13 grm.wt./mm.^{2} at atmospheric temperature. Quite apart from all questions of precision, however, the critical shear stress for crystals of pure metals recorded by different workers may be said to be in the region of 10–600 grm.wt./mm.^{2} which is very small. Single crystals flow extremely easily.

The critical shear stress is very susceptible to small traces of impurity. With cadmium we have found that a contamination of 0·1 per cent. of lead doubles the critical shear stress, all other conditions being the same. We have carried out experiments on single crystals of mercury, since here the metal can be obtained in an extremely pure state. Such crystals show the phenomenon of glide very beautifully: a good example is given in Fig. 5, Plate LVII. We estimate our impurities as in the region of 1 in 10^8, and in any case spectroscopic analysis, carried out by Messrs. Hilger, revealed no impurity. Dr. Greenland has found that, in the case of mercury contaminated with small amounts of silver, the critical shear stress is roughly linear with the logarithm of the quantity of the impurity, one part of silver in a thousand giving a value of about four times that obtained with the purest mercury, while one part in a million gave an easily measurable effect. These experiments seem to me to dispose of any theory that attempts to trace the extreme softness of single crystals to dislocation of the crystal structure produced by foreign atoms.

The other remarkable mechanical property of single crystals is the hardening which they experience when they have been much stressed. This hardening is appreciable for metals of low melting point, such as cadmium, but is much more marked for metals of higher melting point,

FIG. 2.

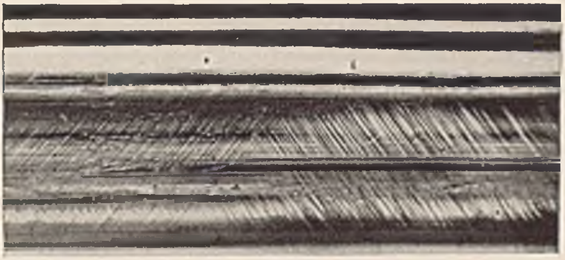

FIG. 3.

FIG. 5.

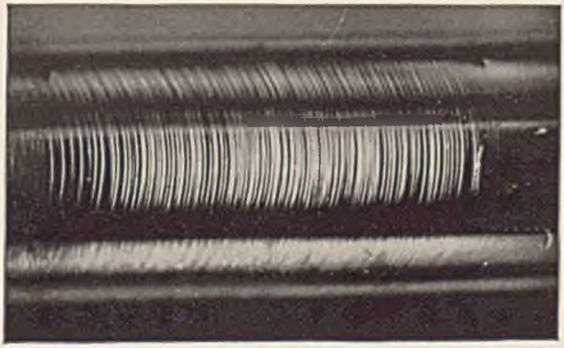

FIG. 6.

[*To face p.* 440.

PLATE LVIII.

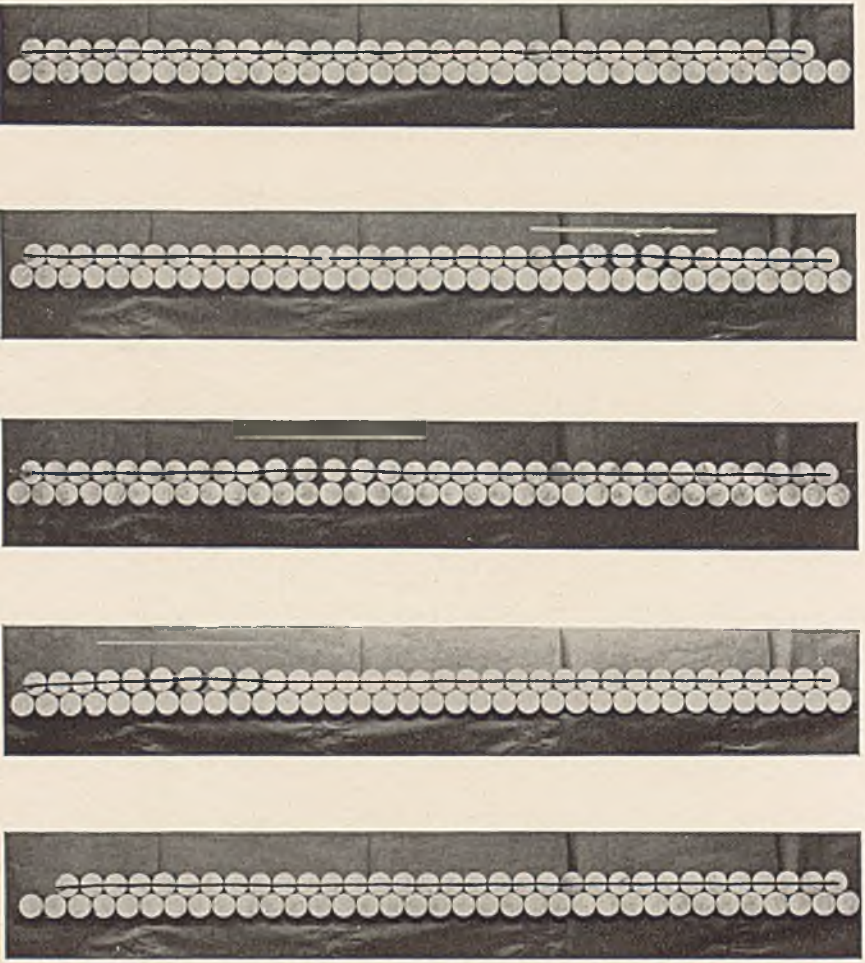

FIG. 8.

especially nickel, as is shown in Fig. 7, taken from Schmid. A very striking demonstration of this was given by Hausser, who prepared single crystals of copper of very large dimensions. Such a crystal, in the form of a rod 16 mm. in diameter, could be very easily bent a little, with difficulty bent into the form of a semicircle, while an athlete could not bend it back again.

We have now reviewed briefly some of the most remarkable properties of single crystals, and come to the difficult task of considering what explanation can be given of these properties. What seems certain is that no picture of a crystal as a perfectly regular lattice is adequate. Energy considerations show that the flow cannot take place as the result of one perfect crystal plane being moved as a rigid whole over another crystal plane. The generally held opinion, put forward in different forms by Polanyi, Orowan, and G. I. Taylor, is that the plane moves by the propagation of a fault, a place of misfit, in the crystal structure, which normally has the atoms to either side of it properly arranged in the lattice. When the crystal is stressed the fault travels along, leaving the atoms behind it regularly ordered, but advanced by one spacing, compared with their previous position. The conception can perhaps be illustrated by a series of rollers, representing one crystal plane, on which rests a second series of rollers, joined to one another by elastic strip, to represent a second crystal plane (see Fig. 8,

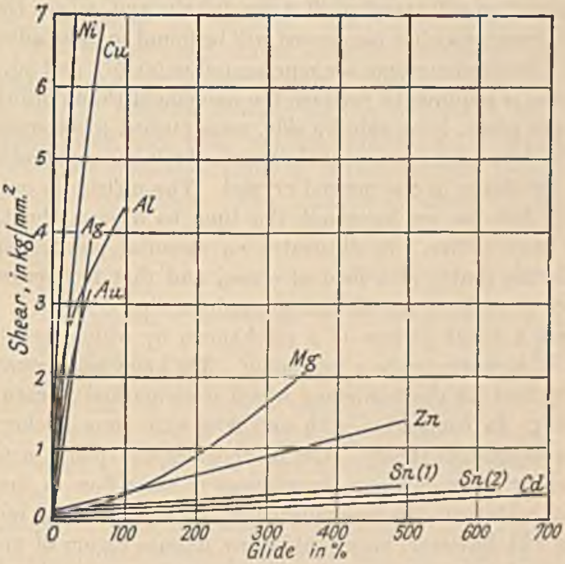

FIG. 7.

Plate LVIII). In the normal crystal, represented at (*a*), each roller of the second plane rests in a hollow of the first plane—and it may be incidentally remarked that no metal crystallizes in the simple (as distinct from the body-centred or face-centred) cubic system, so that the picture has a certain appropriateness. A fault may be created by stretching part of the second plane, so that there are, say, only five rollers where six were before, as represented in (*b*). The region of the fault is indicated by a white line drawn above the model. If now a small shear stress be applied to the upper layer, say by running the hand gently along it, the dislocation will travel until it reaches the end, where the part of the layer through which it has passed will be found to have advanced by one roller. Successive stages are represented in (*c*), (*d*), and (*e*). Clearly far less force is required to produce the movement than if all the rollers of the upper plane, lying side by side, were pushed together as a rigid whole. The depressions represent the points of minimum potential energy occupied by atoms in the normal crystal. The picture is only a very rough one, but, as we have not the time to discuss the theory in detail, it may suffice. It illustrates an essential point, that a dislocation is the centre of a field of stress, and that it requires only a small force to make it travel, and so produce slip.

To have a rough picture of a mechanism by which metal crystals can flow is, however, only a beginning. We have to account for the time factor and for the hardening which is so marked a feature of the distribution. In connection with any flow with time Becker has put forward a suggestive theory. Let us consider any point in the metal where a shear stress S_i exists, insufficient to start flow in the absence of thermal agitation. In consequence of the local thermal movements the stress will, however, vary within any minute region of volume V: for instance clearly if, at a particular moment, several molecules in one layer happened to move in an opposite direction to several molecules in a neighbouring layer, a local shear would be set up which, with favourable conditions of direction, would reinforce the shear due to external stress. Becker's idea is, then, that from time to time thermal agitation will raise the stress to a value S sufficient to produce glide: the glide will take place in a series of small steps, or jumps, at different points. The frequency with which the jumps take place can be found by applying Boltzmann's familiar exponential formula, the energy required for a jump to take place in volume V being $\frac{V(S - S_i)^2}{2G}$, where G is the shear modulus. Supposing all jumps to be of equal magnitude we get

$$v = De^{-\frac{V(S - S_i)^2}{2GkT}}$$

as giving the velocity of glide in terms of the shear and the temperature. This is the type of formula which has been applied by us to express the relation between rate of flow and shear stress in the neighbourhood of the critical shear stress.

It is found, however, in general that if the ordinary shear modulus be taken, flow should not become appreciable except under very much higher forces than those under which flow is actually observed, forces, that is, a thousand or more times the actual ones. Orowan has explained this by assuming that the metal contains flaws, of the type originally assumed by Griffith, and hence often called Griffith cracks. Some such flaws are an essential feature of recent attempts to explain the properties of metals. They have been given various names, but the essential feature for our purpose is that emphasized by Griffith, that any long narrow crevasse in a stressed material will have an enhanced field of stress in the neighbourhood of the greatest curvature. The maximum shear, in fact, will, in the two-dimensional case, be given by a formula of the type $S_{\text{max.}} = \frac{S(a+b)^2}{ab}$, where a and b are the major and minor axes of the supposedly elliptical cross-section, or if a is large compared to b, $S_{\text{max.}} = S\frac{a}{b}$. Such a crack, then, may cause a very high local stress, the limiting value of b being, of course, something like the molecular diameter. Orowan, then, has adapted Becker's formula by putting qS_i instead of S_i, q being a large multiplying factor to indicate the local stress.

Further, we have to consider hardening. G. I. Taylor explains it in terms of his dislocations, which are not the same thing as Griffith cracks, but centres of self-strain.* Two such dislocations exert a force on one another: if they are of opposite sign, that is, if the distortion is healed in an opposite direction in each one, as illustrated in Fig. 9, they will attract one another, and it will require a definite force to separate them, that is, to make them run past one another in their parallel courses, the magnitude of the force being inversely as the distance between them at their nearest approach. On these lines Taylor arrives at an expression for the hardening, but he has to assume that fresh dislocations are created by progressive deformation, and hence will be closer together than the old ones, and so require a greater force to make them run past one another. He also requires a second

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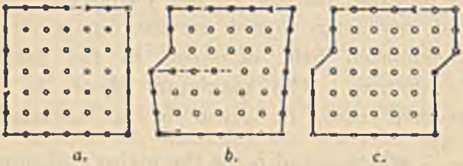
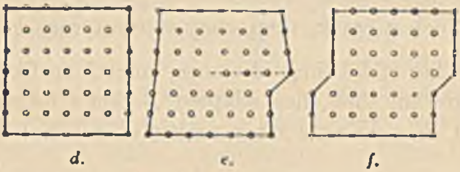
* When a piece is removed from a unstrained body, and the surfaces then rejoined in such a way that the body is strained, the state is said to be one of self-strain. This is a particular case: in general the term is applied when the body is in a state of strain under no external forces, as in the case of temperature stresses.

system of flaws, to prevent them running too far after they pass. The theory is an attractive formal explanation of some of the phenomena.

W. G. Burgers and J. M. Burgers have attempted to combine the best features of the Becker–Orowan and the Taylor theories, so as to make a comprehensive scheme. They start with the assumption of what they call "Lockerstellen" or flaws, corresponding to the Griffith cracks, *i.e.* places where an external stress produces locally a much greater concentration of stress. Here, owing to the temperature fluctuations, jumps take place, with the frequency given by the Becker–Orowan formula. As originally suggested by Orowan, these disturbances lead to dislocations, of the Taylor type, which travel until stopped by a flaw in the crystal, as with Taylor. The arrested dislocations each have round them a field of stress which partly counteracts the external field at intermediate parts of the crystal, and render less likely the occurrence of jumps at cracks that may be there. This accounts for the hardening that takes place. The Burgers also invoke a local curvature of the lattice, although this part of their theory I find less clear.



Positive Dislocation.



Negative Dislocation.

Fig. 9.

This theory has a great deal to commend it, but this is no place to consider it in detail. It does nothing to explain the fact that, with most if not all crystals, the glide takes place along selected planes: the crystal slips in "glide packets." Roscoe and I have shown that with lead, at any rate, the spacing of these glide planes is a real feature of the crystal, independent of a range of factors. I also do not think that it takes sufficient account of crystal break up, which X-ray analysis clearly shows to take place, for the single Laue spots are spread out into long lines, or into a secondary series of spots, as Tsien and I have found when the crystal is much strained. It is not, however, my object this evening to pretend that there is any fully satisfactory theory of the mechanical behaviour of single crystals, or even to put before you such incompletely formulated ideas as I myself may have on the subject of a general theory. All that I wish to do is to present the general problem, and show you the kind of lines along which we may hope to reach a solution when we have sufficient material. The behaviour varies so much with temperature, rate of stressing, and previous strain that more systematic study of single metals is required before we really have the ground firm enough for theorising. But one thing seems certain, that it is no use to seek an explanation in terms of the mathematical crystal, but rather that crystalline imperfections are at the bottom of all these phenomena which I have described, of all phenomena, that is, that take place in real metals.

The interest and practical application of this kind of knowledge may seem very remote to some of you. Since, however, all the metals of engineering are masses of minute crystals, we are unlikely to make any fundamental advance except by learning how the single crystals themselves behave. Dr. Chalmers and I found, for instance, that the electrical behaviour of strained wires of certain polycrystalline metals could be explained roughly in terms of the single crystals, and Orowan has succeeded in explaining roughly the way in which strength varies with the size of the crystal grain in a certain simple case. Not much has been done, but a beginning has been made.

I do not pretend to have given you a balanced account of the subject of flow in metals. Work in which I have been personally interested probably looms too large. I felt, however, that to attempt to give a considered critical summary of the whole field would make impossible demands both upon my powers and upon your patience, and further would suppose that you are already familiar with a great deal of what may with justice be called tedious detail. My object has been the more modest one of trying to show the nature of certain fundamental problems, and the difficulties that have to be overcome before we can really claim to know anything about why metals behave as they do when pushed and pulled.

ACKNOWLEDGMENTS.

The lecturer desires to express his thanks to the Royal Society (Figs. 1 and 9); the Physical Society (Fig. 4), and the publishers of *Science Progress* (Fig. 7) for permission to reproduce certain illustrations.

OBITUARY.

Thomas Bolton, J.P., died at his residence, Blackhurst, Tunbridge Wells, on March 9, 1937, at the age of 78.

He was born at Oakamoor, Staffordshire, and as Chairman of Thomas Bolton and Sons, Ltd., represented a family which for many generations had been prominently connected with the copper and brass industry. His own firm was established in Birmingham in 1783, but in 1852 acquired the works at Oakamoor of the Cheadle Brass and Copper Company which itself had been founded in 1719.

Educated at Harrow and University College, London, and apprenticed to Kitsons of Leeds, he joined his family business at the age of 20 and played an active part in the erection of the Widnes works in 1881 and the Froghall works in 1890. His engineering and technical ability was clearly demonstrated also by his inventions of continuous wire-drawing machinery and other improvements in the rolling and drawing of metals, which have kept his company in the van of a highly competitive industry. As Chairman and Managing Director of his company from 1909 until his death, his outstanding personality and the esteem which his character and power of leadership called forth were of great influence both on its internal and external affairs.

Mr. Bolton was not content to limit his powers to his private commercial interests, nor even to his hobbies, which were many. He always had in view the welfare and progress of industry, and was ready to devote his time and talents to movements which were concerned with these objectives. Thus, we find him amongst the earliest supporters of the Federation of British Industries, when it was formed in 1916; he was elected a Vice-President in 1924 and was Chairman of its Finance Committee for the last five of the 15 years of his service on it. For the British Standards Institution he served as Chairman of the Non-Ferrous Metals Industry Committee and was most active in many other ways. He was also Chairman for over 20 years of the High-Conductivity Copper Association and was closely associated with the other Trade Associations which have played an important part in consolidating the interests and extending the influence of the copper and brass industries of this country. The recently formed Copper Development Association obviously secured his support and membership of its Council and Management Committee.

No record of Mr. Bolton's public services, however sketchy this must be, could fail to refer to his work for the British Non-Ferrous Metals Research Association, for he devoted himself whole-heartedly and continuously to its progress from 1918. He was Chairman of the Provisional Committee which established its plan and scope, and was its first and only Chairman of Council from its inauguration in December 1919 until his death. Largely due to his own gifts of leadership the B.N.F.M.R.A. has become a powerful organization, supported to an ever-growing extent by all throughout the whole non-ferrous field who realize the benefits which science can provide for the advancement of industry. The addresses which Mr. Bolton gave at the Annual Luncheons of the Association greatly stimulated the progress of the Association and exerted an influence for co-operation in industry even beyond its own field. The new plans for an extension of the Headquarters of the Association, which were approved at the last meeting of the Association's Council, which Mr. Bolton presided over, will form a tangible memorial of his period of office. The

Bulletin of the B.N.F.M.R.A. for April 1937 published a more detailed record of his life, and appreciations from many who knew him.

Mr. Bolton was an Original Member of the Institute of Metals and always took a keen interest in its work. He served on the Council from 1923 to 1931 and was a Vice-President from 1926 to 1931. He was also a member of the Institute's Corrosion Research Committee and was instrumental in the formation of the Atmospheric Corrosion Research Committee. Had he so desired he could have assumed the highest office that the Institute has to offer.

Few can have exerted so much influence on the non-ferrous metals industry nor have left such a fine example of courtesy and unselfish devotion. His loss will be deeply felt by all who had the privilege to come in contact with him.

R. S. HUTTON.

GEORGES EMIL BUESS died at his residence on February 22, 1937, in his sixty-third year, after a short illness.

Of Swiss extraction, he joined the clerical staff of Messrs. N. M. Rothschild and Sons' Gold and Silver Refinery in the year 1898. On February 1, 1912, he was appointed manager of the refinery and had thus just completed his Silver Jubilee at the time of his death.

A brilliant refiner, with an enormous knowledge of the precious metals, a true friend, beloved by all his staff, his was a personality with which it was a pleasure to come into contact.

He was elected a member of the Institute of Metals on March 9, 1925.

W. H. WILLIAMS.

PROFESSOR WILLIAM CAMPBELL died suddenly on December 16, 1936, at the age of 60.

Born at Gateshead-on-Tyne, Professor Campbell was educated at King's College, London, and at Oxford. He received the degrees of B.Sc. and of D.Sc. from Durham University, and was research scholar at the Royal School of Mines from 1899 to 1901. He went to Columbia University with a Fellowship in 1902, and taught there continuously from 1904 to his death, being appointed the first Howe Professor of Metallurgy at Columbia University in 1924.

A year after he went to America, he received the Saville–Shaw medal of the British Society of Chemical Industry, and in 1905 the Carnegie Scholarship of the Iron and Steel Institute. During the War he was metallurgist in the New York Navy Yard and rose to the rank of Commander in the U.S. Navy, afterwards becoming consulting metallurgist to the New York Navy Yard. He was a Fellow of the Geological Society of London. During his distinguished career in the United States of America, he held the office of metallographer for the technologic branch of the Geological Survey. He was also at one time a member of the advisory committee of the Bureau of Standards and advisory metallurgist to the New York City Board of Transportation. He edited the *Columbia School of Mines Quarterly*, the *International Journal of Metallography*, and the *Journal of Industrial and Engineering Chemistry*.

Professor Campbell was elected a member of the Institute of Metals on December 29, 1924.

WILLIAM CLARK died on March 13, 1937, at his residence in Skelmorlie, Ayrshire, at the age of 83.

He was born in Mauchline, Ayrshire, in 1854, but early in his life, his family removed to Glasgow. In 1873 Mr. Clark joined the accountants' staff of the Steel Company of Scotland, Ltd., and saw the first cast of Siemens–Martin acid steel made in Scotland. He left in 1875 to take charge of a small wire-rolling mill plant at Brighouse, Yorkshire, but after only twelve months he was offered another appointment with the Steel Company of Scotland, Ltd., where he eventually became accountant, then secretary and, finally, manager. He resigned in 1910 to become manager of Messrs. Vickers' Sheffield works and was shortly afterwards appointed a local director of this company. This was followed by his election as a full director.

During his sixteen years' residence in Sheffield Mr. Clark played an important part in industrial development. He was Master Cutler in 1920 and on the completion of his year of office, he was elected president of the Chamber of Commerce. He did much valuable work during the War when he was called on to control and direct a great number of alterations, extensions, and developments of the manufacture of armaments and munitions. In this connection he was appointed a member of a deputation to meet Lord Kitchener's Committee which was dealing with this matter.

Mr. Clark managed, in spite of his many activities in the world of trade, to find time for social, philanthropic, and welfare work, and he was keenly interested in any movement for helping boys to obtain a good start in life. Mr. Clark was one of the promoters of, and a member of the committee of, the Sheffield branch of the Anglo-American Society which was formed in 1919. He was also an enthusiastic member of the Caledonian Society of Sheffield, and became its president in 1923. He retired from Messrs. Vickers, Ltd., in 1925, and left Sheffield to return to Scotland in 1926.

Mr. Clark was a Past-President of the West of Scotland Iron and Steel Institute and was the first Chairman of the Steel Makers' Association in Scotland, a position he held when he moved to Sheffield. At that time, too, he was a member of the Council of the Institution of Engineers and Shipbuilders in Scotland. He was a member of the Merchant House in Glasgow, a life member of the Glasgow Chamber of Commerce, and a member of the Guild of Hammermen of that city. He was also a member of the Iron and Steel Institute, the Executive Council of the Iron and Steel Federation, and the Grand Council of the Federation of British Industries.

Mr. Clark was elected a member of the Institute of Metals on July 24, 1919.

Dr. Frederick C. Langenberg died on April 4, 1937, three weeks after his forty-seventh birthday.

Dr. Langenberg first became associated with the U.S. Pipe and Foundry Company as consultant metallurgist in 1928. He joined its permanent executive staff in 1929 as organizer and director of the Research Laboratory of the Company.

In planning the buildings and equipping the laboratory he brought to his task a broad experience and a scientific knowledge of ferrous metallurgy which proved to be of great value to the Corporation. He was deeply interested in the education and proper training of young men and gave unstintingly of his time and knowledge to those in his department, or who in any way showed interest not only in his professional but also in his social work. He will be greatly missed by those who knew him.

Dr. Langenberg was elected a member of the Institute of Metals on May 11, 1927.

Crandall Zachariah Rosecrans died on January 7, 1937.

He was born in Chicago, Ill., U.S.A., on January 4, 1897, and was educated at the University of Illinois where he obtained the degrees of: B.S. in Mechanical Engineering 1919, and M.S. in 1921; and also M.E. (professional) in 1929. While at the University, he served successively as Research Graduate Assistant, Research Assistant, and Research Associate. His work chiefly dealt with the study of explosions of gaseous mixtures in closed chambers and thermodynamic analysis of gas engine tests, and resulted in the publication, with collaborators, of several University of Illinois Engineering Experimental Station Bulletins.

Mr. Rosecrans joined the Research Department of the Leeds and Northrup Company in July, 1926, and served successivly as Research Engineer 1926–1928, Chief of Mechanical and Chemical Divisions, 1928–1929, Chief of Mechanical and Metallurgical Divisions, 1929–1935, Assistant Director and Chief of Metallurgical Division 1935–1936. His research work for this firm was in connection with fluid flow meters, thermal conductivity gas analysis, precision governors, combustion control, and carburizing furnaces.

He became Second Lieutenant in the U.S. Engineer Officers' Reserve Corps in 1924, and was attached to the Ordnance Department; was promoted to First Lieutenant in 1926, and was transferred to Coast Artillery Corps Reserve in 1930. In 1935 he was placed on the Coast Artillery Board in addition to his duties in connection with the 603rd Coast Artillery Regiment. In the latter connection he was called on from time to time to give instructional lectures at the bi-monthly meetings and his presence at such times always ensured a good attendance as the other Reserve Officers greatly respected and admired his ability.

Mr. Rosecrans was a member of the American Society of Mechanical Engineers, the American Chemical Society, The Franklin Institute, A.S.R.E., A.A.A.S., the American Institution of Electrical Engineers, the Verein Deutscher Ingenieure, the American Society for Metals, Sigma Ki and Tau Beta Pi. He was also a Past-Master of Western Star No. 240 Lodge A.F. and A.M. and a member of the Commandery and of the Scottish Rite bodies.

Mr. Rosecrans was elected a member of the Institute of Metals on December 19, 1929.

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Printed in Great Britain by Richard Clay & Sons, Limited,
Bungay, Suffolk.