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EDITED BY

S. C. GUILLAN

LONDON
PUBLISHED BY THE INSTITUTE OF METALS
4 GROSVENOR GARDENS, LONDON, S.W.1.
1938

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

Form A. *(Membership Application)*

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

The INSTITUTE of METALS

4 GROSVENOR GARDENS, 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.

....

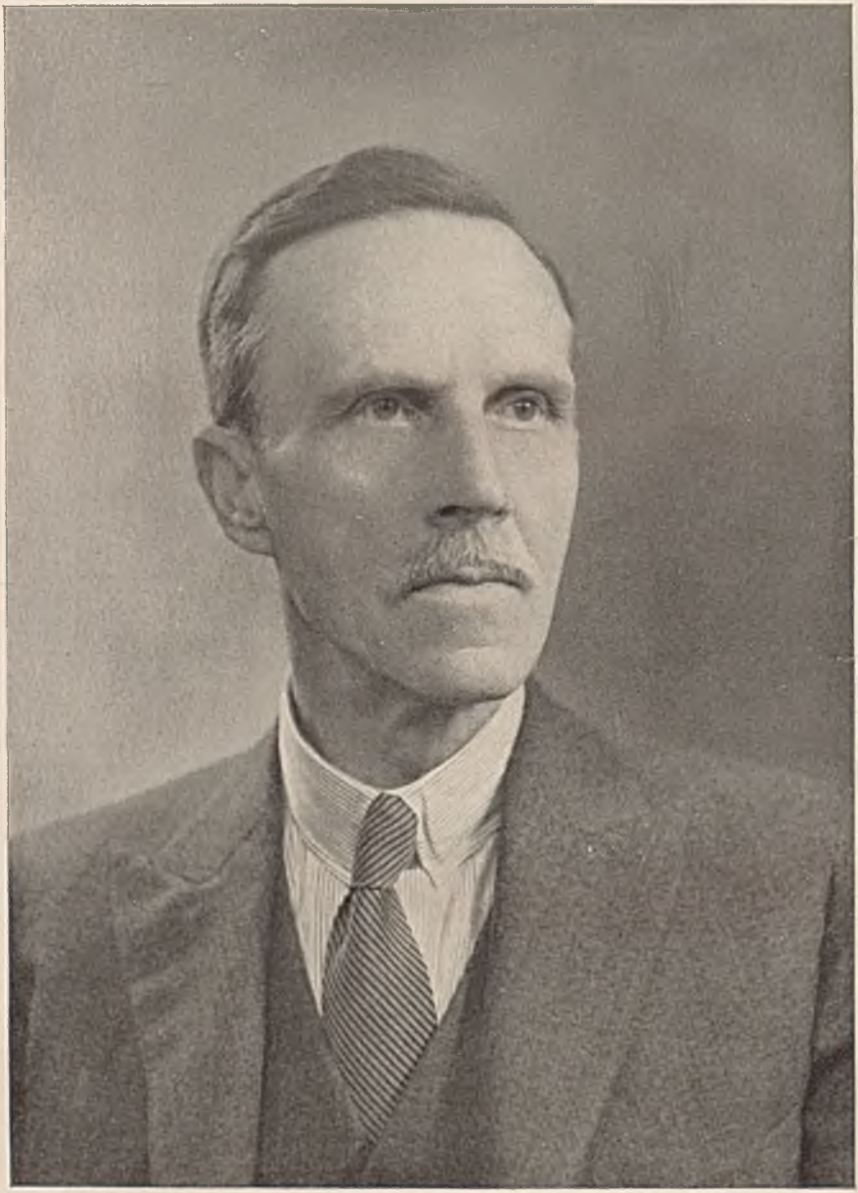
4 GROSVENOR GARDENS, *Chairman.*
WESTMINSTER, LONDON, S.W.1.

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

* 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.)

62.



C. H. DESCH, D.Sc., Ph.D., F.R.S.
President.

[*Frontispiece.*

INSTITUTE OF METALS PUBLICATIONS DEPARTMENT

THE INSTITUTE OF METALS

OFFICERS AND COUNCIL,

1938–1939

PRESIDENT:

C. H. DESCH, D.Sc., Ph.D., F.R.S.

PAST-PRESIDENTS:

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HAROLD MOORE, C.B.E., D.Sc., Ph.D.
RICHARD SELIGMAN, Ph.nat.D.

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C. J. SMITHELLS, M.C., D.Sc.
A. J. G. SMOUT.
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H. S. TASKER, B.A.

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(Chairmen of Local Sections.)

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S. G. HOMFRAY, B.A. (*N.-E. Coast*).
H. BROWN (*Scottish*).
F. MASON (*Sheffield*).
HARRY DAVIES (*Swansea*).

SECRETARY:

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

ASSISTANT SECRETARY:

S. C. GUILLAN.

Telegraphic Address:
Sloane 6233, London.

Telephone:
Sloane 6233.

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 (*deceased*).

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.

W. R. Barclay, O.B.E., 1936–1938.

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.,
3182 The Boulevard, Westmount, P.Q.

France.

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

Germany.

Dr.-Ing. Max Haas, Berlinerstrasse 120, Neubabelsberg.

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,
Laboratorio Chimico Italiano Minero Metallurgico,
Via Carlo Cristoforis 12, Milano.

Japan.

Professor K. Tawara, D.Eng.,
Metallurgical Department, Tokyo Imperial University, Hongo, 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. A. von Zeerleder, Aluminium-Industrie A.G.,
Zentralstrasse 78, Neuhausen.

United States of America.

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

CHAIRMEN AND HONORARY SECRETARIES OF THE LOCAL SECTIONS.

Birmingham.

Chairman : J. A. A. Fraser, B.Sc., Cheylesmore, Brunswick Park Road, Wednesbury.

Hon. Secretary : J. W. Jones, M.Sc., Metallurgical Department, The University, Edgbaston, Birmingham.

London.

Chairman : W. A. C. Newman, B.Sc., A.R.S.M., A.R.C.S., The Royal Mint, E.C. 3.

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

North-East Coast.

Chairman : S. G. Homfray, B.A., Vickers-Armstrongs, Ltd., Elswick Works, Newcastle-upon-Tyne.

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

Scottish.

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

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

Sheffield.

Chairman : Frank Mason, Ivy Bank, 100 Ashdell Road, Sheffield, 10.

Hon. Secretary : Captain F. Orme, M.Met., Department of Applied Science, The University, St. George's Square, Sheffield, 1.

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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LIST OF PLATES

THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS.

EXTRAORDINARY GENERAL MEETING.

AN EXTRAORDINARY GENERAL MEETING was held in Caxton Hall, Caxton Street, Westminster, London, S.W.1. on Thursday, January 13, 1938, Mr. W. R. Barclay, O.B.E., President, occupying the Chair.

The Secretary (Mr. G. Shaw Scott, M.Sc.) read the notice convening the meeting and the following Special Resolution :

"That the Articles of Association of the Institute of Metals be altered as follows :—

(*a*) By inserting after the words 'Ordinary Members' in Article 5 the words 'Associate Members';

(*b*) By inserting in Article 6 after the third paragraph (relating to Ordinary Members) the following new paragraph :

> 'ASSOCIATE MEMBERS shall be persons who are admitted as such at the absolute discretion of the Council, after having satisfied the Council that they are members of some scientific or technical body or society, whether incorporated in Great Britain or elsewhere, whose objects, interests or activities relate to any branch of metallurgy or are otherwise in the opinion of the Council akin or complementary to those of the Institute. They must at the date of admission be at least twenty-one years of age and shall not be eligible for admission to or be entitled to retain Associate Membership if over such age as shall be determined from time to time by the Council or provided by the Bye-laws. An Associate Member shall not be entitled to vote at meetings of the Institute or to nominate candidates for Ordinary or Student membership.'

(*c*) By substituting the words 'Ordinary or Associate Membership' for the words 'Ordinary Membership' at the end of the fourth paragraph of Article 6 (relating to Student Members);

(*d*) By inserting at the end of Article 6 the words :—

> 'The discretion of the Council to admit to any class of Membership shall not be affected by the fact that the person proposed to be admitted is qualified for admission or has previously been admitted, to another class of Membership.'

(*e*) By substituting the words 'Ordinary, Associate or Student Members' for the words 'Ordinary or Student Members' in the opening sentence of Article 8;

(*f*) By substituting the words 'each Associate or Student Member' for the words 'each Student Member' in the opening sentence of Article 9;

(*g*) By altering the first sentence of Article 22 to read :—

> ' At a General Meeting held not less than two months nor more than seven months prior to the Annual General Meeting the Council shall present a list of the Honorary Officers and Ordinary Members of Council previously retired or retiring at such Annual General Meeting and who are eligible for election or re-election (as the case may be) to the respective offices, together with a list of other members, if any, nominated by them for election to honorary office or membership of the Council.'

(*h*) By inserting after the words ' unless he ' in the last sentence of Article 22 the words ' has consented in writing to be nominated and '

(*i*) By making the following insertion at the beginning of Article 23 :—

> ' 23 (*a*). If the candidates validly nominated are not more in number than the vacancies, the persons so nominated shall, as from the next Annual General Meeting, be deemed to be duly elected; (*b*) If the candidates nominated are more in number than the vacancies, any of the candidates in excess of the number to be elected may withdraw or with his consent be withdrawn by the nominators in writing; but if the candidates still remain in excess of the number to be elected, the election shall be conducted by voting papers as hereinafter provided; '
>
> (*c*) [(*c*) will be existing Article 23.]

(*j*) by altering Article 43 to read :—

> ' The Annual General Meeting shall be held in London during the first four months of the year. Other General Meetings shall be held at such time and at such place or places as the Council may determine. The quorum for a General Meeting shall be ten Members of the Institute personally present.' "

The Chairman explained the reasons for the Special Resolution

The Chairman proposed, and it was unanimously agreed that, subject to the approval of the Board of Trade, the words " and entitled to vote " be added to the Clause (*j*) of the Special Resolution.

The Chairman proposed, and it was unanimously agreed, that the Special Resolution, with or without the addition above referred to, be approved.

The Proceedings of the Extraordinary General Meeting then terminated.

ANNUAL GENERAL MEETING.

THE THIRTIETH ANNUAL GENERAL MEETING of the Institute was held in the Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, London, S.W.1., on Tuesday, Wednesday, and Thursday, March 8–10, 1938, the retiring President, Mr. W. R. Barclay, O.B.E., occupying the Chair at the opening of the meeting at 7 p.m. on Tuesday, March 8.

Tuesday, March 8.

The Minutes of the Annual Autumn Meeting held in Sheffield on September 6–9, 1937, were taken as read, and signed by the Chairman.

The PRESIDENT welcomed members attending from overseas.

The SECRETARY (Mr. G. Shaw Scott, M.Sc.) 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, 1937.

The Council has pleasure in submitting its Annual Report covering the thirtieth year of the existence of the Institute.

The year has been one of exceptional activity and of considerable progress in many directions. New schemes for increasing the Institute's usefulness to its members have been put into operation, whilst others are under consideration with a view to their becoming effective in the immediate future.

The Institute's membership has again shown an increase over the previous year, and in the hope that the growth will continue the Council has felt encouraged to develop plans for the improvement of publications and to engage in discussions with the Iron and Steel Institute for closer collaboration and for increased joint responsibilities in several directions.

The raising of an Endowment Fund which now promises to reach £20,000 has appreciably strengthened the financial position and has justified the Council in contemplating forward movements with much greater confidence than has hitherto been possible.

As the result of the work of the Meetings Committee of the Council, and with the ready assistance and co-operation of the Local Sections, the policy of holding some General Meetings of the Institute in the provinces has been adopted, and it is hoped in this and other ways to enlarge the interest of members in the papers and discussions.

Other outstanding features of the year's activities to which more detailed reference is made later are : An invitation from our American friends to hold the 1938 Autumn Meeting in the United States of America in conjunction with the Iron and Steel Institute; the offer (gratefully accepted by the Council) of a platinum medal to be awarded for outstanding services to the Industry; and an internal reorganization and strengthening of the staff of the Institute, which, it is believed, will lead to greater efficiency.

ROLL OF THE INSTITUTE.

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

	Dec. 31, 1933.	Dec. 31, 1934.	Dec. 31, 1935.	Dec. 31, 1936.	Dec. 31, 1937.
Honorary Members	5	5	4	3	4
Fellows . .	8	7	7	8	9
Ordinary Members	2038	1992	1987	2009	2021
Student Members .	80	85	69	64	118
Associate Members	—	—	—	7	14
Total . .	2131	2089	2067	2091	2166

Sir William Bragg, O.M., K.B.E., M.A., D.Sc., P.R.S., and Professor Dr. C. A. F. Benedicks were appointed Honorary Members of the Institute.

The Council nominated Dr. H. Moore, C.B.E. (Past-President) and Mr. W. Murray Morrison (sometime Vice-President) as Fellows of the Institute.

The growth in the membership envisaged in the last Report continued, and the total on December 31, 1937, was the highest reached since the record figure of 2232 was attained in 1931. The large increase in the number of Student Members is particularly gratifying to the Council, as also is that in the number of Associate Members who have joined as a result of the scheme of co-operation with the American Institute of Mining and Metallurgical Engineers. The total of Ordinary Members includes members of the Iron and Steel Institute who have joined under the scheme of co-operation referred to later in this report.

OBITUARY.

It is with much regret that the Council records the deaths of the following members: J. Angus; Major P. C. M. Ash; G. E. Buess; W. Clark; R. S. Corking; E. Curran; A. H. Ivey; A. H. Knight; Dr. F. C. Langenberg; G. W. Mullins; F. V. Ramsden; C. Z. Rosecrans; P. K. Sen; T. Tahara; R. J. Walker; and W. H. Williams.

In addition, the Council records with much regret the deaths of The Rt. Hon. The Lord Rutherford, O.M., F.R.S., an Honorary Member; and Sir John Dewrance, G.B.E., Fellow and Past-President; as well as of T. Bolton and F. Tomlinson, Original Members of the Institute and former Members of Council.

ADDRESS TO THE KING.

A loyal Address of Congratulation was sent to His Majesty King George VI on the occasion of his Coronation. In a reply to the Address, the Home Secretary wrote: "I have been commanded by the King to convey to you Their Majesties' warm thanks for the assurances of loyalty and devotion to which the Address gives expression on behalf of The Institute of Metals."

CO-OPERATION WITH THE IRON AND STEEL INSTITUTE.

The scheme of co-operation between the Institute of Metals and the Iron and Steel Institute in the matter of joint membership, referred to in our last Report, has been carried into effect. Members of either Institute are eligible to join the other at a combined subscription of £5 5*s*. New members also benefit from the scheme as they can join both Institutes on payment of £7 7*s*. instead of £10 10*s*.

MEETINGS OF THE INSTITUTE.

The Annual General Meeting was held in London on March 10 and 11, 1937, the Annual Dinner taking place on March 10. On March 9 members attended a demonstration of television at the London headquarters of the General Electric Company, Ltd., and on March 11 visits were paid to works in the neighbourhood of London.

The May Lecture was delivered in London on May 5 by Professor E. N. da C. Andrade, F.R.S., on "The Flow of Metals."

The Autumn Meeting took place in Sheffield from September 6 to 9. This was the Institute's first visit to Sheffield since 1919. The Autumn Lecture was given by Dr. D. R. Pye, C.B., M.A., F.R.S., on "Metallurgy and the Aero-Engine."

A visit took place on September 23 to the Engineering and Marine Exhibition at Olympia.

A new form of General Meeting, held in Birmingham in association with the Birmingham Local Section, is referred to later in this report under the heading "Local Sections."

The Council co-operated with the Council of the Institution of Automobile Engineers and other bodies in arranging a symposium on "Research in Relation to the Motor Vehicle"; a largely attended meeting was held in London on March 2 to discuss this subject.

A joint meeting with the Manchester Metallurgical Society was held in Manchester on November 3 to discuss the paper by Mr. N. B. Vaughan, M.Sc., on "Inverse Segregation," which had been previously published by the Institute.

The Council was glad to receive a renewed invitation from the American Institute of Mining and Metallurgical Engineers and the American Iron and Steel Institute to hold the 1938 Autumn Meeting in America. The necessary arrangements are being made in co-operation with the Iron and Steel Institute, which has received a similar invitation.

PUBLICATIONS.

During 1937 the publications issued by the Institute consisted, as usual, of three bound volumes—two of the *Journal* and one of *Metallurgical Abstracts*—and twelve issues of the *Monthly Journal.*

With a view to accelerating, and extending the scope of, the Institute's publications a reorganization was introduced, as from January, 1938, which the Council hopes will tend towards greater efficiency on the "publications" side of the Institute's work. This reorganization involves the division of the staff into two sections, one responsible for general administration and the other for the production of the Institute's publications; the Council believes that it should lead to materially improved service to members.

THE INSTITUTE OF METALS MEDAL.

The Council gratefully accepted the offer by The Mond Nickel Company, Limited, of a platinum medal to be awarded annually by the Council for outstanding services to the non-ferrous metals industries, whether on the scientific or industrial side and without distinction of race or country. The first award of "The Institute of Metals Medal" is to be announced and made on the occasion of the Annual General Meeting at which this report is due for presentation.

LIBRARY.

Additions to the Library during the year numbered 108 books. Approximately 3000 books and periodicals were loaned to members, most of these being sent through the medium of the post. Many special enquiries were dealt with by the Librarian, this being a form of service that appears to be much appreciated by members and which, it is expected, will be considerably developed at an early date.

LOCAL SECTIONS.

The activities of the several Local Sections were continued, many useful papers being read and discussed before the Sections. The Council is grateful for the helpful co-operation of the members of the committees of the Local Sections.

The Council has given much consideration, jointly with the local committees, to the question of raising the status of certain of the sectional meetings to that of General Meetings of the Institute at which Institute papers of local interest would be read. The first gathering of this kind was held in Birmingham on March 23, when Dr. M. Cook re-presented his paper on "Directional Properties in Rolled Brass Strip." Plans have been made for an extension of this type of meeting.

The Council co-operated with the Committee of the London Local Section in arranging a Supper-Dance which was held in London on November 24.

COMMITTEES.

The following Committees were appointed for the year 1937–1938 :

Finance and General Purposes Committee.

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

Ex-officio :

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

Local Sections Committee.

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

Ex-officio :

The President.
Immediate Past-President.
Honorary 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.
Brownsdon, Dr. H. W. (*Chair*).
Dorey, Dr. S. F.
Genders, Dr. R.
Griffiths, W. T.
Hanson, Professor D.
Smout, A. J. G.
Stockdale, Dr. D.
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.
Gray, Kenneth (*Chair*).
Genders, Dr. R.
Jenkin, Dr. J. W.
Macnaughtan, D. J.
Morcom, E. L.
Mundey, A. H.
Seligman, Dr. Richard.
Smout, A. J. G.
Weeks, H. B.

Ex-officio :

The President.
Immediate Past-President.
Local Sections Committee's Representative.
Chairman of :
  Birmingham Local Section.
  London Local Section.
  North-East Coast Local Section.
  Scottish Local Section.
  Sheffield Local Section.
  Swansea Local Section.

Publication Committee.

Brownsdon, Dr. H. W.
Desch, Dr. C. H.
Dorey, Dr. S. F.
Genders, Dr. R.
Gough, Dr. H. J.
Griffiths, W. T.
Hanson, Professor D.
Haughton, Dr. J. L.
Murphy, A. J.
Seligman, Dr. Richard.
Smith, Dr. S. W.
Smithells, Dr. C. J. (*Chair*).
Stockdale, Dr. D.
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, etc.): 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 N/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.

GAS TEMPERATURE MEASUREMENT SYMPOSIUM (British Iron and Steel Federation): Mr. S. Robson.

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.

INTERNATIONAL CONGRESS OF INDUSTRIAL CHEMISTRY (17th), 1937: Mr. W. R. Barclay.

LUBRICATION AND LUBRICANTS, GENERAL DISCUSSION, Oct. 1937 (Institution of Mechanical Engineers): Mr. D. J. Macnaughtan.

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.

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. 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. (*Canada*), and Professor K. Tawara, D.Eng. (*Japan*).

Signed on behalf of the Council,

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

G. SHAW SCOTT, *Secretary.*

January 13, 1938.

APPENDIX.

LOCAL SECTIONS' PROGRAMMES, 1937–1938.

BIRMINGHAM LOCAL SECTION.

Chairman : W. F. BRAZENER.

Hon. Secretary : J. W. JENKIN, Ph.D., B.Sc., Messrs. Tube Investments, Ltd., Erdington, Birmingham.

1937.	PROGRAMME.
Oct. 14.	JOINT MEETING WITH THE IRON AND STEEL INSTITUTE.
Nov. 4.	A. C. STREET, Ph.D., B.Sc. "Die-Casting."
Dec. 2.	OPEN DISCUSSION. "Bright-Annealing." *

* Opened by Mr. E. C. Rollason, M.Sc., Mr. A. G. Robiette, B.Sc., and Dr. J. L. Pearson.

Dec. 14.	HAROLD WRIGHTON, D.Sc. "The Expert Use of the Microscope."
1938.	
Jan. 6.	L. W. SCHUSTER, M.A. "The Relationship between Mechanical Properties and Liability to Breakdown in Service."
Jan. 18.	R. W. BAILEY, D.Sc. "Creep of Metals at High Temperatures."
Feb. 18.	KARL SCHERZER, Dr.jur. "Water-Cooled Moulds."
Mar. 3.	J. P. REED. "Non-Destructive Testing."
Mar. 15.	C. E. DAVIES. "High-Speed Strip Rolling."
Mar. 31.	J. D. JEVONS, Ph.D., B.Sc. "Deep-Drawing Problems."
Apl. 14.	W. F. BRAZENER. Chairman's Address. ANNUAL GENERAL MEETING.

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, The General Electric Co., Ltd., Wembley, Middlesex.

1937. Programme.

Oct. 14. H. J. Gough, M.B.E., D.Sc., F.R.S. Chairman's Address.
Nov. 11. Professor R. S. Hutton, D.Sc., M.A. "The Training and Employment of Metallurgists." (Meeting held at the Royal School of Mines, South Kensington, S.W.7, at 8 p.m.)
Nov. 24. Supper-Dance. (Thames House, Millbank, 7.30 p.m.)
Dec. 9. A. J. Murphy, M.Sc. "Magnesium Casting Alloys." (Joint Meeting with the London Branch of the Institute of British Foundrymen.)

1938.

Jan. 13. Bruce Chalmers, B.Sc., Ph.D. "Precision Extensometer Measurements on Tin."
D. W. Ginns, Wh.Sc., B.A. "The Mechanical Properties of Some Metals and Alloys Broken at Ultra-High Speeds."
Feb. 10. Marie L. V. Gayler, D.Sc. "Age-Hardening."
Mar. 3. N. J. L. Megson, M.Sc. "Plastics."
Mar. 31. 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 : J. L. Herbert.

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

1937. Programme.

Oct. 6. J. L. Herbert. Presidential Address.
Oct. 20. H. O'Neill, D.Sc., M.Met. "Metals Used in Railway Work."
Nov. 3. N. B. Vaughan, M.Sc. "Inverse Segregation." (Joint Meeting with the Institute of Metals.)
Nov. 17. A. L. Norbury, D.Sc. "Modern Views of Cast Iron."
Dec. 1. H. W. G. Hignett, B.Sc. "Non-Ferrous Welding."

1938.

Jan. 19. Joint Meeting with the Iron and Steel Institute.
Feb. 2. J. W. Cuthbertson, M.Sc. "Electrodeposition in the Engineering Industry."
Feb. 16. Papers by junior members.
Mar. 2. U. R. Evans, D.Sc., M.A. "Some Researches into the Mechanism of Corrosion."
Mar. 16. H. H. Burton. "Ingots and Ingot Defects." Visit to Manchester Dry Docks. 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 : C. E. PEARSON, M.Met. *Hon. Secretary :* O. KENNEDY, Brass Department, Vickers-Armstrongs, Ltd., Elswick, Newcastle-upon-Tyne.

1937. PROGRAMME.

Oct. 12. C. E. PEARSON, M.Met. Chairman's Address.
Nov. 9. Joint Meeting with the Society of Chemical Industry and Institute of Chemistry. Visit to I.C.I. Metals, Ltd., Coal Hydrogenation Plant, Billingham.

1938.

Jan. 29. F. W. ROWE, B.Sc. "Randrupson Process of Cement Moulding." (Joint Meeting with the Institute of British Foundrymen. Newcastle Branch.)
Feb. 8. Works Visits.
Mar. 15. O. KENNEDY. "Magnesium Alloy Castings." ANNUAL GENERAL MEETING.

The Meetings are held in the Electrical Engineering Lecture Theatre, King's College, Newcastle-upon-Tyne, at 7.30 p.m.

SCOTTISH LOCAL SECTION.

Chairman : H. BROWN. *Hon. Secretary :* H. BULL, Bull's Metal and Melloid Co., Ltd., Yoker, Glasgow, W.4.

1937. PROGRAMME.

Oct. 11. H. BROWN. Chairman's Address.
Nov. 8. Works Visit, G. & J. Weir, Ltd., Cathcart.
Dec. 14. F. HUDSON. "Modern Non-Ferrous Castings and their Engineering Interest." (Joint Meeting with the Institution of Engineers and Shipbuilders in Scotland.)

1938.

Jan. 10. J. C. CHASTON, B.Sc., A.R.S.M. "Lead—Its Industrial Uses and Mechanical Properties."
Feb. 14. G. MORTIMER. "Some Notes on Aluminium Alloys in Road Transport." (Joint Meeting with the Institution of Automobile Engineers, Scottish Centre.)
Mar. 14. G. W. AUSTIN, O.B.E., M.Sc. "What Conventional Mechanical Properties tell us about Materials." ANNUAL GENERAL MEETING.

All Meetings (except the second) 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.

1937. PROGRAMME.

Oct. 8. W. R. BARCLAY, O.B.E. "Some Recollections of the Nickel Industry."
Nov. 9. J. C. CHASTON, B.Sc., A.R.S.M. "Powder Metallurgy." (Joint Meeting with the Sheffield Metallurgical Association.)

1938.
Feb. 11. J. E. Newson, M.Met. "Large Non-Ferrous Castings."
Mar. 1. Frank Mason. "Electrodeposits: Chromium, Rhodium, Cadmium. Some Difficulties and Suggestions." (Joint Meeting with the Sheffield Metallurgical Association.)

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 : Harry Davies.

Acting Hon. Secretary : Roosevelt Griffiths, M.Sc., University College, Swansea.

Programme.

1937.
Oct. 12. Harry Davies. Chairman's Address. "The Application of Science to the Non-Ferrous Industry."
Nov. 9. Miss I. H. Hadfield. "Qualitative Analysis of Minute Inorganic Samples."
Dec. 14. D. J. Macnaughtan. "Hot-Dipped and Electrodeposited Tin Coatings."
1938.
Feb. 8. J. Fallon. "Industrial Furnaces."
Mar. 15. R. D. Burn, M.Sc. "Recent Developments in the Production of Copper." Annual General Meeting.

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

The President: It is now my duty to move the adoption of the Report of the Council. There are some things that I am sure you would like me to say with regard to it, and I select a few outstanding points only.

Firstly, it has been a great pleasure to me during the past two years to have had the opportunity to represent the Institute at meetings abroad, particularly in the United States of America and Canada, France, Germany, and Sweden; I have also had the privilege of meeting, either in London or in their own homes, Corresponding Members to the Council in a number of other foreign countries. I can assure you that, although we have a relatively small number attending our meetings in London (necessarily so, because our membership is world-wide), the interest of the members of the Institute is thoroughly well maintained in every country with which I have been in contact, and I can recall no period in the history of the Institute when its repute and the interest shown in its proceedings were at a higher level than they are to-day.

Secondly, I had hoped to be able to announce to-night the completion of the Endowment Fund, but the ways of Boards of Directors are sometimes inscrutable and some replies that I had hoped to receive have not yet arrived. The amount raised up to the present is about £19,000, and I have every hope that during the next few weeks we shall have been promised very little short of the £20,000 aimed at. I should like to emphasize that we would particularly welcome contributions, however small, from individual members. A number of members have spoken to me on the subject, but there seems to be a shyness in filling up the perhaps somewhat formidable covenant form which can be obtained from the Secretary.

I wish also to refer to the reorganization of the Staff. We have made considerable alterations in our internal organization, and I would like to pay a warm tribute to Mr. Shaw Scott, Mr. Guillan, and the members of the Staff generally for the good will and spirit of compromise that they have shown in accepting recommendations which, to some extent, were rather revolutionary. I am at the end of my period of office as President, and I feel to-night particularly grateful to the Staff of the Institute for their loyalty and hard work during the two years of my Presidency.

Finally, I must refer briefly to the American Meeting. The Iron and Steel Institute and this Institute have received very warm invitations to visit the United States of America in the autumn of this year. An exceptionally attractive programme has been drawn up, covering periods varying from three to five weeks. It is hoped very soon to circulate fairly complete details to every member of the Institute.

I have great pleasure in moving the adoption of the Report of Council.

Dr. L. B. PFEIL (Member) seconded the motion, which was put to the meeting and carried unanimously.

REPORT OF THE HONORARY TREASURER

(MR. JOHN FRY)

For the Financial Year ended June 30, 1937.

There is better news to tell the members in reference to the year which ended on June 30 last. We again lived within our income, and there was a small surplus of £49 15*s.* 10*d.*; in addition, thanks to the fine initiative and spade-work of the President in connection with the Endowment Fund, the capital strength of the Institute is in course of being considerably improved.

Annual subscriptions have again increased, on this occasion by £199. On the other hand, current requirements of the Institute necessitated additional expenditure. Printing and stationery needed an extra £55, mainly due to a new List of Members and work in connection with the Endowment Fund. Subscriptions and grants to Local Sections show an increase of £92, partly due to a donation of £50 voted to the International Association for Testing Materials. A general increase in the Institute's activities accounts for most of the increase of £43 shown under postages, etc.

The " Publications Account " item—a net figure reached after deducting expenditure from revenue—shows a reduction of £44, as compared with last year. There was actually an increase in the cost of production of publications; happily this was offset by welcome increases in sales and in advertisement revenue.

Entrance Fees amounted to £259 7*s.*, and are again carried direct to the Balance Sheet. This Fund now amounts to £2,220 7*s.* 5*d.*

The cash position shows an improvement, and the Council feels that the financial outlook is definitely stronger.

Reference is made earlier in this report and also in the previous Treasurer's Report to the efforts that are being made to strengthen the financial structure of the Institute.

These efforts have materialized during 1937 in the shape of the Endowment Fund. The sum of £10,993 13*s.* had been received by June 30, 1937, and this is represented by a separate holding of £9,500 3½% War Stock—the balance of this sum has been placed temporarily on deposit with Lloyds Bank. Further sums are promised and anticipated; the Council hopes to have even better news for members during the current year.

The Industrial Fund, too, makes its first appearance in the Balance

Sheet and shows a balance of £445 15*s*., which has been deposited in the Post Office Savings Bank. The Industrial Fund has been allowed to go into suspense—temporarily, at any rate—in order to concentrate on securing contributions for the Endowment Fund. Some promises under the Industrial Fund have already been transferred, by agreement with the donors, to the Endowment Fund.

The Silver Jubilee Fund remains unchanged at £672 5*s*.

The House Fund shows an increase of £178, a sum which was received on the liquidation of the Association for the Promotion of Co-operation between Scientific and Technical Societies and Institutions.

The new Funds which have been received in recent years, viz. the Silver Jubilee Fund, the Industrial Fund, and now the Endowment Fund, which is in process of attaining a substantial figure, will, if there is no falling away in other directions, considerably increase the income of the Institute. It is the intention of the Council that this increase of income shall mainly be used "to assist the Institute's publications"; most of it has, in fact, actually been given for this express purpose.

May I, as Treasurer, be allowed here to add a few words of advice?

During the past three years there have been very narrow credit balances—a total of £300 in 3 years. Prior to that, for four years we actually overspent our income by a total of £1,739. At the time, the Council was seriously disturbed. It would be prudent finance, before spending too large a share of our newly-acquired income, if a determined effort were made—for a short period at any rate—to improve the Income and Expenditure position, so that the danger of overspending might be further removed.

We should be guided by our experience of the last depression and seize this excellent opportunity to strengthen our finances still further. The Publication Committee realizes the position, and is willing to co-operate. The welcome increase in the sales of publications and also in advertising revenue has been very helpful lately, and it may be that it can be developed still further to enable us to bridge the gap until our income is more able to cope regularly with increased expenditure.

Mr. John Fry, Honorary Treasurer (in moving the adoption of the Report): It is my privilege to present officially the annual accounts of the Institute made up to the end of June, 1937. The Accounts and Report are in your hands and seem to require no further explanation at this stage.

Members will have noted with satisfaction the very considerable strengthening of the financial structure, in particular the capital account. We are grateful to the President for the inspiration which guided him to create the Endowment Fund, and for the able and energetic way in which he has carried it to such a really successful total.

The Institute has reason to thank our retiring President for many benefits. In consolidating our finances he has done not only the Institute, but the whole metallurgical world, a great service.

The strengthening of the capital increases our income at the same time. It has arrived at the opportune moment.

Recently, as members have learned, the amenities of the Institute have been considerably increased: improved premises, dual membership with the Iron and Steel Institute, internal staff alterations, etc. These all cost money and we shall require all we have—and *more*.

The Income and Expenditure Accounts will need careful handling in the future. The Council and Publication Committee are alive to the situation and are determined not to live on capital. We do not believe in the old adage: "A short life and a merry one."

THE INSTITUTE OF METALS

BALANCE SHEET AS AT JUNE 30, 1937.

30.6.1936. £	£	LIABILITIES.	£ s. d.	£ s. d.
		Creditors :		
	92	Sundry Creditors for accrued Expenses, *less* proportions in advance	105 3 9	
	731	Publications Accounts	879 19 10	
	871	Subscriptions paid in advance	928 19 9	
	7	Entrance Fees paid in advance	6 6 0	
1,701				1,920 9 4
		Entrance Fees Account :		
	1,770	Balance as at June 30, 1936	1,961 0 5	
	191	Amounts recoverable for the year to June 30, 1937	259 7 0	
1,961				2,220 7 5
		Endowment Fund :		
		Balance as at June 30, 1937		10,993 13 0
		Industrial Fund :		
	21	Balance as at June 30, 1936	246 15 0	
	226	Contributions during the year	199 0 0	
247				445 15 0
		Silver Jubilee Fund :		
672		Balance as at June 30, 1937		672 5 0
		Woodhouse Fund :		
13		Balance as at June 30, 1937		14 4 6
		House Fund :		
1,050		Balance as at June 30, 1937		1,228 1 2
		Excess of Assets over Liabilities :		
	1,614	Balance as at June 30, 1936	1,699 0 5	
	85	*Add* Excess of Income over Expenditure for the year to June 30, 1937	49 15 10	
1,699				1,748 16 3
£7,343				£19,243 11 8

30.6.1936. £	£	ASSETS.	£ s. d.	£ s. d.
		Office Furniture :		
200		Balance as at June 30, 1936		200 0 0
		Library Books, &c. :		
100		Balance as at June 30, 1936		100 0 0
		Sundry Debtors :		
	8	For Entrance Fees.	30 9 0	
	357	" Subscriptions	320 13 10	
	207	" Publications Accounts (Sales and Advertisements)	237 14 1	
	572		588 16 11	
	139	*Less* Reserve for Doubtful Subscriptions	44 2 0	
433				544 14 11
		Stock of Publications :		
1		At Nominal Valuation		1 0 0
		Investments :		
4,411		£4,438 16*s.* 8*d.* 3½% War Stock at cost		4,410 14 10
		Endowment Fund :		
		£9,500 3½% War Stock at cost	9,679 5 9	
—		Lloyds Bank, Ltd., Deposit Account	1,314 7 3	
				10,993 13 0
		Industrial Fund :		
—		Post Office Savings Bank		445 15 0
		Silver Jubilee Fund :		
672		£672 5*s.* 0*d.* 3½% War Stock at cost		672 5 0
		Woodhouse Fund :		
13		Balance at Lloyds Bank, Ltd.		14 4 6
		House Fund :		
	1,045	£1,000 3½% War Stock at cost	1,044 19 1	
	5	Balance at Lloyds Bank, Ltd.	183 2 1	
1,050				1,228 1 2
		Cash :		
	450	Lloyds Bank, Ltd., Current Account	615 9 1	
	5	" " Deposit "	3 18 3	
	8	Petty Cash in hand	13 15 11	
463				633 3 3
£7,343				£19,243 11 8

Approved on behalf of the Council,
W. R. BARCLAY, *President*,
R. B. DIXON, *Chairman, Finance Committee.*
G. SHAW SCOTT, *Secretary.* January 13, 1938.

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, 1937, according to the best of our information and from the explanations given to us and as shown by the Books of the Institute.

November 16, 1937.

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

THE INSTITUTE OF METALS

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED JUNE 30, 1937.

30.6.1936. £		£ s. d.	30.6.1936 £		£ s. d.
2,125	To Salaries	2,155 0 0	*6,086*	By Annual Subscriptions	6,284 15 11
1,036	" Wages and National Insurance	1,072 14 5	*179*	" Interest on War Loan	178 17 8
1,299	" Publications Account	1,255 14 5	*35*	" House Fund Rent	35 0 0
801	" Rent, Telephone, Lighting, and Insurance	808 3 4	*9*	" Sundry Donations	9 9 0
191	" Printing and Stationery	246 12 10	*2*	" Miscellaneous Receipts	11 5 2
410	" Postages, Travelling, and Sundry Expenses	453 18 0			
70	" Library Expenses	61 5 9			
128	" Subscriptions and Grants to Local Sections	220 7 0			
115	" Expenses of Meetings	110 9 2			
18	" Repairs and Renewals	43 14 0			
30	" Audit Fee and Legal Charges	41 1 8			
3	" Bank Charges, *less* Interest	11 4			
85	" Excess Income over Expenditure for the year	49 15 10			
£6,311		£6,519 7 9	*£6,311*		£6,519 7 9

PUBLICATIONS ACCOUNT FOR THE YEAR ENDED JUNE 30, 1937.

£	£		£ s. d.	£ s. d.
1		To Stock of Publications at June 30, 1936		1 0 0
	3,308	" Cost of Production and Abstractors' Fees, Payments made during the year	3,419 17 11	
	698	Amounts owing at June 30, 1937	843 14 4	
	4,006		4,263 12 3	
	773	*Less* Amounts owing at June 30, 1936	697 15 2	
3,233				3,565 17 1
£3,234				£3,566 17 1

£	*Advts.* £	*Sales.* £		*Sales.* £ s. d.	*Advertisements.* £ s. d.	£ s. d.
			By Net Sales of Publications and Advts.:			
	810	*1,190*	Receipts during the year	1,460 5 1	819 0 9	
	195	*11*	Amounts owing June 30, 1937.	17 2 5	220 11 8	
	1,005	*1,201*		1,477 7 6	1,039 12 5	
	198	*74*	*Less* Amounts owing June 30, 1936	11 11 11	195 5 4	
	807	*1,127*		1,465 15 7	844 7 1	
1,934						2,310 2 8
1			" Stock of Publications June 30, 1937.			1 0 0
1,299			" Net Cost of Publications for year			1,255 14 5
£3,234						£3,566 17 1

THE INSTITUTE OF METALS

HOUSE FUND ACCOUNT FOR THE YEAR ENDED JUNE 30, 1937.

30.6.1936. £		£	s.	d.	30.6.1936. £		£	s.	d.
35	To Rent paid to the Institute of Metals	35	0	0	*1,050*	By Balance at June 30, 1936	1,049	19	8
1,050	,, Balance at June 30, 1937	1,228	1	2	—	,, Amount received from the liquidation of A.S.T.I.	177	8	3
					35	,, Interest on War Loan	35	0	0
					—	,, Bank Interest		13	3
£1,085		£1,263	1	2	*£1,085*		£1,263	1	2

THE WOODHOUSE BENEVOLENT FUND FOR THE YEAR ENDED JUNE 30, 1937.

30.6.1936. £		£	s.	d.	30.6.1936. £		£	s.	d.
—	To Donations to Members Subscription	4	4	0	*13*	By Balance at June 30, 1936	13	8	6
13	,, Balance at June 30, 1937	14	4	6	—	,, Donation received	5	0	0
£13		£18	8	6	*£13*		£18	8	6

ENDOWMENT FUND FOR THE YEAR ENDED JUNE 30, 1937.

30.6.1936. £		£	s.	d.	30.6.1936. £		£	s.	d.
	To Proportion of War Loan Interest, to date of Purchase written off Investment Account	98	15	0	—	By Subscription and Donations received	10,926	3	0
—	,, Balance at June 30, 1937	10,993	13	0	—	,, War Loan Interest	166	5	0
		£11,092	8	0			£11,092	8	0

SILVER JUBILEE FUND FOR THE YEAR ENDED JUNE 30, 1937.

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

Professor R. S. Hutton, D.Sc., M.A. (Fellow), seconded the motion for the adoption of the Report, which was put to the meeting and carried unanimously.

ELECTION OF OFFICERS FOR 1938–1939.

The Secretary read the list of officers elected to five vacancies on the Council for the year 1938–1939:

President.

Cecil H. Desch, D.Sc., Ph.D., F.R.S.

Vice-President.

Professor J. H. Andrew, D.Sc.

Members of Council.

J. W. Donaldson, D.Sc.
Engineer Vice-Admiral Sir George Preece, K.C.B.
H. S. Tasker, B.A.

ELECTION OF MEMBERS, STUDENT MEMBERS, AND ASSOCIATE MEMBERS.

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

MEMBERS ELECTED ON OCTOBER 29, 1937.

Adamoli, Comm. Carlo	Milan, Italy.
Ashworth, Wilfred, B.Sc.	Avonmouth.
Brivonesi, Comm. Bruno	London.
Clewlow, Walter George	Birmingham.
Cook, Leslie	Scunthorpe.
Decoux, Arthur	Marchienne-au-Pont, Belgium.
Dewsnap, George Garside	Birtley, Co. Durham.
Dyson, George Malcolm, B.A., B.Sc., Ph.D.	Loughborough.
Harris, Harry Edwin	Oldham.
Herzig, Alvin John, M.S.E.	Detroit, Mich., U.S.A.
Humfrey, John Charles Willis, O.B.E., B.A., M.Sc., M.Eng.	London.
Mann, Helmut, Dr.-Ing.	Düren/Rhld., Germany.
Ortlepp, Julius Adolph Leopold, M.Sc.	Pretoria, South Africa.
Owston, Joseph Edward	Darlington.
Pietsch, Erich, Dr.-phil.	Berlin, Germany.
Ratcliffe, John Alfred	Bushey.
Sheppard, Herbert	Birmingham.
Sussmann, Carl	London.
Tritton, Julian Seymour	London.
Vigers, Colonel Thomas Whitehair, O.B.E., M.C., T.D.	London.
Walker, Cyril Jackson	Brooklands, Cheshire.
Walker, John, B.Sc., A.R.S.M.	New Malden.

STUDENT MEMBERS ELECTED ON OCTOBER 29, 1937.

Hodapp, Walter Leonard, B.S.	Maplewood, N.J., U.S.A.
Jakeman, Kenneth Stephen Christopher, B.Sc.	Banbury.
Smith, William Anderson, B.Sc.	Kettering.
Vorrath, Carl Cortissos.	Melbourne, Australia.

ASSOCIATE MEMBER ELECTED ON OCTOBER 29, 1937.

Thompson, David H., B.S.	Waterbury, Conn., U.S.A.

Members Elected on December 9, 1937.

Allen, Colonel Leonard Sandeman	London.
Beauchamp, Herbert Reginald	London.
Clark, Professor Karl Adolf, M.A., Ph.D.	Edmonton, Canada.
Davison, George Harley	Stocksbridge.
Gardner, Henry	Kilmarnock.
Holden, John William, B.Met.	London.
Howitt, Frederick, B.Sc., Assoc.Met.	Streetly.
Iitaka, Ichiro, D.Eng.	Tokyo, Japan.
Jakobi, David	London.
Jakobi, Leo, Dr.-phil.nat.h.c.	Edgware.
Janssen, Dr. Cornelis, Czn.	Arnhem, Holland.
Knight, John T.	Greenford.
McLeod, Alastair	London.
Mills, Gordon Cooke	Perambur, India.
Stokeld, Francis Ernest	Birmingham.
Sutaria, Dhansukhlal C., B.Sc.	Bombay, India.
Swift, George Parsons, S.M.	Cambridge, Mass., U.S.A.
Thomson, George Basil	Richmond.
Veltman, Berndt, Dr.-Ing.	Finow/Mark, Germany.

Student Members Elected on December 9, 1937.

Ball, Frank Armitage, B.Sc.	Birmingham.
Barnett, Frederick Roe, B.Sc.	Port Kembla, Australia.
Brown, Ronald Henry	Birmingham.
Clegg, Oliver Raymond	Birmingham.
Davison, Donald William, B.Sc., Ph.D.	Sheffield.
Hale, Geoffrey Howard	Wolverhampton.
Holway, William Gabe	Swansea.
Hopkins, Bernarr Eugen	Swansea.
Jones, Cyril Gwynne	Carmarthen.
Lake, Henry	London.
Lewis, Dewi Morgan	Merthyr Tydfil.
Morgan, Bernard Henry	Swansea.
Turnbull, William Shaw	Greenock.
Whitney, George Selfe, B.Sc.	Sydney, Australia.
Williams, Lewis Rhoslyn	Swansea.

Associate Member Elected on December 9, 1937.

Jarrett, Tracy Charles, D.Sc.	Southbridge, Mass., U.S.A.

Members Elected on January 13, 1938.

Ash, Joseph Tempest	London.
Barham, Ronald Jack, B.Sc.	Junin, Buenos Aires, Argentine.
Bennett, Herbert Edgar	Hampton Hill.
Bridgett, Cyril Douglas Selwyn, B.Sc.	Breadsall, Derby.
Brooke, William Joseph	Scunthorpe.
Butler, Basil Harding, M.C.	Leeds.
Clark, Professor Donald Sherman, M.S., Ph.D.	Pasadena, Cal., U.S.A.
Curtis, Algernon Lewin	Chatteris.
Duffield, Frederick Lindley	London.
Finlay, Jack	Lithgow, N.S.W., Australia.
Henderson, James	London.
Hockey, Richard Francis	Melbourne, Australia.
Hyslop, George Thomas	Birmingham.
Kugel, Ernest Emeric, Dipl.-Ing.	Dusseldorf, Germany.
Lake, Norman Cecil	Thornaby-on-Tees.
Meyer, Hans Ulrich, Dr.mont.	Schaffhausen, Switzerland.
Moss, Francis Charles	Rotherham.

Ohashi, Teruichi, B.Eng.	London.
Reavell, James Arthur	London.
Salmon, Ronald Percy	West Wickham.
Talent, Walter	Sheffield.
Tresidder, Alfred Henry	London.
Westman, Ernst Bianco	London.

Student Members Elected on January 13, 1938.

Brown, James Albert	Newcastle-upon-Tyne.
Lismer, Roy Edward, Assoc.Met.	Sheffield.
Russell, Frank William Fisher	Sheffield.
Spraggon, Walter	Newcastle-upon-Tyne.

Members Elected on February 10, 1938.

Appleby, Allen Almond, B.Sc.	London.
Biers, Howard William Richard, Sc.M.	Brussels, Belgium.
Blot, Maurice Adrien	Paris, France.
Bowen, Henry Blanc	Montreal, Canada.
Clayton, Gerald Charles	London.
Crafts, Walter, A.B., M.S.	Niagara Falls, N.Y., U.S.A.
Curran, John	Cardiff.
Danielsen, Peter John	London.
Edwards, Harold	Chester.
Foerst, Wilhelm, Dr.-phil.	Berlin, Germany.
Good, Robert Charles	Pittsburgh, Pa., U.S.A.
Graham, Alexander Barbour	Glasgow.
Houdremont, Professor Eduard, Dr.-Ing.	Essen, Germany.
Junner, Gordon Mackenzie	London.
Keating, Frederick Hamilton	Norton-on-Tees.
Libotte, Charles-René	Rodange, Luxembourg.
Marsden, Walter	New Barnet.
Mason, Professor Clyde Walter, B.A., Ph.D.	Ithaca, N.Y., U.S.A.
Medlock, Reginald Stuart, B.Sc.	Gidea Park.
Morgan, Emrys, B.Sc.	London.
Mort, Eric Roland, B.Sc.	London.
Murray, Gerald, M.Sc.	Cowley.
Paul-Cavallier, Marcel, Dr.-ès-Sci.	Nancy, France.
Peake, Theodore James, B.Sc.	Farnborough.
Reavell, Brian Nobel, B.Sc.	Bromley.
Richards, Edwin John	Birmingham.
Roberts, Joseph George	Barrhead, nr. Glasgow.
Spannagel, H.	The Hague, Holland.
Stuart, James Horace	Edinburgh.

Student Members Elected on February 10, 1938.

Casewell, Edward William George	Birmingham.
Lee, Oscar Rene Jackson, M.Sc.	Stockport.

Re-Election of Auditors.

Dr. A. G. C. Gwyer proposed, Mr. John Cartland, M.C., M.Sc., seconded, and it was unanimously agreed, that Messrs. Poppleton and Appleby be re-elected auditors for the ensuing year.

Co-operation with the Iron and Steel Institute.

The President: Two years ago my friend and predecessor, Dr. Moore, was able to make a tentative announcement to the effect that negotiations and discussions had begun for co-operation with the Iron and Steel Institute. He was not able to give further details, but you received his announcement with great enthusiasm. It is a pleasure to me to be able to announce that, in addition to the joint membership scheme, particulars of which you have already received, we have now come to an agreement for a joint building and library. We have agreed to take No. 4, Grosvenor Gardens, until recently the American Embassy, a building particularly well suited to our requirements, and containing ample accommodation for Committee and Council meetings, and also, we hope, Local Section meetings. In this building there is accommodation for a joint library. The amalgamation of the libraries of the two Institutes will enable metallurgists, ferrous and non-ferrous, to have convenient access to a great range of literature, instead of as now, only by separate visits and by consulting different authorities. The joint library is a valuable part of the new scheme, and, in commending it to you, I feel sure that you will realize that it will place at the disposal of the members of the two Institutes, and particularly the younger members, conveniences and privileges which have great potential value for the future. An official announcement of this new scheme has been sent to all members of both Institutes.

The necessary negotiations have been conducted in the friendliest spirit, and I should like to say that those who represented this Institute on the Joint Committee appreciated the courtesy, consideration, and sincere good will shown by our friends of the Iron and Steel Institute.

INSTITUTE OF METALS MEDAL.

The PRESIDENT: A number of members of the Institute who have evinced a keen interest in its welfare have felt the need for a means whereby suitable acknowledgment could be made of outstanding service rendered to the industry we represent, on both the scientific and the industrial sides. I should like to acknowledge our indebtedness to those members, who would not, I am sure, desire any publicity, for the conception of the idea of a medal which could be presented by the Institute, at the entire discretion of its Council, to a distinguished servant of the industry. Further, we are most grateful to The Mond Nickel Company, Limited, for the generosity which inspired them to make this abstract idea concrete. That Company has often evinced its keen interest in, and enthusiasm for, scientific research, and has contributed handsomely on many occasions to public and private funds for research. We are now still further indebted to them.

I am able to announce the gift of a medal in platinum, which it is in the power of your Council to award every year, or less frequently if thought fit, for services which are regarded as outstanding, either on the scientific or technical sides.

To-night is the occasion of the first award of the Medal. The Council has unanimously chosen Sir William Bragg as its recipient. (*Applause.*) I believed that the Council's choice would be received most enthusiastically, and you have confirmed my thought.

Turning to Sir William Bragg, the PRESIDENT said:

Sir William Bragg, your brilliantly-conceived application of X-rays to the study of the structure of matter has influenced scientific research far beyond the boundaries of the particular branch of applied science represented by this Institute, and has brought to you many and well-deserved honours from universities and scientific bodies throughout the world. We feel, Sir, a very great pleasure to-night in being able to add one more to the many tributes that have already been paid to you, and in particular to have the privilege of recognizing the value of your work in investigations into the structure of metals. Through that work, in which you have received, we are happy to recall, the collaboration of your highly gifted son, Professor W. L. Bragg, you have placed at the service of scientific research workers in our field an entirely new technique, the enormous value and potentialities of which we are only just beginning to realize. We are very glad indeed, Sir, to have the opportunity now, in the form of the first award of the Institute of Metals Medal, of saying "Thank you."

I am sure that I am correctly interpreting the feelings of all the members of the Council and the very large body of members outside the range of the Council, who know you, when I say that we have also a personal pleasure in presenting this medal to you, for, in addition to your scientific services, you have for many years evinced a keen and enthusiastic interest in the welfare of our Institute. You have attended our functions, you have often given us the pleasure of hearing your wise counsels at our dinners, you have honoured us by becoming an Honorary Member, and we have also had the great pleasure of numbering you amongst our May Lecturers. Through these and many other channels we feel that we can almost call you one of ourselves. There is, therefore, a warm personal element, Sir William, in this recognition of your services to us, and, in handing you this medal, I desire to say that it carries with it the warmest personal regard and the highest esteem of the members of the Institute of Metals.

Sir William H. Bragg, O.M., K.B.E., P.R.S.: I am a proud man to-night. I feel this honour very deeply. There are indeed many special reasons why I should esteem it so highly. It is not only that it is the first award of its kind, which in itself is a great distinction, nor is it only that the medal is a very beautiful piece of work, which anyone might be proud to possess, but the chief pleasure it gives me is the thought that I, and those who have worked with me, have been able to help you and have won your regard.

I should like to say a word about the history of my work. When my son had just finished his course at Cambridge he asked me what sort of job he might take up—a very natural and proper question, of course, for a son to put to his father—and it happened that at that time I was in rather deep water. I had been advocating a certain theory as to what the nature of X-rays might be, and certain brilliant experiments in Germany had seemed to upset all my theories; I thought they had all gone astray. I appealed to my son to come and see if we could save something out of the wreck. We conferred and we made models, and before very long he sent from Cambridge to say that he thought that he had found the secret of it—that was, that the new phenomena which had been discovered in Germany by Laue were really, as Laue said, a result of a diffraction of X-rays, and that it opened up the whole possibility of examining the internal structure of matter and its crystalline formation. That launched us both off on a kind of voyage of discovery, and in the course of that voyage we have been to many lands, that is to say, to many other sciences, and have found a harbour, I think, in every one.

Since that early beginning, the inquiry has spread very widely, so that the number of workers engaged in the world is now quite considerable, and perhaps in metallurgy more than in any other field, workers have been engaged in the application of the new methods. I have taken only a very small share in that work, and, in receiving this medal from you, Sir, and thinking, as I always shall, with pride and great happiness of the fact that it has been presented to me and the way in which you have presented it, I should like, without in any way minimizing my own satisfaction, to take the medal as a present not to me only but to all the body of those X-ray and crystal workers who have now made a great subject from what was only a small beginning. I know that the subject is well launched now, and I know that in years to come the interior structure of the solid will be a subject of wide and keen investigation, and that from it will flow an immense amount of scientific discovery and, I believe, also of practical application.

In the name not only of myself but of all those who have worked to make this new subject worthy of its place amongst the other sciences, I thank you very heartily and accept this medal with the greatest pride and pleasure.

INDUCTION OF NEW PRESIDENT.

The RETIRING PRESIDENT: Anyone occupying the position which I occupy to-night must approach the last stages of the holding of his honourable and responsible office with mixed feelings, and it is impossible for me to put into adequate language all that I feel or all that I would desire to say. I should like, amongst other things, to say a great deal about the responsibilities of the office of President and something also about its many privileges, but the feeling which is uppermost in my mind just now is the personal pleasure that an outgoing President feels when he is able, as I am to-night, to induct into the Chair a successor so outstandingly fitted for the office as is Dr. Cecil Henry Desch. Dr. Desch is so well known to almost every member of the Institute of Metals, although its membership is scattered through every part of the known world, that it is unnecessary for me to attempt to give any account of his career. I would only remind you that he is an original member of the Institute, that he contributed to the proceedings of its first provincial meeting nearly thirty years ago in Birmingham, and that he has served on the Council for ten years, during the last five of which he has been a Vice-President. Throughout the whole of his membership of the Institute and of its Council, Dr. Desch has rendered conspicuous service, and has been regarded as one of our leading scientific metallurgists. His name appears in the distinguished roll of our May Lecturers, and both by original papers and by contributions to our discussions he has played no small part in bringing the Institute to its present position of high repute, both nationally and internationally.

It was a matter of great gratification to your Council, and to myself, that Dr. Desch accepted our unanimous invitation to the Presidential Chair. Some of us feel that the honour is long overdue, but we are happy that at last we shall have the pleasure of seeing Dr. Desch in the Chair of the Institute. From my own experience I can assure him that he will receive, as all Presidents have received, the sympathy and support of the Council and of all the members of the Institute.

The work which falls to the lot of the President of any technical society of the size and standing of the Institute of Metals is both responsible and onerous, but I am convinced that Dr. Desch will realize during his term of office that the work brings with it proportionate compensations, and that, being essentially a worker, he will appreciate these compensations to the full.

I am happy that it has fallen to my lot to induct Dr. Desch into the Presidential Chair, for I have had the honour of his friendship for a number of years. I have learned to esteem him not only for his outstanding attainments as a scientist, but for his qualities as a man. Dr. Desch's sympathies are by no means confined to the science of metallurgy; he possesses, in addition to scientific ability of the very highest order, those great qualities of human sympathy and sincerity which are absolutely essential to leadership in any sphere.

Mr. Barclay then vacated the Chair, which was taken, amid applause, by the new President, Dr. C. H. Desch, F.R.S.

The PRESIDENT (Dr. DESCH): After the almost overwhelming kindness of the remarks made by Mr. Barclay, it is very difficult for me to express my appreciation of the honour which has been done me. As I have to speak again officially later in the evening, I will, as my first duty as President, call on Mr. Horace Clarke to propose that the thanks of the Institute be conveyed to the Retiring President.

VOTE OF THANKS TO THE RETIRING PRESIDENT.

Mr. **HORACE W. CLARKE** (Member of Council): You will all agree that Mr. Barclay has served the Institute with distinction, and that he has also acquired great renown during the time that he has occupied the Presidential Chair. He has upheld and enhanced the high traditions of the office which were created by the many eminent men who have preceded him.

Mr. Barclay's charm of manner would qualify him to preside over almost any society. We in this Institute, however, demand something more than charm of manner; our Presidents have all been men who have made their mark in the world of science or of industry. It is difficult—indeed it is nearly impossible—to become what our American friends call a " big noise " in science while being at the same time a " big noise " in industry; Mr. Barclay however, has achieved the almost impossible by acquiring eminence and distinction in both of the branches in which we in this Institute are interested; he has developed the scientific side, but has never lost sight of the industrial aspect. I think that he has managed it very well.

I first met Mr. Barclay twenty-five years ago, when I think that he made the first stride forward towards his ultimate development. The first move, I think, was when he was selected by the Minister of Munitions to teach manufacturers how to make metal. Some of you, I know, will agree with me that for that task Mr. Barclay needed more than metallurgical knowledge to have the temerity to come to Birmingham and actually teach brass manufacturers how to make brass! He needed not only moral, but also physical courage for that task. Events have proved that he had an abundance of those great virtues. That was twenty-five years ago, and it is a little different now. It is evident that Mr. Barclay succeeded in that important task exceedingly well, because as soon as he was released by the Ministry of Munitions a very big and influential firm offered him an important position on its staff.

I must come back, however, to Mr. Barclay's work for the Institute. You have heard about the high standing of this Institute abroad. A great deal of that is due to Mr. Barclay. I have met him in many corners of the globe. I have met him when he has been coming back from Sweden or from Germany, and when I have asked him what he has been doing he has replied, " Well, I certainly had a job to do, but it so happened that my job there coincided with a meeting of some society or other." We should pay a tribute to Mr. Barclay's firm, which has so conveniently arranged his commercial visits abroad so as to coincide with scientific meetings in the countries he was visiting.

There are many landmarks which will stand out in Mr. Barclay's career. Of some of them you have heard, but I think that the greatest landmark is the inauguration of the Endowment Fund. I can assure you, now that it has all been settled, that that work was not done by writing letters from Victoria Street. I had some experience of the worries of Mr. Barclay, because he worried me personally three or four times a week for about eight weeks! It is almost entirely due to his perseverance that this Endowment Fund has been such a success, and we ought to pay him a great tribute for that.

I formally move that the best thanks of this Institute be accorded to our Retiring President, Mr. Barclay, for his services during the past two years.

Lieutenant-General Sir **RONALD CHARLES**, K.C.B., C.M.G., D.S.O. (Member of Council): In seconding this vote of thanks, I wish to associate myself with everything that Mr. Horace Clarke has said. I have served with and under Mr. Barclay on the Council of the Institute for the past three or four years, and the aspect of his character which has struck me most is that he is essentially a man of action. With all his charm of manner and his unfailing tact, he has, during his period of office as President, proved himself to be a real leader of the Council, and one who has never failed to shoulder his responsibility, and who in addition, if I may say so, has taken more than his fair share of the Council's work.

It is largely owing to his own initiative that his task has been a heavy one. Mr. Clarke referred to the inauguration of the Endowment Fund. Mr. Barclay's activities in the interests of the Institute have extended in many other directions. It was due to his vigorous prosecution of the schemes for allying ourselves with other scientific bodies that the scheme for combined membership of our Institute and the Iron and Steel Institute has been brought to fruition, and further, the scheme under which we have a mutual associate membership with the American Institute of Mining and Metallurgical Engineers was brought about almost entirely by his personal efforts. Last but not least comes the inauguration of the Institute of Metals Medal. Whilst acknowledging fully the generosity of the donors, I would remind you that the institution of an award of this description does not begin and end with the production of the token itself. Mr. Barclay has played a very important part in the inauguration of our first medal, the award of which we all hope will be regarded as a coveted honour. I have much pleasure in seconding the vote of thanks.

The **President** (Dr. **Desch**): I feel that I must say a few words about the work which Mr. Barclay has done for the Institute. He is one of the hardest workers that I know, but as President of this Institute he has worked with extraordinary energy. He has not only performed all the normal duties of a President, but has invented and carried out all kinds of new duties. It will be very difficult for other Presidents to follow him, and I know that it will be quite impossible for me to do all the things that he has done.

I am glad that mention has been made of his very frequent journeys abroad. Mr. Barclay has done splendid work in making connections with metallurgists in many different countries, and in that way has greatly extended the influence of the Institute.

The motion having been put to the meeting, the vote of thanks was carried unanimously, with prolonged applause.

Mr. W. R. **Barclay**, O.B.E.: I deeply appreciate the remarks of my old friend and colleague, Mr. Clarke. We have met in many different circumstances, and, knowing me as well as he does, praise from him is praise indeed. He said that I had worried him about the Endowment Fund in its early stages. I certainly did, but the Institute owes a great deal to the patient way in which Mr. Clarke endured that worrying, and to the very warm and generous response that he was able to inspire from his hard-headed Birmingham colleagues.

It is quite impossible for me after two years of office to give vent to even a fraction of what I feel, but I wish you to believe that although the work of the Presidency has been onerous—and, as my friend Sir Ronald Charles hinted, that has probably been my own fault as much as that of anyone else—it has brought with it so many opportunities of service and so many compensations that I have been more than rewarded for any effort which I have made on your behalf.

As I move, as Dr. Seligman once said, into the shadows of the past, and go on to that shelf adorned by distinguished men—Sir Harold Carpenter, Dr. Moore, Dr. Seligman, and others—I do so with feelings of great pleasure in having had for two years what I consider the greatest privilege that a metallurgist engaged in the non-ferrous metal industry can possibly have, namely the occupancy of the Chair of the Institute of Metals.

PRESIDENTIAL ADDRESS.

The PRESIDENT then delivered his Presidential Address. "A Chemist's View of Metallurgy" (see pp. 41–61).

Professor J. H. ANDREW, D.Sc. (Vice-President): I should like to read a telegram which has arrived from the Scottish Local Section, signed by its Chairman, Mr. Bull; it reads: "The Scottish Local Section send their heartiest congratulations to Dr. Desch on his elevation to the Presidential Chair, and to their fellow members of the Institute for their perspicacity in thus honouring the Scottish Local Section's first Chairman."

A formal vote of thanks to Dr. Desch for his Presidential Address is almost superfluous, because a sincere note of appreciation must have arisen spontaneously in the minds of all the members present when they realized at the conclusion of this Address how wonderfully they had been entertained to a delightful account of scientific realities, delivered in such a manner as almost to convey the impression that we have been listening to a scientific romance, were it not for the fact that every statement was supported by scientific, and in many cases by experimental evidence.

Trained as a chemist, and, notwithstanding his pursuit of almost every conceivable science, and indeed I think that I may say almost every form of learning, Dr. Desch has always been faithful to the profession of his youth, and in his Address he spoke of the chemist who, by accumulating through a number of years a copious supply of bricks and mortar, has assisted the physicist in designing and constructing his atomic edifices, along the lines of modern architecture, which, judging by what we see outside, is tending towards the cubic.

Dr. Desch has given us many of these intellectual treats; we always expect the very best from him, and have never yet been disappointed. His encyclopædic knowledge not only of the sciences but also of the more humanitarian studies has given him that breadth of vision and that power of expression which has made his Address to-night such a delight to listen to and a joy to remember. It is with the greatest pleasure that I propose that a very hearty vote of thanks be conveyed to our President for his Address.

Dr. D. STOCKDALE, M.A. (Member of Council): I have been wondering why the honour of seconding this vote of thanks has devolved on me; it is perhaps because I, too, am an organic chemist who has strayed from—or into—the proper path. The President to-night has touched on many of the problems of this Institute and its members, and not the least of those problems is this enormous mass of literature which we have somehow to digest. A new kind of scientist is developing to overcome this difficulty, and the first of these is our President. We all know how widely read and how hard-working Dr. Desch is, and perhaps no one but he could have given us this Address to-night. It is a far cry from Lucretius to Bragg; from the conservation of metals to the conservation of space in our *Journal*.

Now, if the precision of a statement is not proportional to the number of syllables used in its terms, it is also true that the warmth of a speech is not proportional to its length, and I have therefore very great pleasure in seconding this vote of thanks.

The motion was then put to the meeting and carried with acclamation.

The PRESIDENT: I thank you most warmly for the kind reception which you have given me, and I hope that I shall be able to justify my election to this very important post.

Wednesday, March 9.

On the resumption of the meeting, Dr. C. H. Desch, F.R.S., President, occupying the Chair, communications by the following authors were presented and discussed: W. R. D. Jones and K. J. B. Wolfe (789); J. L. Haughton and A. E. L. Tate (797); G. H. S. Price, C. J. Smithells, and S. V. Williams (798); D. Hanson and E. J. Sandford (791); M. Cook (792); L. Northcott (793); W. D. Jones (787); and R. Chadwick (790). In each case a hearty vote of thanks to the authors was proposed by the President and carried with acclamation.

Annual Dinner and Dance.

The Annual Dinner and Dance was held at the Grosvenor House Hotel, Park Lane, London, W.1, and was presided over by the President. Nearly 400 members and guests were present.

Thursday, March 10.

The President, Dr. C. H. Desch, F.R.S., occupied the Chair when the meeting was resumed in the morning.

Discussion on the Training and Employment of Metallurgists.

A discussion took place on the subject of "The Training and Employment of Metallurgists," based on a paper on this subject by Professor R. S. Hutton, D.Sc., M.A., printed in the *Monthly Journal*, 1937, 4, (12).

Votes of Thanks.

The President moved: That the best 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. The General Electric Company, Limited, for permission to visit their Lamp and Glass Works at North Wembley;
(3) The London Passenger Transport Board for permission to visit their Chiswick omnibus works.

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

Visits.

In the afternoon members and their ladies visited, by invitation, the Lamp and Glass Works of Messrs. The General Electric Company, Ltd., at North Wembley, or the Chiswick omnibus works of the London Passenger Transport Board.

GENERAL MEETING IN BIRMINGHAM.

A General Meeting of the Institute was held in the Chamber of Commerce Buildings, New Street, Birmingham, on the evening of Thursday, March 24, 1938, Dr. C. H. Desch, F.R.S., President, in the Chair.

The minutes of the Annual General Meeting held in London on March 8–10, 1938, were taken as read and signed by the Chairman.

Mr. R. Chadwick, M.A., then re-presented his paper on "The Influence of Surface Alloying on the Strength of Soft Soldered Joints," which had previously been presented at the Annual General Meeting in London on March 9, 1938.

After the discussion, a record of which appears on pp. 299–305, the President proposed, and there was carried with acclamation, a vote of thanks to the author of the paper.

ANNUAL MAY LECTURE.

At a General Meeting of the Institute held in the Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, London, S.W.1, on the evening of Wednesday, May 4, 1938, Dr. C. H. Desch, F.R.S., President, in the Chair, Professor G. I. Taylor, F.R.S., delivered the Twenty-Eighth May Lecture on "Plastic Strain in Metals" (see p. 307) before a large audience.

The Chairman proposed, Professor J. H. Andrew, Vice-President, seconded, and there was carried with acclamation, a hearty vote of thanks to Professor Taylor for his lecture.

The Minutes of the General Meeting held in Birmingham on March 24, 1938, were taken as read and signed by the Chairman.

Election of Members and Student and Associate Members.

The Secretary announced that the following members, student members, and associate member had been elected on March 31 and May 4 :

Members Elected on March 31, 1938.

Allison, Harry, B.Sc.	Sale, Cheshire.
Bennett, Ronald Orton, B.E., M.A.	Bushey.
Dance, Jack Beech, B.Met.E.	New Guinea.
Erichsen, Sven F.	Slough.
Hepburn, Jack Reginald Irons, D.Sc., Ph.D.	London.
Heuser, Paul, Dipl.-Ing.	London.
Kornfeld, Konrad, Inz.Met.	Warsaw, Poland.
Preston, Geoffrey William	London.
Pullan, Charles	Harrogate.
Smith, Arthur	West Bromwich.
Smith, David William	Barnehurst, Kent.
Smith, Samuel Spenceley, M.Met.	Birmingham.
Spanner, Jakob, Dr.phil.nat.	Neu-Isenburg, Germany.
Swiderski, Major Jan	Warsaw, Poland.
Symonds, George Henry	Enfield.
Thomas, Bernard	Wolverhampton.
Wiecke, Kurt, Dipl.-Ing.	Düren/Rhld., Germany.

Student Members Elected on March 31, 1938.

Ball, John Geoffrey	Birmingham.
Harding, John Viney	Birmingham.
Hoskins, Henry Guildford	London.
Lowe, Frederick Mervyn, B.Sc.	Crosskeys, Monmouthshire.
Poole, Lionel George	London.
Powell, Lancelot, B.Sc.	Clydach.
Ritchie, John Gowar, B.Met.E.	Melbourne, Australia.
Skelton, Leslie George Victor	London.
Taylor, Dennis Wellington	London.

Associate Member Elected on March 31, 1938.

Floe, Professor Carl Frederick	Notre Dame, Ind., U.S.A.

Members Elected on May 4, 1938.

Chase, Frederic L., B.Sc.	Dayton, O., U.S.A.
Clark, Norman Arbuthnott, B.Sc.	Birmingham.
Das, Salya Ranjan, M.Sc.	Calcutta, India.
Davis, Edwin, M.Sc.	Birmingham.
Frommer, Leopold, Dr.-Ing.	London.
Gould, A. J. Ph.D.	Cambridge.
Grant, Alexander Hugh Williamson	London.
Harrison, Edward Joseph	Mitcham.
Hutt, George Manson, B.Sc., A.R.S.M.	Farnborough.
Lilley, George Harry	Walton-on-Thames.
Morgan, Stephen William Kenneth, B.Sc., A.R.S.M.	Avonmouth.
Parrett, Flight-Lieutenant Ernest, R.A.F. (Retd.)	Shefford, Bedfordshire.
Pearson, Andrew	London.
Pope, Clive Fairbridge	Bangalore, India.
Rawson, Stanley Walter, M.A.	London.
Shuffrey, Leonard Bentley, B.Sc., A.C.G.I., D.I.C.	London.
Soens, James	Liverpool.
Stott, Louis Lathrop, Ph.B.	Reading, Pa., U.S.A.
Swan, John Carey, M.Met.	Woodford Green, Essex.
Thomas, Richard Emrys	London.
Twyman, Frank, F.R.S..	London.
Vickers, George Westlake	Sheffield.

Student Members Elected on May 4, 1938.

Atkins, Lawrence John	Stockport.
Cooper, Sidney	Beddington, Surrey.
Dilley, Donald C., B.S.	Cleveland, O., U.S.A.
French, Albert Henry Randall	Heston, Middlesex.
Holland, Edgar, B.Sc.	Manchester.
Howie, Thomas Wyllie, B.Sc., A.R.T.C.	Sheffield.
Johnson, Stanley Clarence, B.Met.E.	Melbourne, Australia.
Nicholson, Oswald Pritchard	Manchester.
Wilks, Allan Dudley	Birmingham.

A CHEMIST'S VIEW OF METALLURGY. 799

PRESIDENTIAL ADDRESS

DELIVERED BY DR. C. H. DESCH, F.R.S.

March 8, 1938.

IN thanking you for the great honour you have done me in electing me as your President, and in expressing the hope that I may be able to fulfil the responsible duties of the post, I cannot, although an original member, claim that intimate experience of the work of the Institute and of the organization of the non-ferrous industries that is possessed by both of my immediate predecessors. They have done admirable work for us, and we shall shortly be in a position to reap the benefit of their labours. I am fortunate in taking office at a time when there is every prospect, with the marked expansion of industry, of our entering upon a period of advance. It is when industry is flourishing that we have the best opportunity of strengthening our position, remembering that, in the present organization of Society, fluctuations are certain to occur, and it may be confidently said that technical societies, which serve for the collection and interchange of knowledge, can themselves play an important part in assisting to ward off fluctuations of an extreme kind. Systematic planning of industry is still in a very imperfect stage, but that it may be possible at all there must exist a mass of accurate and ordered information, technical as well as economic. Such an Institute as this, which makes possible the full and frank exchange of technical knowledge, is helping in that direction, not only by its collection of facts, but also by fostering a spirit of co-operation in the industry.

It is natural that the greater number of papers offered to us should come from research laboratories, and be written by scientific workers. For this there are several reasons. In the course of a research, it can be clearly seen when a stage is reached at which the results can be communicated to the public, and, although the rush of publications at the present day, with the exaggerated importance given to questions of priority, sometimes leads to the presentation of papers which would be better for postponement until the conclusions are more complete, the Publication Committee strives to ensure that only work deserving its place in the *Journal* is admitted. Those in charge of technical operations do not so easily realize the point at which their results become of interest, and, being less accustomed to the production of papers than their colleagues in the laboratory, hesitate to offer to the Institute matter which would, if suitably presented, arouse great interest. This is a difficulty to which attention has often been directed, and I can only repeat what has been said by several of my predecessors, that papers having a direct practical bearing will be welcomed by the Institute, and that aid will be willingly given, if needed, in putting material into a form suitable for publication. The desire for secrecy concerning technical improvements, although legitimate and comprehensible in some instances, plays, I believe, a diminishing part in governing the supply of communications, and we can congratulate ourselves that the existence of the Institute has itself done much to break down old prejudices in this respect.

There is room for a third type of paper. The work summed up in the form of an equilibrium diagram, especially if established by means of X-rays, is often understood only with difficulty by those technical metallurgists to whom the information implicit in the diagrams would have practical value. A paper describing experimental results cannot well be written in a popular form, although I should like to urge upon authors the desirability of using the simplest language consistent with accuracy. The precision of a statement is not proportional to the number of syllables used in its terms, and it is worth while, after writing a paper, to go through it again with the object of replacing complex expressions by simpler ones wherever it can be done without injury to the sense. I feel sure that many readers would be grateful for this extra labour.

Even when this has been done, however, since a published research cannot go back to the beginning, but must assume a knowledge of the subject, there remains a gap between the ideas of the research worker and the apprehension of the works manager or technician. We shall need, and increasingly so, papers in which the results of investigations, perhaps necessarily abstruse, may be made known to industrialists whose experience is on the practical side. Such papers may perhaps take the form of special monographs, directly aiming at interpretation in clear language, and their preparation will call for particular care. I make the suggestion, which is, of course, not new, for consideration during the coming year.

We are not here concerned with the economic aspects of metallurgy, but we must be aware that industry is not the affair of one country alone, but that it profoundly affects, and is affected by, international relations. From the number of overseas members of our body, this Institute has acquired a pronounced international character, and we are glad to welcome members from abroad to our meetings, and to receive from them contributions to our publications. The autumn meetings which we have held from time to time in Continental countries have been both enjoyable and instructive, and we have deeply appreciated the hospitality that we have received and the opportunities of visiting metallurgical plants and laboratories. In the coming autumn we are to go farther afield. The plan of a visit to America, in company with the Iron and Steel Institute, has been welcomed by many of our members, and there is every prospect of a most successful tour. Those of us who have previously visited the United States must have come to the conclusion that the knowledge and interest to be gained from such a visit, both by scientific workers and by those engaged in production, are so great as to justify a serious effort to make the journey. We are assured of a most hospitable reception, and we shall value the opportunity of meeting our American colleagues and friends.

The tour has been so arranged that members will have an opportunity of visiting plants of interest, either ferrous or non-ferrous, in some of the chief industrial centres, whilst those who are specially interested in the equipment for research will be able to see some of the great laboratories for which America is famous. The meetings, which will not occupy an undue proportion of the whole time, will afford facilities for discussion with our own members in that country, and with the members of American societies concerned with similar problems. For those who can spare the time, the extension to Canada will provide much of metallurgical interest, as well as an occasion for making acquaintance with an attractive part of that great Dominion.

During the past year, mainly through the untiring efforts of Mr. Barclay, the resources of the Institute have been set on a new footing by the establishment of an Endowment Fund, to provide a permanent income apart from the annual subscriptions of members. The sum aimed at, £20,000, is in sight, and we are grateful to the generosity of a number of leading firms. The Fund is not, however, closed, and I would urge on our industrial members the great advantages to be gained by a permanent provision for the future of our publications, and for those other services which the Institute is able to render. Among these we look forward to a great extension of library facilities, which become more and more valuable as technological practice advances and the need for scientific information is more strongly felt.

In the days when the metallurgical industries of this country depended mainly on native ores—on copper and tin from Cornwall, lead from Derbyshire, the Mendips, Alston Moor, and Leadhills, calamine from Somerset and Gloucester—they had a reputation for conservatism and secretiveness. That stage is past, and with the expansion of the industry has come a belief in the advantages of interchange of knowledge and a willingness to adopt improvements of technique suggested by the advance of metallurgical science. Under these conditions, the value of a flourishing Institute associated with the industry becomes more and more obvious.

The past year has seen other changes in our organization. We have made new arrangements of staff which will, we believe, result in more prompt publication and in greater effectiveness generally. This is, however, only a beginning. The joint American visit to which I have referred is a further step in the policy of co-operation with the Iron and Steel Institute which began last year with the arrangement for joint membership, an arrangement of which many members have taken advantage. You have heard to-day of a decision which must necessarily bring the two Institutes still closer together. That their headquarters will be in the same building, with a joint library and joint use of council and committee rooms, is a great step in advance, and must prove of benefit to the metallurgical world.

The scope of the two Institutes differs in one important respect. The field of the Iron and Steel Institute embraces the mining and smelting of the ore and the coking of the coal used in the process, as well as the conversion of iron into steel and ultimately into finished products. Our own Institute deals only with these later stages, the mining and smelting of non-ferrous ores being the province of yet a third body of long standing: the Institution of Mining and Metallurgy. The work of this last lies largely abroad, especially among other units of the British Commonwealth of Nations, and its members are able to compare experiences gained in many remote regions of the world. It therefore needs three distinct Institutes to cover the whole field of metallurgy, and I cannot leave this point without calling attention to the fact that Sir Harold Carpenter enjoys the unique distinction of having successively occupied the presidential chair of all three.

This does not complete the tale, for there remain several important bodies concerned with special branches of metallurgy, notably the Institute of British Foundrymen and the Electroplaters' and Depositors' Society, the latter, by its affiliation to the Faraday Society, indicating its special relation to the study of physical chemistry. The British Non-Ferrous Metals Research Association and the British Cast-Iron

Research Association, again, although organized on a different basis, are also closely associated with the progress of metallurgical science. Each of these bodies has its distinct function, and, as a considerable degree of interlinking occurs through common membership, they are able to co-operate in many ways, with mutual advantage.

In the course of 23 years of teaching both ferrous and non-ferrous metallurgy, and of later experience in a great research laboratory, I have had occasion to survey the subject of metallurgy as a whole, and I have mentioned these facts of organization in order to show the practical difficulties in the way of so treating it on a large scale. The separation between the ferrous and non-ferrous industries and between the industry of smelting and refining on the one hand, and of alloying, casting, working, and finishing on the other, presents a real obstacle to unification, except on the educational side. There is, however, one department of metallurgy in which no such difficulty need arise. That is the study best known as metallography, which is concerned with the structure and properties of metals and alloys, making use of methods based on physics and on chemistry. The metallographer, whether dealing with ferrous or non-ferrous metals, finds himself faced by similar problems, and is forced to consider them in the same way. The structure of ingots has received most attention from research workers on steel, on account of the large scale of operations in steel making and of the known profound effects of heterogeneity on properties, but as research proceeds it is found that the problems of the mechanism of freezing are common to both branches of metallurgy. The distinction between columnar and equiaxed crystallization, the effects of differential freezing, and the factors which produce inverse segregation, interest the maker of ingots of brass or of light alloys as well as the steel maker, and investigations carried out for the one throw light on the problems of the other. The hardening of steel by quenching has seemed to the practical man, and for long also to the scientific worker, to be a process unique of its kind, since the increase in hardness so produced is far greater than in any other system, whilst softening as the result of quenching is actually the more usual effect. On the other hand, age-hardening, first observed in the light alloys of aluminium and now found to be producible in an extraordinary variety of alloys, proves to involve internal changes in the crystalline edifice which are closely analogous with those in the hardening of steel. Whether we are investigating changes of this kind or those which are brought about in metals and alloys by deformation and by annealing, we find that there is no essential difference between the alloys of iron and those of other metals, and that facts observed in the study of one group may be used to illuminate the behaviour of the other, so that the distinction between ferrous and non-ferrous metallurgy in this field becomes purely artificial.

This fact brings with it certain administrative difficulties. An investigator who is making a complete study of a binary system of alloys containing iron can send his papers to this Institute so long as the percentage of iron (whether atomic or by weight I am not sure) is less than 50, but after that point has been passed he should publish through the Iron and Steel Institute. Such minor difficulties can no doubt be adjusted; I only mention them as illustrating the essential unity of the scientific study of metals, a unity which, I feel assured, will be more widely felt with the advance of our organization. Such divergence as exists has to be borne in mind in devising any scheme for increased co-operation in publishing and in the abstracting of metallurgical literature. This task is a formidable one. The mass of such literature has grown rapidly in recent years, being notably swollen by the great output of Soviet Russia, and the problem of co-ordinating abstracts is receiving serious attention on both sides of the Atlantic. It is a problem which we shall have to face in the coming years.

Metallurgical science is based on physics and chemistry. Historically, its connection with chemistry is much the older, since in fact chemistry arose out of the empirical knowledge acquired by the craftsman in the preparation and handling of materials, notably of metals. The view that we were once taught, that chemistry developed out of alchemy, can no longer be maintained. Although it lasted many centuries, alchemy was an aberration, and not a stage in the linear historical filiation of science. The modern transmutation of elements, one of the triumphs of the science of to-day, owes nothing to alchemy either on the side of theory or on that of practice. During all the lifetime of that aberration, however, facts concerning chemical substances, including metals, were being accumulated, and by the time of Agricola's great work, published in 1556,[1] a great body of metallurgical knowledge, purged of alchemical and astrological superstition, was ready for the scientific chemists of the two following centuries. The study of the oxidation of metals played a great part in the growth of modern ideas of chemical combination, from the time of Boyle to that of Lavoisier, and Davy, Faraday and their contemporaries constantly used the reactions of metals as a means of advancing their science.

Within the last few years, we have seen a great transformation of metallographic research by the introduction of new physical methods of study. Chief among these is the determination of crystal structure by means of X-rays. The original discovery of Laue, so brilliantly applied and extended by Sir William Bragg and his son, has proved of incalculable value in metallurgical research, giving us a new insight into the internal structure of solids, assisting us greatly in the study of changes during cold-working, recrystallization, age-hardening, and other processes, and furnishing a rapid and accurate method of determining phase equilibria in systems of alloys. The physicists, having been brought into contact with metals in this way, have found that metallic structures lend themselves well to theoretical treatment, and we are indebted to Professors Bragg, Mott, Borelius and others, for an explanation of changes in certain alloys, such as those of gold and copper, which had puzzled metallurgists, and now reveal themselves as changes from a disordered to an ordered arrangement within a lattice which otherwise retains its character. These discoveries have a wide-reaching importance, and seem certain to throw light on other processes in alloys which affect profoundly their technical properties.

It is clear that metallographic research tends more and more to become an application of physics to the special case of metals. It must not be thought, however, that this constitutes the only approach. Without anticipating the discussion on the training of metallurgists which is to be opened by Professor Hutton, I would suggest that, for the research worker of the future, metallurgy should be essentially a post-graduate subject, to be studied after a thorough training in physics or in chemistry. (I regard this as distinct from the more technical courses in metallurgy which are usually given, which aim at training men for the control of works operations.) It may well be that we shall draw more largely in the future for our metallurgical research workers on those students who have distinguished themselves in physics, but not exclusively on them. Like several of my academic colleagues, I came to metallurgy by way of chemistry, even of organic chemistry, and this fact leads me to dwell this evening for a short time on the chemical approach to metallurgical problems, without seeking in the least to undervalue the precious help that is given by physics.

It is characteristic of chemistry that its astonishing growth during the nineteenth century has been made with the use of a bare minimum of hypothesis. Atomic theories are very old. From the Greeks onwards, thinkers from time to time have found an intellectual satisfaction in picturing the world around them as being made up of atoms, and of explaining natural phenomena in terms of those atoms, but knowledge was not advanced thereby, nor was it possible to base scientific predictions on such speculations. Successful prediction is the true test of the value of an hypothesis, and these conceptions remained barren. When, 134 years ago, John Dalton took up this ancient hypothesis and used it in chemistry, he gave it a form which bore no real relation to the doctrines of Democritus and Lucretius. He said that the quantitative laws of combination of elements were such as would hold *if* each element were made up of similar atoms, and certain ratios existed between their weights. On that simple foundation the whole of chemistry has been built up. And observe, it was not necessary that the atoms should have a real existence. Some chemists thought it unnecessary to assume them except as a convenient working hypothesis, but by so using them they were able to build up a great body of chemical knowledge. It soon became evident, from a study of chemical reactions, that some atoms in a molecule were more closely connected with one another than with other atoms, and the notion of structure was introduced. Even after, by the discovery by Berzelius in 1832 of isomerism (the existence of compounds with different properties, although containing the same number and the same kind of atoms), it had become necessary to arrange the atoms composing a compound into a pattern which could be varied, Crum Brown could write, in 1867 :

" While there can be no doubt that physical research points to a molecular constitution of matter, it is perfectly indifferent to a chemist whether his symbols represent atoms or units; and graphical formulæ would be as useful as they are now, were it conclusively proved that matter is continuous."

Lastly, when it became necessary to find some explanation of Pasteur's discovery of the optically different isomerides of tartaric acid, van t'Hoff and Le Bel proposed a tetrahedral arrangement around the carbon atom, and structural formulæ became three-dimensional, making possible a whole new field of prediction. In all this progress there was no new hypothesis. The arrangement of the atoms was based on the chemical reactions of the substances, the accumulated experience of organic chemists making it possible to distinguish with certainty between alternative groupings. It has been said, with much truth, that the successive steps by which an organic chemist establishes the constitution of a complex natural substance, for instance, furnishes one of the most perfect illustrations of the logic of scientific method. I would suggest to chemical hearers the study of Professor Robinson's Royal Institution lecture [2] on the red colouring matter of the pelargonium as an admirable example of this kind of logic.

Now that the progress of physics has given new grounds for believing in the existence of the chemical atom, many lines of evidence converging to the same point, the structural formulæ of the organic chemist gain new reality, and the foresight of their inventors becomes strikingly evident. Kekulé's benzene ring is found to be real, although Kekulé himself had said that "whether atoms exist or not has but little significance from a chemical point of view; its discussion belongs rather to philosophy." The complex groupings of rings in the heavier aromatic hydrocarbons find equally their justification in the results of X-ray analysis, as does the tetrahedral carbon atom of van t'Hoff. I believe that it is correct to say that in no instance has a structure established on chemical grounds been shown by X-ray investigation to be erroneous. On the other hand, the new method often provides a rapid means of deciding between possible alternatives, and thus furnishes organic chemistry with one more means, and that an efficient one, for the determination of structure. Chemical and physical methods now go hand in hand, and are rapidly transforming our knowledge of such complex groups of compounds as the proteins.

The cautious methods of the chemist, then, have fully justified themselves, and chemistry remains a model of a science built up directly on experiment, with the aid of only such a working hypothesis as was needed to link together the results of its observations. The X-ray method is, of course, not the only physical method to be adopted as an auxiliary; dipole moments, Raman spectra, and electron diffraction by vapours are all employed as aids in the determination of structure, but the old methods of structural chemistry retain all their validity, and have not had to be modified as a result of the new knowledge. The fact that the present edition of Beilstein's Handbuch contains an account of over 200,000 compounds of carbon, and only comes down to the year 1919, is sufficient evidence that the methods of the chemist are successful in predicting the existence of new compounds and in determining their constitution.

I have had occasion lately to study the writings of Henry Le Chatelier, a chemist who also ranks as one of the founders of the scientific metallurgy of to-day. I was aware that he insisted on the use of as few hypotheses as possible, but I was surprised to learn that he deliberately chose to dispense with the idea of atoms, using chemical formulæ and equations to express reacting proportions and nothing more. His work was not in the field of organic chemistry, where he would have been obliged to consider questions of structure, and would have found the conception indispensable, but even so it is surprising how great was the progress that he was able to make in the study of cements, of gas reactions, of the dynamics of chemical equilibrium, and lastly in metallurgy. This was possible because he had great experimental gifts, and true chemical insight.

sometimes a most sensitive detector of the beginnings of change. A striking example is that of an aluminium alloy containing 5 per cent. of copper, rendered homogeneous by quenching from 540° C. By using a suitable etching reagent, a kind of faint Widmanstätten pattern soon appears on ageing, parallel with the increase in hardness, even at atmospheric temperature.[4] At higher temperatures it appears in a shorter time, but even when the temperature is as high as 200° C. this difference in etching properties is apparent long before there is any change in the lattice parameter, and still longer before any new phase can be detected by X-rays. This behaviour was first noticed in the alloys of copper containing about 2·5 per cent. of beryllium, which have to be aged at a relatively high temperature. A change in the appearance on etching, producing a hazy Widmanstätten pattern, accompanies the increase in hardness, and is earlier than the change in lattice parameter.[5] Similar effects are found in the alloys of copper and silver, and in those of aluminium and magnesium.

It is not difficult to see why this should be so. If, as has several times been suggested, an early stage in age-hardening is the formation of two-dimensional sheets of foreign atoms, parallel with some set of closely-packed planes in the parent lattice, the resistance to chemical attack on such planes as have been changed must be altered, probably diminished, by the setting up of minute local electrolytic couples. The scale is far too small to represent distinct particles, hence the hazy pattern, but the directional effect is very obvious. There is, in the early stages of the process, nothing that can be called a second phase, but we are in a region of minuteness to which the phase rule does not apply.

Chemical attack can also tell us something of the process of mechanical deformation which is not so clearly shown by other methods. That the plastic deformation of a metallic crystal is not homogeneous has long been known. Slip-bands are formed, representing parallel planes of slip, usually separated from one another by some thousands of atomic distances. They appear on a polished surface as changes of level, but mostly vanish on etching. When the cold-working has been severe, and also when the metal has been subjected to alternating stresses, bands appear, more widely spaced than the early slip-bands, and showing, by their increased rate of attack by the reagent, that they represent narrow regions of highly-deformed material. Such "strain lines" are well seen in cupro-nickel, which has the advantage of giving clear etching patterns even when the degree of distortion has been very great. These bands take up very definite positions relatively to the direction of stress, and form a kind of Lüders lines on a microscopic scale. When crystallization sets in on annealing, the nuclei of the new crystals always make their appearance in these bands, and the new grains grow into the less deformed parts of the crystal.[6] Their special interest lies in the evidence they afford that the deformation of a metallic crystal is highly localized. The X-ray indications of breakdown to units of about 10^{-4} cm. probably refer to these regions,[7] and we cannot at present say what is the condition of the intervening metal. Fatigued specimens show similar localized bands of chemically altered material. For a complete account of the processes of rupture under static and under alternating stresses, then, we must supplement the remarkable evidence recently obtained by X-ray methods by that of the microscope, which depends again on chemical properties. The matter has some importance in connection with corrosion, which is known to be hastened by the contact of plastically-strained and unstrained metal. A minute microscopical study of the early stages of corrosion under such conditions might lead to useful results.

The subject of etching has scarcely received all the attention that it deserves. We choose etching reagents mainly for the contrast which they give, so that we may obtain the best photographs, and only rarely for their specific reactions. There are a few exceptions. The phases in the ternary and more complex alloys of aluminium are very difficult to distinguish by their appearance, and much empirical information has been collected on the selective effects of different reagents. Rather less has been done on the identification of the carbides in alloy steels, and here more experiments are certainly needed. The survey of ternary systems by means of X-rays, as developed by Dr. A. J. Bradley, does indeed tell us the composition of the phases present in a given alloy when in equilibrium, but we have often to examine alloys which are not in equilibrium, either in the course of industrial processes or when studying the rate of change in a solid transformation, and for such purposes more refined chemical methods would be most useful.

By varying the concentration of etching reagents or the time during which they act, their effects may be greatly altered, and in some etching processes, especially if electrolytic, an actual reversal may occur. Such effects probably depend on local polarization, but we have no quantitative knowledge of them.

It is not necessary to say much as to the importance of chemical analysis for metallurgical research. As a means of control of industrial processes it is the oldest and still the most generally applied. Analytical laboratories were introduced into metallurgical works before any use was made of the microscope or of physical measurements. (Mechanical testing is, of course, still older.) Even now, establishments which have no other scientific control may employ a works chemist, even though he be confined to the simplest of routine analyses, but analytical methods in the more highly developed industries are undergoing a profound change. With the increased use of highly-purified metals—aluminium, copper, zinc, lead, and cadmium are all obtainable in commerce with a purity of 99·99 per cent. or better—interest is being taken in the estimation of very minute amounts of foreign elements.

That interest is by no means purely academic. The removal of a few hundredths or even thousandths per cent. of impurity may have a profound effect on the properties of certain metals, aluminium, for instance, becoming self-annealing like lead at a certain stage, and there is little doubt that before long we shall see a greatly increased practical use made of the special properties, both chemical and mechanical, of metals in the highest attainable state of purity. This is one of the reasons for the growing popularity of spectrographic methods, made quantitative by such devices as the logarithmic sector and the photometer. Some of the non-metallic elements do not lend themselves even to these improved methods, and special means have to be devised for their estimation. I would instance the determination of oxygen, hydrogen, and nitrogen in iron and steel. The total oxygen can now be determined with great accuracy by fusion in a graphite crucible and analysis of the evolved gases. The principle is simple, but it has taken much research, and the co-operation of many laboratories, to arrive at a satisfactory form of apparatus. The high-frequency vacuum furnace devised at the National Physical Laboratory embodies a number of improvements on earlier forms, and is now being adopted elsewhere. This method of estimating oxygen, and incidentally hydrogen and nitrogen, has now reached the stage at which workers in different laboratories obtain results as concordant as those expected in analytical work generally. Since skill in vacuum technique is essential, it can scarcely become a routine method until more trained workers are available, but the analyses now being made, in which institutions at home and abroad are co-operating, are proving most valuable in the study of the effects of manufacturing processes on the properties of steel.

The estimation of total oxygen is chiefly of interest to the ferrous metallurgist, but the second problem, that of determining how the oxygen in a metal is distributed, in inclusions of oxides or otherwise, has a wider application. Since it is essential to isolate non-metallic inclusions without altering their composition, solvents have to be found which will dissolve the metal and nothing else, without causing secondary reactions. This problem has been solved for the simpler steels, but certain elements interfere, and the conditions for obtaining correct results are also being sought through co-operative research, at the National Physical Laboratory and elsewhere.

Two other developments in the analytical examination of metals deserve a short notice. Microchemical methods, for some time used only in biochemistry, are becoming more popular, and much ingenuity is being expended in perfecting them for more general use. It is often an advantage to be able to make a complete analysis on a few milligrams of material, as in a study of the local changes during corrosion or abrasion. In the course of an investigation of ancient copper and bronze it has been found possible, by relating the impurities in metal objects from ancient sites to the composition of ores from different geographical regions, to supplement the well-known methods of comparing the shapes of objects and the types of pottery, and so to assist in tracing out the migrations of early peoples.[8] A difficulty in the way of such work has been the natural reluctance of museum curators to allow drillings for analysis to be taken from a valuable object. Now that a complete analysis of a bronze can be made on 10 mg. of metal, the sample can be taken without any noticeable disfigurement. This is just one illustration of the usefulness of micro-chemical methods which, from their simplicity and cleanliness, are particularly attractive to a worker with skilful fingers. The micro-balance, an admirable product of the instrument-maker's art, has become a valuable auxiliary in the laboratory.

The second development in this field is that of contact printing. The sulphur print has rendered great services to the steel industry as a means of controlling the quality of ingots and forgings. It can be extended by impregnating paper with various reagents, such as those which have been developed for the method of "drop reactions," so as to identify constituents other than sulphides, and to detect the segregation of elements in non-ferrous ingots. This method offers interesting possibilities.

The study of corrosion is clearly a part of metallurgical research which is mainly chemical. Much has been done on the external conditions affecting corrosion, but less on the relation between internal structure and liability to chemical attack. An alloy may exist in conditions differing widely in their resistance to corrosion, without any change in chemical composition, merely through an alteration in the distribution of the constituents, an alteration which may be on a submicroscopic scale, or possibly even through still more subtle changes.

This is particularly true of intercrystalline corrosion, which is profoundly affected by heat-treatment, time, and stress. When, as in some of the light alloys of aluminium, quenching in cold water will give a resistant material, whilst quenching in boiling water causes it to crack between the crystal grains with remarkable ease, we are evidently dealing with processes at the grain boundaries which produce effects large in proportion to their cause. Intercrystalline corrosion is by no means confined to the alloys of aluminium, but is met with in many alloys. The mechanism of corrosion-fatigue, in which the local failure is not as a rule at the crystal boundaries, is a closely allied problem, as to which our knowledge is still imperfect.

In metallographic writings of 25 years ago or earlier, a prominent place was occupied by intermetallic compounds. That alloys often differed so greatly in properties from their components was put down to the formation of definite compounds, which were identified in various ways, by singular points on property–composition curves, by direct separation of crystals from the melt, or by analysis of residues remaining after attack by reagents. Heycock and Neville compiled a list of 37 compounds in 1909, and when in 1914 I compiled a monograph on the subject,[9] the formulæ of 263 such compounds were taken as known with more or less certainty, whilst it was considered that many more must exist in systems which had not been completely examined. They were mainly based on thermal and microscopical analysis, but other evidence was derived from breaks in the e.m.f. curves at certain atomic compositions, or even from marked changes in colour, the bright purple of Cu_2Sb and the violet of Al_2Au being conspicuous examples. These compounds puzzled chemists for two reasons. Their formulæ usually disregarded all the rules of valency to which chemists had become accustomed, and many of them had the remarkable property of taking an excess of one or both of their component metals into solid solution while retaining their homogeneous structure and their principal properties. Such formulæ as $NaHg_2$, $AlAu_2$, and $AuSn_4$ were quite inconsistent with the known valencies of the metals. It was therefore clear that they differed in constitution on the one hand from salts and on the other from organic compounds, from a consideration of which the doctrine of valency had arisen. A "metallic" linking had to be assumed, differing from both the ionic and the homopolar linkings already familiar.

The second difficulty was of another kind. The existence of a homogeneous phase extending over a range of composition, but including a simple atomic ratio, was again foreign to chemical ideas. When Berthollet, in 1832, impressed by the influence which he had discovered of the masses of the reacting substances on the course of a chemical reaction, called into question the law of constant proportions, a long controversy was started, which ended in a complete victory for the Daltonian view. The behaviour of such solid phases as the β phase of the copper–zinc system, with its indication of a compound CuZn, seemed to contradict the accepted view, and it was even proposed to distinguish these compounds of apparently variable composition as Berthollides, in contrast with the normal Daltonides.

There was, however, evidence to show that even within these Berthollide phases the simple atomic ratio had some significance. When a metal which is a good conductor of electricity takes another element into solid solution, the conductivity is rapidly lowered by even small additions. The typical intermetallic compound was found to have, in many instances, a remarkably high conductivity, which was lowered by the addition of either of its components, so that the conductivity–composition curve showed a sharp upward-directed cusp at a simple atomic ratio, such as AgMg or CuZn. Similar cusps were found in the curves illustrating the variation of other properties, such as thermo-electric power or temperature-coefficient of conductivity, with composition. This seemed to reconcile the idea of the intermetallic compound once more with the facts, but many systems behaved anomalously.

X-ray methods brought new light. It was discovered how the two kinds of atoms were distributed on the lattice, and how the greater regularity corresponding with a simple atomic ratio led to a higher conductivity, thus accounting for the cusps. The Hume-Rothery principle,[10] soon extended to other phases, attaching importance to the ratio of valency electrons to atoms in a phase, introduced a new kind of valency, strangely different from the original but yet intelligible. Incidentally, the X-ray observations made it necessary to alter some of the accepted formulæ. Cu_2Zn_3 became Cu_5Zn_8, Cu_4Sn became $Cu_{31}Sn_8$, and so on, apparently more complex, but actually fitting better into a definite scheme. It seemed doubtful, however, whether the conception of an intermetallic compound, in the sense in which a chemist would use the term, had much further value.

Next came the study of the order–disorder changes in solid solutions. Professor W. L. Bragg, in particular, has studied the relation between the rate at which atoms can change places in a given phase and the temperature of ordering.[11] In some instances, as in the β phase of the copper–zinc system, the change to the ordered state takes place so rapidly that no quenching succeeds in preserving the disordered condition. In the alloys of gold and silver no ordering can set in at a temperature at which the atoms have appreciable mobility, so that they remain permanently disordered. In such systems as copper–gold and iron–aluminium the velocities and temperatures are such that the conditions can be controlled, and the transformations studied under a great variety of conditions. Again, there are some phases which are completely ordered as they crystallize from the melt, and never become disordered. They are most often marked by a strong maximum on the freezing-point curve, and that they persist in the ordered condition even in the molten state is shown by the fact that on a conductivity–composition curve of the liquid alloys they correspond with an upward-directed cusp, such as is found in solid solutions. It seems right to speak of these phases as true intermetallic compounds. $NaHg_2$ is a typical example. That the atoms in phases of this kind are held together differently from those of most other alloys is shown by their heat of formation. When two metals are alloyed, the linking being metallic, the energy set free may be expected to be small. A high heat of formation suggests an ionic linking, as in salts. Quite recently, the heats of mixture of a number of alloys have been determined directly, the results confirming and greatly extending earlier experiments by an indirect method.[12] In many systems the heat of formation rises linearly from each end, with a single sharp peak at a definite composition. When the component metals are, for instance, sodium and bismuth, and a single sharp peak is found at the composition Na_3Bi, we can, in view of the great electrochemical difference between the components, fairly regard this as an ionic compound. Even in much more complex systems, however, such compounds as FeSi and CoSi appear as single peaks, the linear relation being scarcely disturbed by the presence of other compounds in the system. In the highly complex alloys of nickel and aluminium the peak is at NiAl, and only a slight change of slope occurs at the compositions Ni_3Al and $NiAl_2$. Here, then, we have strong evidence that some alloys have an ionic character, a conclusion which, it is fair to say, has been reached by physicists on quite independent grounds. I mention the subject here because it shows that the well-established laws of chemical combination, which seemed to have lost their meaning in the field of alloy systems, are found once more when the properties of the metallic state are more searchingly studied. I am confident that in the immediate future, while the recent great additions to our knowledge of solids are being completed, chemical considerations will be found to play an important part. The doctrines of valency and of structure, which served so unfailingly in building up the great edifice of organic chemistry, often proved less certain guides in the study of inorganic compounds other than salts, but now that it is possible, in the light of the discoveries concerning crystal structure, to understand better how metallic atoms group themselves, those doctrines reappear, and are still of service.

I have dealt, very sketchily, with a few of the chemical aspects of metallography. Evidently, this is only one of the applications of chemistry to metallurgy. Leaving aside altogether the extraction of metals from their ores, many industrial processes are essentially chemical. Electrodeposition is one such, whilst refining by means of slags or vapours, pickling, and bright-annealing are others. So, too, the whole field of corrosion, whether by the atmosphere, by liquids, or by heated gases, belongs mainly to the chemist. There is no likelihood that the connection between chemistry and metallurgy will become less, however increasingly the scientific study of metals may seem to be based on physics, or however great the development of industrial plant on the engineering side.

To turn for a few moments from the laboratory, I come now to a very difficult problem. The chemist, in the course of his studies, is inevitably impressed by the great principle of the conservation of matter. A substance can neither be created nor destroyed, a conviction which modern physical theory has done little to disturb. It is true that on the cosmic scale the annihilation of matter is believed to be proceeding at a prodigious rate, while serving as a source of radiant energy, but we do not meet such processes in our terrestrial life. Again, the transmutation of elements has been found to be practicable, and the artificial production of radio-active elements seems likely to supplement in a most valuable way the natural supplies of radium, but such processes involve a great expenditure of energy in proportion to the yield, and there seems to be no likelihood of the production of, say, copper or tin in quantities by such a method. It follows, then, that we are confined to the deposits of those metals existing in the earth's crust for the future supplies of metals and alloys. Those deposits, forming an important part of the natural resources of the world, are not inexhaustible. For some of them, perhaps, the time when they will be exhausted can be calculated only too easily. There is an obvious and understandable tendency to exploit the supplies of a particular metal to the utmost, without reference to the needs of future generations, but the chemist must necessarily look on such a policy with mistrust. All utilization of metals involves waste; the processes of corrosion and abrasion continually diminish the stock available for use, so that production has not only to meet new demands but must make good the unavoidable losses. Is not some plan of conservation needed?

Surveys of existing resources are not lacking. Geologists and prospectors, sometimes using the modern resources of geophysics, have explored the greater part of the earth's surface, and although extensive new discoveries are always possible, the advancing knowledge of the structure of the earth makes them increasingly unlikely. Estimates of the stocks remaining in the known worked or unworked deposits must be subject to very large errors, but we know that certain metals will be exhausted long before others. There is plenty for our own and a few more generations, but will posterity find itself lacking in what we regard as necessaries through our thriftlessness? It is a question which naturally presents itself to a chemist, and one which metallurgists may be asked one day to answer.

Moreover, the metallic ores are very unequally distributed over the world, and as many of them are essential to the economy of any nation having a mechanical culture, their availability is a matter of great international significance. Without entering into the field of politics, we must be aware that this problem—the distribution of natural resources—is one which the most thoughtful statesmen regard as of the utmost importance. The subject bristles with difficulties, but it is clear that efforts will have to be made to study it in all its bearings. I am not thinking of war conditions, although they bulk so largely in the public mind, but of the peaceful conduct of international commerce, which must continue and develop if the world is not to lapse into barbarism. The relative importance of the several metals varies from time to time with the progress of technology, and with the policy of states seeking to conserve their resources or to avoid the importation of metals from abroad. Note, for example, the vast increase in production of aluminium, and more recently also of magnesium, in Germany, replacing copper and its alloys and even steel in order to use so far as possible raw materials of native origin. A study of the regulations of the Four Years Plan and the explanatory articles, as published week by week in *Metallwirtschaft*, is most instructive in showing to how great an extent one metal may be substituted for another, and alloys produced for new services, when sufficient technical skill and knowledge are applied to the problem. Experts have collected much information on this and kindred subjects, and reference can only be made to a few publications.[13]

To discuss these questions, tempting as they are, would be to travel far beyond the scope of this Institute. I mention them only to illustrate the proposition that a knowledge of the production and uses of the non-ferrous metals has far-reaching public importance. Modern civilization is closely bound up with technological progress. Conscious as we may be of the deficiencies of the Machine Age, it is impossible to return to a purely agricultural state of life, and Society has to accept the inventions of the present and strive to turn them to their best uses. More and more, the community is dependent on the technologist, a fact still too little appreciated by the public, and even by its leaders. The scientific world is only slowly realizing its own function, in spite of the ample evidence of current events.

To approach such questions as these, the first requisite is accurate knowledge. To arrive at a great invention by way of a happy guess is becoming less and less likely, and it is now generally recognized that industry must progress by means of increasing research, based on the accumulated knowledge of a great body of workers of the present, and still more of past, generations. To make such knowledge as available as possible, and to encourage, by the interchange of ideas, further additions to it, is the function of this Institute and of similar organizations. I conclude, then, by urging that an Institute devoted to metallurgical science and practice has a great public function to perform, and that its continued flourishing is an object which should appeal to all concerned with the great metallurgical industries, on which the prosperity of this country so largely depends.

REFERENCES.

[1] G. Agricola, "De Re Metallica." English translation by H. C. and L. H. Hoover, **1912**.

[2] R. Robinson, *Proc. Roy. Inst.*, 1936, 29, (1).

[3] P. Jacquet, *J. Chim. Physique*, 1936, **33**, 226; *J. Electrodepositors' Tech. Soc.*, 1937, **13** (Paper No. 20).

[4] W. L. Fink and D. W. Smith, *Trans. Amer. Inst. Min. Met. Eng.*, 1936, **122**, 284.

[5] G. Masing, *Z. Elektrochem.*, 1931, **37**, 414.

[6] F. Adcock, *J. Inst. Metals*, 1922, **27**, 73.

[7] H. J. Gough and W. A. Wood, *Proc. Roy. Soc.*, 1936, [A], **154**, 510.

[8] Reports to Sumerian Committee of British Association, 1928–1936.

[9] C. H. Desch, "Intermetallic Compounds," London: **1914**.

[10] W. Hume-Rothery, "The Structure of Metals and Alloys" (*Inst. Metals Monograph*, No. 1), **1936**.

[11] W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.*, 1935, [A], **151**, 540.

[12] F. Korber, *Stahl u. Eisen*, 1936, **56**, 1401; W. Seith and O. Kubaschewski, *Z. Elektrochem.*, 1937, **43**, 743.

[13] W. Y. Elliott, *et al.*, "International Control in the Non-Ferrous Metals" (Bureau of International Research, Harvard University and Radcliffe College), **1937**.

"Technological Trends and National Policy." (National Resources Comm., N.Y.), Washington: **1937**.

Sir Thos. Holland, "The Mineral Sanction," Edinburgh: **1935**.

"International Sanctions" (Roy. Inst. Internat. Affairs), London: **1938**.

"Raw Materials in Peace and War" (Council of Foreign Relations), New York: **1937**.

THE INFLUENCE OF IRON AND MAGNESIUM ON THE AGE-HARDENING OF COPPER–ALUMINIUM ALLOYS.* 796

By D. A. PETROV,† Member.

Synopsis.

The room-temperature age-hardening of copper–aluminium alloys is practically prevented by very small additions of iron, and is completely eliminated by greater amounts of iron, *e.g.* 2 per cent. iron with 4 per cent. copper, which leads to the formation of an insoluble compound Al_7Cu_2Fe. Commercial copper–aluminium alloys, the room-temperature age-hardening capacity of which has been lost because of the presence of iron, regain the capacity when small additions of magnesium are made, *e.g.* 0·03 per cent. Discrepancies between previous investigators' results for the age-hardening of commercial copper–aluminium alloys at room temperature probably result, therefore, from the presence of magnesium as an impurity in some grades of aluminium. The origin of the effects of iron and magnesium is obscure, but it is clear to the author that the explanation must be sought in the lattice structure of the copper–aluminium solid solution.

The results of previous investigations on the age-hardening of copper–aluminium alloys at room temperature are contradictory. Thus, Wilm[1] discovered Duralumin, which age-hardens at room temperature, only when he introduced 0·5 per cent. magnesium into his earlier copper–manganese–aluminium alloy. Yet Merica, Waltenberg, and Scott,[2] who were the first to suggest an explanation of the phenomenon of ageing in Duralumin, regarded magnesium as of minor importance and thought that $CuAl_2$ is the hardening agent. The age-hardening at room temperature of copper–aluminium alloys free from magnesium was reported also by Portevin and Le Chatelier.[3] On the other hand, Rosenhain, Hanson, and Gayler,[4, 5, 6, 7] as well as Fraenkel and his collaborators[8, 9, 10] and Konno,[11] have pointed out that the explanation of the hardening at room temperature of copper–aluminium alloys is inadequate to account for that of Duralumin.

These references admittedly relate to an early period, but a similar lack of agreement is shown in more recent papers. For example, Kempf and Dean, in the discussion of a paper by Gayler and Preston,[12] expressed disagreement with the statement that copper–aluminium

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alloys of commercial purity do not harden at room temperature, and stated that these alloys harden to a lesser degree and at a slower rate than do copper–aluminium alloys of the highest purity. More recently, Koch and Nothing [13] have asserted that there is no essential difference between the age-hardening of pure copper–aluminium alloys and that of commercial alloys, either at room temperature or at higher temperatures. According to these authors, in either case the hardness of both the freshly-quenched and the age-hardened material decreases almost linearly with increase in iron content. Results obtained by Meissner,[14] Fraenkel,[15] Gayler and Preston [12, 25] lead, however, to different conclusions.

In Table I figures are given which show the wide variations between the hardness values obtained by the various workers who have studied the room-temperature age-hardening of commercial copper–aluminium alloys.

Additional data, indicating the effect of iron on the age-hardening of copper–aluminium alloys, are given in Table II. In passing, it may be noted that repeated statements are to be found in the literature [13, 14, 19] to the effect that the deleterious effect of iron on room-temperature age-hardening is compensated to a certain extent by silicon. This problem, however, has not been studied systematically, and the author holds the opinion that the beneficial effect of silicon is never very marked.

TABLE I.—*Hardness Changes of Copper–Aluminium Alloys Resulting from Age-Hardening at Room Temperature.*

Alloy No.*	Composition, Per Cent.			Brinell Hardness.		Hardness Increment, Per Cent.	Authority.
	Cu.	Fe.	Si.	As Quenched.	After Age-Hardening.		
1 (AC4O)	4·07	0·209	0·032	34·7 † (545°)	39·2 †	13·0	Kokubo and Honda [16]
2 (FY)	4·09	0·32	0·008	50·0 (500°)	55·1	10·2	Gayler and Preston [12]
3	4·00	0·32	0·29	46·8 ? (525°)	68·8	47·0	Koch and Nothing [13]
4 (N9)	4·00	0·35	0·011	46·8	66·5	40·2	do.
5	4·50	‡	‡	64·0 (500°)	63·0	—1·6	Gayler and Preston [17]
6	5·78	0·54	0·061	64·2	76·7	19·5	Kempf and Dean [12]
7	5·80	0·61	0·33	64·2	84·9	32·2	do.

* The original designations of the alloys are given in parentheses.

† Rockwell hardness, B scale.

‡ Iron and silicon contents not stated; alloy prepared from commercial aluminium.

The points on which all authorities are in complete agreement are : (*a*) that copper–aluminium alloys free from iron harden at room temperature[12–15, 19, 25], and (*b*) that commercial copper–aluminium alloys harden to a considerable extent at elevated temperatures.[2, 4, 13, 16, 17, 18, 25]

TABLE II.—*Influence of Iron on the Age-Hardening at Room Temperature of Copper–Aluminium Alloys.*

Alloy No.*	Composition, Per Cent.			Brinell Hardness.		Hardness Increment, Per Cent.	Authority.
	Cu.	Fe.	Si.	As Quenched.	After Age-Hardening.		
1 (C_4)	3·96	0·01	0·01	60·0	84·2	40·3	Gayler and Preston[12]
2 (FY)	4·09	0·32	0·008	50·0	55·1	10·2	do.
3	5·00	†	†	60·7	85·7	41·2	Fraenkel[15]
4	5·00	1·00	†	56·7	59·7	5·3	do.

* The original designations of the alloys are given in parentheses.

† Alloys prepared from high-purity aluminium (with intentional addition of iron to alloy No. 4).

INFLUENCE OF MAGNESIUM ON COMMERCIAL COPPER–ALUMINIUM ALLOYS.

In view of the varied results obtained in previous investigations of the room-temperature age-hardening of commercial copper–aluminium alloys, an investigation has been undertaken of the effect of the addition of small amounts of magnesium on the age-hardening of these alloys. A description of this work is given below.

The alloys under investigation fall into four groups according to their copper contents : 4, 3, 2, and 1 per cent. copper. The magnesium contents of each group were 0·01, 0·03, 0·05, 0·1, 0·3, &c., up to 1·5 per cent. All the alloys and hardeners were prepared from stocks of aluminium of uniform composition made by melting together several ingots of virgin aluminium in one crucible. A copper–aluminium hardener containing 50 per cent. copper was also prepared, and was used to prepare four copper–magnesium–aluminium hardeners, containing 4, 3, 2, and 1 per cent. copper, respectively, and 10 per cent. magnesium, and also two hardeners containing iron, employed in a later section of the work (see p. 69). The procedure followed in making up the first group of alloys was to prepare from the aluminium and the copper–aluminium hardener a charge containing 4 per cent. copper; after casting the first ingot, magnesium-free, the remainder of the melt was poured into a second, pre-heated crucible and weighed. Enough of the copper–magnesium–aluminium hardener (4 per cent. copper, 10 per cent. magnesium) was then added to produce an alloy with 0·01 per cent.

magnesium. After casting this alloy, crucible and contents were weighed again, and the melt converted into a 0·03 per cent. magnesium alloy by adding the hardener, and so on. In order to reduce, so far as possible, loss of alloying constituents, the times of weighing and of other operations were reduced to a minimum. The crucible was cleaned and the oxide film carefully removed before each weighing.

The remaining three groups of alloys were prepared by the same method, which resulted in an almost constant content of iron and silicon in all the alloys, and of copper in the alloys of each group, as shown by check analyses of a number of the alloys (Table III).

TABLE III.—*Compositions of the Alloys Investigated.*

Alloy No.	Composition, Per Cent.					
	As Calculated.		By Analysis.			
	Cu.	Mg.	Cu.	Mg.	Si.	Fe.
27–1	4·0	0·0	4·09	...	0·24	0·15
27–2	4·0	0·01	4·02	0·008	0·28	0·18
27–3	4·0	0·03	4·01	0·03	0·25	0·16
27–4	4·0	0·05	3·96	0·06	0·27	0·18
27–5	4·0	0·1	4·01	0·12	0·26	0·19
27–6	4·0	0·2	4·01	0·19	0·24	0·16
23–4	4·0	0·4	3·99	0·44	0·26	0·19
27–7	4·0	0·6	...	0·57	0·28	0·15
27–8	4·0	1·0	...	0·93	0·31	0·16
27–9	4·0	1·4	4·01	1·28	0·26	0·16
27–10	4·0	1·8	3·98	1·64	0·28	0·17
40–1	3·0	0·0	2·80	...	0·31	0·14
40–2	3·0	0·01	2·80	...	...	...
40–3	3·0	0·03	2·82	0·035	...	...
40–4	3·0	0·05	...	...	...	...
46–1	3·0	0·1	2·86	0·11	0·26	0·15
46–2	3·0	0·3	...	0·30	...	...
46–3	3·0	0·6	...	0·58	...	...
46–4	3·0	0·9	...	0·92	...	...
46–5	3·0	1·2	2·83	1·16	0·25	0·14
38–1	2·0	0·0	1·94	...	0·29	0·15
38–2	2·0	0·2	1·87	0·25	...	...
38–3	2·0	0·4	1·98	0·38	...	...
38–4	2·0	0·6	1·99	0·64	...	...
38–5	2·0	0·8	1·95	0·69	...	...
38–6	2·0	1·0	1·95	1·04	0·31	0·12
48–1	1·0	0·0	...	...	0·26	0·16
48–2	1·0	0·03	0·94	...	...	...
48–3	1·0	0·05	0·92	0·07	...	...
48–4	1·0	0·1	0·93	0·13	...	...
48–5	1·0	0·3	...	...	0·27	0·16
48–6	1·0	0·6	0·92	0·60	...	...
48–7	1·0	0·9	1·00	0·83	...	...
48–8	1·0	1·2	0·96	1·12	0·26	0·15
48–9	1·0	1·5	...	...	...	...

The alloys were cast in cast-iron noulds as ingots 30 mm. in diameter nd 100 mm. in height. After discarding he upper portion of each ingot, the emainder (60 mm. high) was forged to a diameter of 60 mm. and prepared for aardness tests. Specimens so produced were quenched after being heated in a salt-bath for 2 hrs. at 510° C. Hardness tests were carried out immediately after quenching and again after six days' ageing at room temperature.

Fig. 1 shows the hardness of the alloys immediately after quenching and after ageing, while Fig. 2 gives the curves of increase in hardness due to ageing (age-hardening curves). Fig. 1 shows clearly that the hardness of the quenched alloys (curves 1) increases almost linearly with increase in the magnesium content, while that of the age-hardened alloys with 4, 3, and 2 per cent. copper (curves 2) increases rapidly up to 0·03–0·04 per cent. magnesium, and then the curves rise much less steeply. In the case of the 2 per cent. copper alloys, the effect of magnesium contents below 0·2 per cent. has not been studied experimentally and the curve has been extrapolated below this point. The age-hardening capacity curves (Fig. 2) are similar in form to the hardness curves after age-hardening.

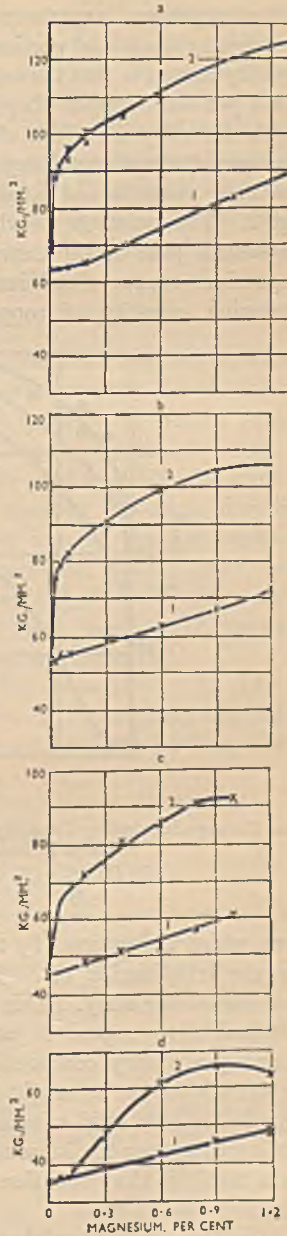

FIG. 1.—Hardness of Commercial Magnesium–Copper–Aluminium Alloys in Relation to Magnesium Content: (1) Immediately After Quenching; (2) After Age-Hardening at Room Temperature for 6 Days.

(*a*) Cu 4%; (*b*) Cu 3%; (*c*) Cu 2%; (*d*) Cu 1%.

magnesium. After casting this alloy, crucible and contents were weighed again, and the melt converted into a 0·03 per cent. magnesium alloy by adding the hardener, and so on. In order to reduce, so far as possible, loss of alloying constituents, the times of weighing and of other operations were reduced to a minimum. The crucible was cleaned and the oxide film carefully removed before each weighing.

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Alloy No.	Composition, Per Cent.					
	As Calculated.		By Analysis.			
	Cu.	Mg.	Cu.	Mg.	Si.	Fe.
27–1	4·0	0·0	4·09	...	0·24	0·15
27–2	4·0	0·01	4·02	0·008	0·28	0·18
27–3	4·0	0·03	4·01	0·03	0·25	0·16
27–4	4·0	0·05	3·96	0·06	0·27	0·18
27–5	4·0	0·1	4·01	0·12	0·26	0·19
27–6	4·0	0·2	4·01	0·19	0·24	0·16
23–4	4·0	0·4	3·99	0·44	0·26	0·19
27–7	4·0	0·6	...	0·57	0·28	0·15
27–8	4·0	1·0	...	0·93	0·31	0·16
27–9	4·0	1·4	4·01	1·28	0·26	0·16
27–10	4·0	1·8	3·98	1·64	0·28	0·17
40–1	3·0	0·0	2·80	...	0·31	0·14
40–2	3·0	0·01	2·80	...	...	...
40–3	3·0	0·03	2·82	0·035	...	...
40–4	3·0	0·05	...	...	...	...
46–1	3·0	0·1	2·86	0·11	0·26	0·15
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38–3	2·0	0·4	1·98	0·38	...	...
38–4	2·0	0·6	1·99	0·64	...	...
38–5	2·0	0·8	1·95	0·69	...	...
38–6	2·0	1·0	1·95	1·04	0·31	0·12
48–1	1·0	0·0	...	...	0·26	0·16
48–2	1·0	0·03	0·94	...	...	...
48–3	1·0	0·05	0·92	0·07	...	...
48–4	1·0	0·1	0·93	0·13	...	...
48–5	1·0	0·3	...	...	0·27	0·16
48–6	1·0	0·6	0·92	0·60	...	...
48–7	1·0	0·9	1·00	0·83	...	...
48–8	1·0	1·2	0·96	1·12	0·26	0·15
48–9	1·0	1·5	...	...	...	...

The alloys were cast in cast-iron moulds as ingots 30 mm. in diameter and 100 mm. in height. After discarding the upper portion of each ingot, the remainder (60 mm. high) was forged to a diameter of 60 mm. and prepared for hardness tests. Specimens so produced were quenched after being heated in a salt-bath for 2 hrs. at 510° C. Hardness tests were carried out immediately after quenching and again after six days' ageing at room temperature.

Fig. 1 shows the hardness of the alloys immediately after quenching and after ageing, while Fig. 2 gives the curves of increase in hardness due to ageing (age-hardening curves). Fig. 1 shows clearly that the hardness of the quenched alloys (curves 1) increases almost linearly with increase in the magnesium content, while that of the age-hardened alloys with 4, 3, and 2 per cent. copper (curves 2) increases rapidly up to 0·03–0·04 per cent. magnesium, and then the curves rise much less steeply. In the case of the 2 per cent. copper alloys, the effect of magnesium contents below 0·2 per cent. has not been studied experimentally and the curve has been extrapolated below this point. The age-hardening capacity curves (Fig. 2) are similar in form to the hardness curves after age-hardening.

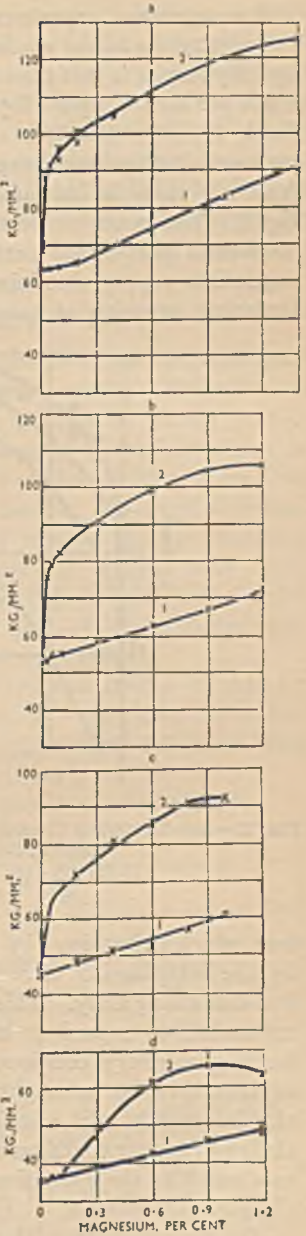

Fig. 1.—Hardness of Commercial Magnesium–Copper–Aluminium Alloys in Relation to Magnesium Content: (1) Immediately After Quenching; (2) After Age-Hardening at Room Temperature for 6 Days.

(*a*) Cu 4%; (*b*) Cu 3%; (*c*) Cu 2%; (*d*) Cu 1%.

An important experimental fact, which must be considered in interpreting the initial portions of both the hardness and age-hardening capacity curves, is that the extent of age-hardening (24·2 Brinell) found in a 4 per cent. copper alloy of high-purity by Gayler and Preston[12] (Table II, alloy No. 1) is closely similar to that (24·6 Brinell) of a commercial alloy containing 0·03 per cent. magnesium. Gayler and Preston's value is indicated by the symbol △ on the ordinate of Fig. 2. The point △ clearly lies on the backward continuation of the second part of the curve for the 4 per cent. copper commercial magnesium–copper–aluminium alloys. It is evident that the age-hardening capacity of copper–aluminium alloys at room temperature, which is destroyed by the presence of iron, is completely restored by the introduction of as little as 0·03 per cent. magnesium to the iron-containing alloy. This amount of magnesium is so small that it is impossible to regard it as directly responsible for hardening by forming a binary compound (Mg_2Si) or a ternary compound. The explanation must be sought in its effect on the lattice structure of the aluminium-rich solid solution, though Archer's suggestion[19] that the ability of copper to diffuse through the aluminium lattice is increased as a result of the expansion of the lattice produced by magnesium is obviously inadequate.

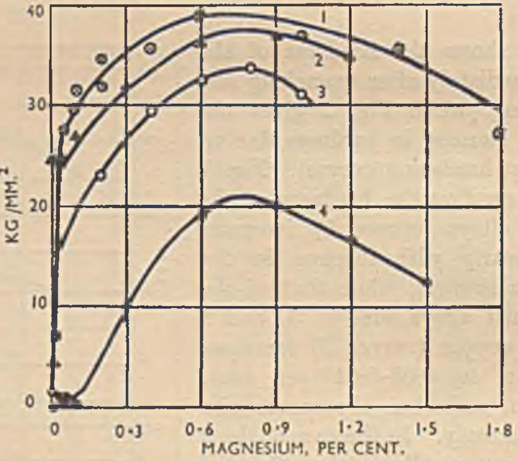

Fig. 2.—Age-Hardening Capacity of Commercial Magnesium–Copper–Aluminium Alloys in Relation to Magnesium Content.
(1) Cu 4%; (2) Cu 3%; (3) Cu 2%; (4) Cu 1%.
⊗ ▲ ○ ●

On the assumption that commercial copper–aluminium alloys to which 0·03 per cent. magnesium has been added behave as pure copper–aluminium alloys as regards age-hardening, an additional conclusion may be reached from Fig. 2, viz. that copper–aluminium alloys with 3 or 2 per cent. copper, prepared from aluminium of high purity, should harden at room temperature, but that a similar alloy with 1 per cent. copper should not exhibit room-temperature age-hardening. This is fully borne out by results obtained by Fraenkel,[15] so that an approximately quantitative estimate of the extent of age-hardening in high-purity copper–aluminium alloys may be obtained from these curves.

EFFECT OF LARGER AMOUNTS OF IRON.

It is also noteworthy that the establishment of the fact that small additions of magnesium result in almost complete elimination of the deleterious effects of iron makes it possible to obtain properties similar to those of pure binary copper–aluminium alloys in commercial copper–aluminium alloys by adding 0·03 per cent. or more magnesium. This fact has been used in the work described below on the effect of large amounts of iron on the age-hardening of copper–aluminium alloys. Two series of alloys have been prepared, one with 4 per cent. copper and 0·3, 0·6, 0·9, 1·4, and 2·0 per cent. iron, and the other with 4 per cent. copper, 0·05 per cent. magnesium, and the same amounts of iron, see Table IV.

The method of preparation of the alloys was similar to that for the magnesium–copper–aluminium alloys, a copper–iron–aluminium hardener and a magnesium–copper–iron–aluminium hardener being

TABLE IV.—*Compositions of the Iron–Copper–Aluminium Alloys Investigated.*

Alloy No.	Composition, Per Cent.						
	Calculated.			By Analysis.			
	Cu.	Mg.	Fe.	Cu.	Mg.	Fe.	Si.
44–1	4·0	...	0·3	3·96	...	0·28	0·40
44–2	4·0	...	0·6	...	...	0·55	...
44–3	4·0	...	0·9	...	...	0·84	...
44–4	4·0	...	1·4	...	...	1·32	...
44–5	4·0	...	2·0	3·90	...	1·80	0·36
45–1	4·0	0·05	0·3	3·86	0·055	0·20	0·34
45–2	4·0	0·05	0·6	...	...	0·56	...
45–3	4·0	0·05	0·9	...	...	0·89	...
45–4	4·0	0·05	1·4	...	...	1·38	...
45–5	4·0	0·05	2·0	3·92	0·05	1·94	0·35

employed. These contained 4 per cent. copper and 10 per cent. iron, with or without 0·05 per cent. magnesium. The casting and forging of the ingots were also carried out in the way described above.

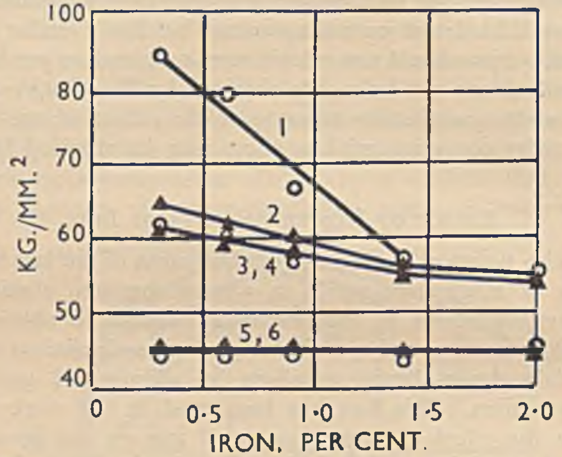

FIG. 3.—Hardness of Copper–Aluminium Alloys in Relation to Iron Content. Curves (3) (4)—Immediately after Quenching from 500° C.; curves (1) (2)—After Age-Hardening for 6 Days at Room Temperature; curves (5) (6)—After Annealing for 24 Hrs. at 350° C. (▲ = Alloys with 4% Copper; ⊙ = Alloys with 4% Copper, 0·05% Magnesium.)

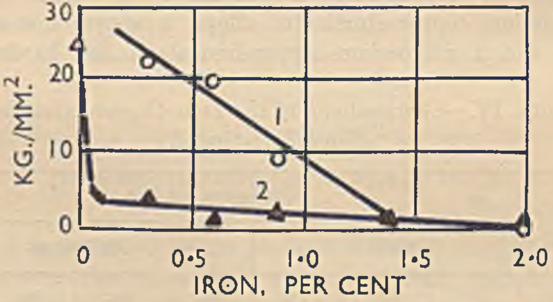

FIG. 4.—Age-Hardening Capacity of Copper–Aluminium Alloys in Relation to Iron Content. (▲ = Alloys with 4% Copper; ⊙ = Alloys with 4% Copper, 0·05% Magnesium.)

The specimens were quenched from 500° C., and hardness tests carried out immediately afterwards and again after 6 days' age-hardening at room temperature; then the specimens were annealed at 350° C. for 24 hrs., slowly cooled in the furnace to room temperature, and subjected to further hardness measurements. The results are shown in Figs. 3 and 4.

The hardness curves for alloys in the quenched condition (Fig. 3, curves 3 and 4) are coincident for the alloys with and without magnesium. The curve for age-hardened magnesium-free alloys (Fig. 3, curve 2) scarcely rises above the curve for quenched alloys, while, in agreement with previous results, the values for the alloys containing 0·05 per cent. magnesium (Fig. 3, curve 1) are much higher at small iron contents. The curve falls gradually with increase in iron content, and is coincident with that for magnesium-free alloys beyond 1·4 per cent. iron.

The age-hardening capacity for the two groups of alloys yields similar curves (see Fig. 4), that for the magnesium-free alloy being extended arbitrarily to the point △ on the ordinate which indicates, as before, the age-hardening obtained by Gayler and Preston [12] in an alloy containing 4 per cent. copper prepared from aluminium of high purity (Alloy No. 1, Table II).

The following conclusions have been reached regarding the part played by iron in the age-hardening of copper–aluminium alloys:

With small additions of iron, the age-hardening capacity at room temperature of copper–aluminium alloys decreases sharply to a very small value at a composition probably corresponding to the limit of solid solubility of iron in aluminium, which is believed to be less than 0·05 per cent. The work of Gayler [25] has shown that 0·1 per cent. iron practically prevents room-temperature age-hardening of copper–aluminium alloys. Beyond 0·05 per cent., the age-hardening capacity continues to decrease gradually with increase in iron content, and becomes practically zero at 2 per cent. iron.

Thus the age-hardening capacity of copper–aluminium alloys is almost completely lost in the presence of small amounts of iron. The present results may be compared with those of Koch and Nothing,[13] who found that the hardening capacity of pure copper–aluminium alloys is also sharply diminished by small additions of cobalt, nickel, and molybdenum. The explanation of this phenomenon must be sought in the lattice structure of the solid solution formed by copper with aluminium, as has already been suggested above in referring to the effects of magnesium.

Large amounts of iron reduce the age-hardening capacity of copper–aluminium alloys, even in the presence of magnesium, the effect being proportional to the iron content of the alloy. Increase in iron content causes the hardness of the quenched alloys to decrease, but does not alter markedly the hardness of annealed and slowly-cooled alloys (Fig. 3, curves 5 and 6). Hence, iron reduces the effect of quenching, *i.e.* the solid solution has a lower copper content, due either to a reduction in the solubility of copper in aluminium as a result of the presence of iron, or to the formation of an insoluble compound of iron, copper, and aluminium. The first explanation seems improbable, in view of the small solubility of iron itself in aluminium, but the second suggestion is confirmed by microscopical examination of the alloys.

In the microstructure of the alloy containing 4 per cent. copper and 0·3 per cent. iron annealed at 500° C. for 10 days and cooled during 7 days to room temperature, a considerable quantity of $CuAl_2$ appears, together with a lesser amount of a ternary compound of aluminium, copper, and iron. This compound is called the N-constituent by Gwyer, Phillips, and Mann [20] and denoted by the formula Al_7Cu_2Fe by Yamaguchi and Nakamura.[21] Koch and Nothing,[13] citing the last reference erroneously, give the formula Al_2Cu_2Fe. In the alloy containing 4 per cent. copper and 2 per cent. iron, heat-treated similarly to the above-mentioned alloy, the ternary constituent predominates, and no $CuAl_2$ is seen microscopically, though it seems that the presence of small amounts of it is indicated by the increase of hardness of this alloy effected by quenching. In neither of the alloys examined is $CuAl_2$ found microscopically after quenching, which is in accordance with the copper–aluminium equilibrium diagram.

Koch and Nothing [13] obtained similar microscopical evidence when investigating the effect of iron on the age-hardening of high-purity copper–aluminium alloys. Kroenig,[23] working with Duralumin alloys, also found the ternary compound referred to above, which he describes as a phase more complex than $FeAl_3$. Koch and Nothing's hardness results, which have already been mentioned in connection with Table I, are shown more completely in Fig. 5, where their age-hardening capacity curve is compared with the present results and those of other investigators. The results of Koch and Nothing are widely at variance with those of other workers on commercial copper–aluminium alloys. Their curve approaches very closely to the curve now obtained for alloys containing 0·05 per cent. magnesium, and lies considerably above the curve for magnesium-free alloys. This suggests that in Koch and Nothing's alloys magnesium was present to a small extent as an impurity, probably 0·03 per cent., and this affected the hardness results. The hardness results obtained by Kempf and Dean may perhaps be similarly explained (see Table I, Alloys Nos. 6 and 7). Traces of magnesium may be present as an impurity in certain grades of aluminium and evidently account for discrepancies in the results obtained in different investigations of the age-hardening of commercial copper–aluminium alloys. In this connection it is interesting to note, for example, that 0·03 per cent. magnesium was found by Göler and Sachs [22] together with the usual impurities—iron and silicon—in a commercial 5 per cent. copper–aluminium alloy, for which the average values of tensile strength obtained were: immediately after quenching from 525° C., 34·3 kg/mm.^{2}; after 3 days at room temperature, 39·4 kg/mm.^{2}. An alloy of approximately the same copper content, 4·5 per cent., prepared by Gayler and Preston [17] from commercial aluminium, had a tensile strength of only 31·5 kg/mm.^{2} after quenching from 500° C. and age-hardening for 7 days at room temperature.

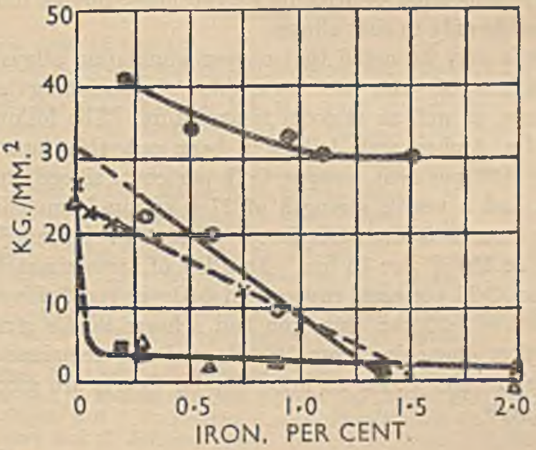

Fig. 5.—Age-Hardening Capacity of Copper–Aluminium Alloys in Relation to Iron Content:

△ Gayler and Preston's Data (Alloys 1 and 2, Table II).
■ Kokubo and Honda's Data (Alloy 1, Table I).
× Koch and Nothing's Data.
● Kroenig's Data for Duralumin Containing Copper 4·6, Magnesium 0·5, Manganese 0·6, Silicon 0·3 Per Cent.
▲○ Author's Data.

Fig. 5 also shows interesting results obtained by Kroenig [23] in his research on the influence of iron on the age-hardening of Duralumin, from which it may be seen that the hardening capacity decreases with increase in iron content, although the effect is not so marked as in the binary copper–aluminium alloys. The deleterious effect of iron in Duralumin doubtless results again from the formation of the compound Al_7Cu_2Fe, but its influence is lessened by the presence of a comparatively large amount of magnesium, viz. 0·5 per cent. Kroenig considers that for iron to have a purely mechanical action is improbable, but explains its effect in a different way from that of the present author. He believes that a ternary eutectic of aluminium, copper, and iron is formed and this reduces the proportion of copper free to enter solution in the aluminium. The formation of a ternary eutectic of this sort is, however, possible only beyond the limit of solubility of copper, and the presence of considerable quantities of eutectic in Kroenig's alloys containing 4·6 per cent. copper, when quenched from 540° C. (this is scarcely probable, since 540° C. is above the solidus temperature of these alloys—525° C. or below), could be explained only by non-attainment of equilibrium. This explanation does not seem probable for sheets 2 mm. in thickness rolled from ingots 95 mm. thick. Fuss [24] has put forward a modification of Kroenig's hypothesis, but he indicates that it is applicable only to cast alloys.

Finally it may be noted that copper–aluminium alloys containing large additions of iron are incapable of hardening at elevated temperatures, as well as at room temperature. The following results obtained by Archer and Jeffries [18] bear out this fact. An alloy containing 3·95 per cent. copper, 0·21 per cent. silicon, and 0·35 per cent. iron had a tensile strength of 27·4 kg/mm.^{2} immediately after quenching from 540° C.; this increased to 33·7 kg/mm.^{2} after age-hardening at 150° C. for 48 hrs. An alloy of approximately the same composition, 3·94 per cent. copper and 0·31 per cent. silicon, but with the addition of 1·22 per cent. iron had a lower tensile strength of 22 kg/mm.^{2} after quenching from 530° C., and this remained unchanged after ageing at 150° C. for 22 hrs. Similar figures are given by Koch and Nothing.[13]

CONCLUSIONS.

The experimental investigation described in the paper shows that the age-hardening capacity of copper–aluminium alloys at room temperature is almost completely lost in the presence of an amount of iron which is very small and which corresponds, in all probability, to the limit of solid solubility of iron in aluminium. At a certain iron content, about 2 per cent. for a 4 per cent. copper alloy, room-temperature age-hardening is completely suppressed.

In the present investigation it has been shown that when the capacity for room-temperature age-hardening of commercial copper–aluminium alloys has been lost because of the presence of iron, the hardening capacity is completely restored by addition of a very small amount of magnesium, viz. 0·03 per cent. Discrepancies between the results of various workers for the room-temperature hardening of copper–aluminium alloys may be explained by the presence of magnesium as an impurity in certain grades of aluminium. With high iron contents, the iron forms an insoluble ternary compound

Al_7Cu_2Fe, which causes the age-hardening capacity of copper–aluminium alloys at room temperature gradually to decrease even in the presence of magnesium. The deleterious effect of iron on the age-hardening of copper–aluminium alloys at higher temperatures, found by Archer and Jeffries, may also be due to the formation of Al_7Cu_2Fe.

The effects of very small amounts of iron and magnesium on the age-hardening of copper–aluminium alloys is regarded by the author as related to their influence on the lattice structure of the solid solution of copper in aluminium.

REFERENCES.

[1] *Aluminium*, 1936, **18**, 366–367.
[2] P. D. Merica, R. G. Waltenberg, and H. Scott, *Sci. Papers* (*U.S.*) *Bur. Stand.*, 1919, (**347**), 271–316.
[3] A. Portevin and F. Le Chatelier, *Rev. Mét.*, 1924, **21**, 233–246.
[4] W. Rosenhain, S. L. Archbutt, and D. Hanson, *11th Report Alloys Res. Cttee. Inst. Mech. Eng.*, 1921.
[5] D. Hanson and M. L. V. Gayler, *J. Inst. Metals*, 1921, **26**, 321–359.
[6] M. L. V. Gayler, *J. Inst. Metals*, 1922, **28**, 213–252.
[7] M. L. V. Gayler, *J. Inst. Metals*, 1923, **29**, 507–528.
[8] W. Fraenkel and R. Seng, *Z. Metallkunde*, 1920, **12**, 225–237.
[9] W. Fraenkel, *Z. Metallkunde*, 1920, **12**, 427–430.
[10] W. Fraenkel and E. Scheuer, *Z. Metallkunde*, 1922, **14**, 49–58, 111–118.
[11] S. Konno, *Sci. Rep. Tôhoku Imp. Univ.*, 1922, [i], **11**, 269–294.
[12] M. L. V. Gayler and G. D. Preston, *J. Inst. Metals*, 1932, **48**, 197–219.
[13] W. Koch and F. W. Nothing, *Aluminium*, 1935, **17**, 535–546.
[14] K. L. Meissner, *Z. Metallkunde*, 1929, **21**, 328–332.
[15] W. Fraenkel, *Z. Metallkunde*, 1930, **22**, 84–89.
[16] S. Kokubo and K. Honda, *Sci. Rep. Tôhoku Imp. Univ.*, 1930, [i], **19**, 365–409.
[17] M. L. V. Gayler and G. D. Preston, *J. Inst. Metals*, 1929, **41**, 191–247.
[18] R. S. Archer and Z. Jeffries, *Trans. Amer. Inst. Min. Met. Eng.*, 1925, **71**, 828–863.
[19] R. S. Archer, *Trans. Amer. Soc. Steel Treat.*, 1926, **10**, 718–747.
[20] A. G. C. Gwyer, H. W. L. Phillips, and L. Mann, *J. Inst. Metals*, 1928, **40**, 297–358.
[21] K. Yamaguchi and I. Nakamura, *Rikwagaku Kenkyû-jo Iho* (*Bull. Inst. Phys. Chem. Res. Tokyo*), 1932, **11**, 815–833.
[22] (Frhr.) v. Göler and G. Sachs, *Metallwirtschaft*, 1929, **8**, 671–680; also *Mitt. Material.*, *Sonderheft* **10**, 1930, 33–43.
[23] W. Kroenig, *Z. Metallkunde*, 1931, **23**, 245–249.
[24] V. Fuss, "Metallographie des Aluminiums und seiner Legierungen," Berlin: 1934, pp. 120–122, 134–135.
[25] M. L. V. Gayler, *J. Inst. Metals*, 1937, **60**, 75–99.

CORRESPONDENCE.

DR. MARIE L. V. GAYLER * (Member): The author has presented most interesting data on the effect of magnesium on the age-hardening of commercial copper–aluminium alloys. He remarks (p. 68): "The amount of magnesium is so small (*i.e.* 0·03 per cent.) that it is impossible to regard it as directly responsible for hardening by forming a binary compound (Mg_2Si) or a ternary compound."[1] Direct evidence in support of this view is to be found in the data

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published by the writer and Preston,* which are summed up in Table A, where, in spite of the extremely small amount of silicon present, a very marked effect is observed on adding 0·5 per cent. magnesium to a 4 per cent. copper alloy.

TABLE A.

Composition, Per Cent.				Brinell Hardness Number.	
Cu.	Si.	Fe.	Mg.	Immediately after Quenching from 500° C.	Aged 6 Days at Room Temperature.
4·12	0·01	0·01	—	60	80
4·12	0·01	0·01	0·46	66	107
4·09	0·008	0·32	—	49	55
4·04	0·012	0·32	0·58	59	99

Magnesium has a far greater effect than that alone of restoring the capacity of room-temperature age-hardening to commercial copper–aluminium alloys.

An examination of the data in Table A shows that: (*a*) the maximum age-hardness of an alloy containing 4 per cent. copper only, is considerably raised by the addition of 0·5 per cent. magnesium; (*b*) apart from restoring the property of age-hardening at room temperature, the addition of 0·5 per cent. magnesium to the iron-bearing 4 per cent. copper alloy also causes a very marked increase in age-hardness.

It is not possible to put forward an explanation of this phenomenon based on the data at our disposal, and it is unlikely that a true explanation will be found until a very intensive X-ray examination has been carried out—using a highly-specialized technique—on the effect of added elements on the structure of the copper–aluminium solid solution.

From the results of a recent investigation on the constitution of copper–silicon–iron–aluminium alloys,† it is clear that a complex phase containing copper, iron, and silicon is formed in the alloys under consideration. The present writer adopted the nomenclature of Dix and Heath, and the phase Al_7Cu_2Fe was designated β Fe–Si. Until the structure of such a complex phase has been determined by X-ray analysis, the actual composition is indefinite and it will probably avoid confusion in the future if such constituents are not given definite chemical formulæ unless confirmed by X-ray data.

Mr. L. W. KEMPF,‡ M.S. (Member), and Dr. W. A. DEAN ‡: The author suggests at the bottom of p. 72 that the room-temperature hardening of our alloys, the data on which were presented in a discussion of Gayler and Preston's paper,§ may be due to the presence of concentrations of magnesium of the order of 0·03 per cent. The magnesium content of the alloys referred to, as determined by spectrographic analysis, was:

Alloy No.	Magnesium, Per Cent.
7987	0·003
7988	0·003
7989	0·002
7990	0·003

While it would be rash to conclude that such concentrations of magnesium have no effect on the tendency of copper–aluminium alloys to age-harden at

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* M. L. V. Gayler and G. D. Preston, *J. Inst. Metals*, 1932, 48, 197.

† M. L. V. Gayler, *J. Inst. Metals*, 1937, 60, 75.

‡ Aluminum Research Laboratories, Aluminum Company of America, Cleveland, O., U.S.A.

§ M. L. V. Gayler and G. D. Preston, *J. Inst. Metals*, 1932, 48, 197.

room temperature, nevertheless our alloys were probably as free from magnesium as those of other investigators who have used high-purity aluminium in their experiments. At any rate, the magnesium content of our alloys was about one-tenth the minimum postulated by the author for appreciable effect.

It appears to us that there are many things regarding the age-hardening of copper–aluminium alloys much less explicable than the effect of iron. The presence of a complex constituent containing iron and copper in aluminium alloys containing both these elements may be considered as definitely established, at least for the conditions prevailing in commercial alloys and in most experimental alloys which have been used to study age-hardening effects in the copper–aluminium system. The solubility of this constituent in solid aluminium is apparently quite low. The composition of the constituent is not known, and it is quite conceivable that it varies somewhat with the conditions of casting, fabrication, and heat-treatment. It is known that the volume of this constituent increases with iron content in alloys containing upwards of perhaps 2·5 per cent. copper. Also, the precipitation hardening of copper–aluminium alloys at room temperature in the absence of iron, or at very low concentrations of iron, may be considered as definitely established. It is to be expected, and some data in the literature confirm this, that the amount and rate of hardening at room temperature increase with the concentration of copper in the supersaturated solid solution, and, therefore, that increasing concentrations of iron will decrease the tendency of an alloy of specific copper concentration to age at room temperature, by reducing the amount of copper available for the supersaturated solid solution. The minimum concentration of copper in the supersaturated solid solution for appreciable ageing at room temperature has not been determined, so far as we are aware. The data given in Table B, collected in these laboratories, indicate appreciable room-temperature age-hardening in an alloy containing 2·67 per cent. copper, together with iron 0·45, silicon 0·42, and magnesium 0·003 per cent., which was rolled to sheet 0·064 in. thick from an ingot 3¾ × 12 × 24 in. The properties were determined in the conditions indicated in the table.

TABLE B.

Heat-Treatment.	Yield Strength, Lb./in.^{2}.	Tensile Strength, Lb./in.^{2}.	Elongation, Per Cent. on 2 in.
Heated 1 hr. at 520° C., quenched in water at room temperature, and tested immediately after quenching . . .	9,700	29,350	26·8
As above, but tested after ageing for 25 days at room temperature	14,820	33,480	19·0
Quenched as above and aged for 139 hrs. at 150° C.	23,310	37,390	14·3

From the solid-solubility curve of copper in aluminium, it is to be expected that in high-purity alloys, ageing effects at room temperature should be noticeable at least down to concentrations of copper in the neighbourhood of 1 per cent. Regardless of the absolute minimum amount of copper for appreciable age-hardening at room temperatures, it is obvious that, with a specific copper content, on continuously increasing the iron concentration, sufficient copper will finally be removed from the supersaturated solid solution completely to inhibit ageing at room temperature.

Dr. Gayler, in her reply to our discussion of the paper cited, asked whether we suggested the formation of a compound other than that designated as "N" by Gwyer, Phillips and Mann,* which is formed on prolonged annealing. As indicated above, the composition of this constituent has not been determined, unless we accept, as the author appears to, that its composition has been satisfactorily established at Al_7Cu_2Fe, and that it is the same after short as after long times of annealing at the solution heat-treating temperatures. Dr. Gayler also asked why the addition of a small amount of magnesium appears to annul the effect of iron when there is little evidence of a combination of magnesium with iron. It seems to us that the effects of magnesium and iron are quite independent.

It has been demonstrated many times that magnesium greatly accelerates the hardening of supersaturated copper–aluminium solid solutions at room temperature. This accelerating effect increases within definite limits with the degree of supersaturation of the solid solution and with the concentration of magnesium. Little is known regarding the mechanism of the effect, but it appears to be generally accepted that it is the result of an influence of magnesium on the solid solution lattice. At any rate, the effect is probably present to some degree at any concentration of copper in the solid solution above the minimum at which room-temperature ageing effects can be noted in the pure binary alloy. On this basis, magnesium will accelerate the room-temperature ageing of the copper–aluminium solid solution regardless of the presence of the Al–Cu–Fe constituent, and the effect will be noticeable so long as there is a concentration of copper in supersaturated solid solution above the minimum required for room-temperature hardening.

The AUTHOR (*in reply*): I am in complete agreement with Dr. Gayler that the composition of the complex phase, containing iron and copper, which she designates β Fe–Si, is not exactly described by the formula Al_7Cu_2Fe. More work must be carried out in order to establish the precise composition of this phase as well as its extent in the equilibrium diagram. I think it admissible, however, to use this formula in as much as it shows approximately the relation of copper and iron in the phase. Its composition probably depends on the state of the alloy, and, consequently, on the conditions of casting, fabrication, and heat-treatment, as noted by Kempf and Dean, as well as on the relative proportions of the constituents of the alloy. A detailed study of this phase and its behaviour in alloys of the Duralumin type will doubtless contribute to a correct understanding of a number of hitherto unexplained phenomena, and particularly to the understanding of the nature of complex alloys of the RR 56 and RR 59 type.

It should be noted, however, that the influence of small quantities of iron and magnesium on the age-hardening capacity of copper–aluminium alloys at room temperature ought not to be explained by structural changes observed by the usual methods of physico-chemical analysis. The cause lies in the lattice structure of the solid solution, and the elucidation of this demands the application of very precise methods, and, first of all, of the X-ray method, as Dr. Gayler suggests.

Mr. Kempf and Dr. Dean conclude that the effects of magnesium and of iron on the age-hardening of commercial copper–magnesium–aluminium (and Duralumin) alloys are quite independent. This does not appear to me to be likely, since magnesium forms a ternary phase with copper and aluminium in alloys of the Duralumin type as I have shown in my other paper (pp. 88–89). Therefore, even if it be admitted that the deleterious effect of iron is manifested only in the removal of copper from the supersaturated solid solution, it must be conceded that magnesium and iron do affect each other, since both form

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* A. G. C. Gwyer, H. W. L. Phillips, and L. Mann, *J. Inst. Metals*, 1928, **40**, 297.

complex phases with copper and aluminium. (Mr. Kempf and Dr. Dean evidently do not attach any importance to my statement that iron, present in small quantity probably corresponding to its solid solubility in aluminium, effectively exerts its deleterious influence by completely suppressing the age-hardening capacity of copper–aluminium alloys at room temperature.)

In this connection the results in Table C, obtained with iron-bearing alloys, are of considerable interest.

TABLE C.

Alloy No.	Composition, Per Cent.				Brinell Hardness, Kg./mm.^{2}.		Hardness Increment.
	Cu.	Fe.	Mg.	Si.	As Quenched.	After Age-Hardening at Room Temperature.	
55–1	0·00	2·00	0·52	0·23	41·3	41·9	0·6
44–5	4·01	2·03	—	0·21	54·4	55·7	1·3
55–5	4·0	1·95	0·50	0·24	62·8	88·6	25·8
50–5	3·99	3·00	0·51	0·25	63·1	87·3	24·2

Doubtless the effect of magnesium in alloy 55–5, and in particular in alloy 50–5, cannot be ascribed to its accelerating effect, since the whole of the $CuAl_2$ should normally be contained in a ternary compound with iron, of which evidence is provided by the absence of any age-hardening effect in alloy 44–5. If an independent rôle be ascribed to magnesium, say, through the compound Mg_2Si, it is difficult to explain why alloy 55–1 shows no age-hardening whatever. The whole of the silicon in this alloy is obviously combined with iron in a compound of aluminium.

As regards the observation made by Mr. Kempf and Dr. Dean on the minimum quantity of magnesium necessary for the restoration of the age-hardening capacity of copper–aluminium alloys, a more detailed investigation is desirable in as much as the chemical analysis of such small quantities of magnesium is very difficult. The quantity of magnesium which was introduced into our alloys was converted to magnesium oxide, and was determined as such, together with metallic magnesium.

It is possible that the age-hardening capacity of copper–aluminium alloys at room temperature may also be restored by other metals besides magnesium.

ON THE PROBLEM OF THE AGE-HARDENING OF DURALUMIN.*

795

By D. A. PETROV,† Member.

Synopsis.

Hardness determinations after ageing at elevated temperatures show that silicon, either as Mg_2Si or an aluminium–magnesium–silicon–copper complex, enters into the age-hardening of copper–magnesium–silicon–aluminium alloys. This is, however, not the case with room-temperature age-hardening, in which silicon plays no part; here the hardening constituents both of high-purity copper–magnesium–aluminium alloys and of commercial Duralumin are $CuAl_2$ and the ternary compound $Al_5Cu_2Mg_2$, the presence of which has been detected microscopically in slowly-cooled alloys.

The remarkable rôle of magnesium in the age-hardening of Duralumin at room temperature was first shown by Wilm.[1, 2] Merica, Waltenberg, and Scott[3] state that copper–aluminium alloys containing a small percentage of magnesium (0·5 per cent.) undergo considerably greater hardening at room temperature than do those without magnesium. These authors concluded from their investigations, however, that the room-temperature age-hardening of Duralumin is due only to copper, and that magnesium does not play any direct part. The cause of the greater hardening of the magnesium-bearing alloys may be that magnesium combines with silicon, present in aluminium as an impurity, to form Mg_2Si, and so the action of silicon in partially suppressing the hardening power of copper is removed. It is also possible that the presence of magnesium affects the mode of precipitation of $CuAl_2$ during age-hardening.

English investigators[4–10] attribute to magnesium quite a different rôle, and consider that it is firmly established that the compound of magnesium with silicon (Mg_2Si), in addition to $CuAl_2$, plays a direct part in the age-hardening of Duralumin at room temperature. This view has also been expressed from time to time by other investigators,[11, 12, 13] and is at present that most generally accepted, in spite of a number of facts which conflict with this point of view. For instance, Archer[14] found, in 1926, that the hardening effect in copper–mag-

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TABLE I.—*Age-Hardening of Copper–Magnesium–Aluminium Alloys with and without Silicon: Changes in Tensile Strength.*

Alloy* No.	Composition, Per Cent.					Tensile Strength, Kg./mm.²			Increase in Tensile Strength as a Result of Age-Hardening, Per Cent.		Reference.
	Cu.	Mg.	Mn.	Si.	Fe.	Directly after Quenching.	After Age-Hardening at Room Temperature.	After Age-Hardening at 150° C. for 48 Hrs.	At Room Temperature.	At 150° C.	
1	3·55	0·48	....	0·02	0·03	(533°) 25·3	37·3	....	47·5	....	Archer [14]
2 (7)	4·51	0·51	....	0·04	0·04	(510°) 27·6	39·3	40·0	42·4	45·0	Schmid & Wassermann [18]
3 (16)	4·07	0·53	....	0·31	0·08	27·5	40·4	46·0	46·9	67·2	
4 (5)	4·2	0·5	....	0·01	0·02	(515°) 26·2	38·3	...	46·2	...	Meissner [30]
5 (5A)	4·2	0·5	....	0·30	0·02	26·8	38·3	...	42·9	...	
6 (1)	4·2	0·5	0·6	0·01	0·02	32·5	43·5	...	33·8	...	
7 (6)	4·2	0·5	0·6	0·30	0·02	32·9	44·8	...	36·2	...	

* The designations of the alloys in the original papers are given in parentheses.

TABLE II.—*Age-Hardening of Copper–Magnesium–Aluminium Alloys with and without Silicon: Hardness Changes.*

Alloy * No.	Composition, Per Cent.				Brinell Hardness.			Increase in Hardness as a Result of Age-Hardening, Per Cent.		Reference.
	Cu.	Mg.	Si.	Fe.	Directly after Quenching.	After Age-Hardening at Room Temperature.	After Age-Hardening at 200° C. (Maximum Values).	At Room Temperature.	At 200° C.	
1	3·55	0·48	0·02	0·03	(533°) 78	107	...	37·2	...	Archer [14]
2	4·00	0·50	0·02	0·03	(550°) 73	112	...	53·4	...	
3 (CMF)	4·04	0·58	0·012	0·32	(500°) 60·4	98·7	101·0	63·5	67·3	Gayler and Preston *, [18]
4 (H_2)	4·00	0·51	0·30	†	66·0	98·0	143·0	48·5	116·8	
5 (C_2M_1)	1·96	0·54	0·01	0·01	45·2	82·1	71·0	81·5	57·1	
6 (H_4)	2·00	0·425	0·25	†	44·0	80·0	112·0	81·9	154·8	
7	4·08	0·63	0·056	0·045	(510°) 64·6	105·3	106·6	63·0	65·0	Kempf and Dean [18]
8	4·02	0·60	0·43	0·065	67·9	106·3	140·7	65·0	107·4	
9	4·05	0·54	0·065	0·54	60·0	99·4	93·1	65·7	55·2	
10	3·95	0·60	0·43	0·59	64·0	100·3	132·4	56·7	107·0	

* The designations of the alloys in the original papers are given in parentheses.
† Iron content is not indicated; alloys were prepared from commercial aluminium.

nesium–aluminium alloys is not increased by the addition of silicon (see Tables I and II), and concluded that for the age-hardening of Duralumin the presence of Mg_2Si is not necessary. This was later confirmed by Schmid and Wassermann [18] and Meissner,[30] whose data are also given in Tables I and II. Meissner has also shown that the age-hardening of Duralumin containing manganese (alloys 6 and 7, Table I) is equally unaffected by the presence of silicon. Table II contains also results of the investigations of Gayler and Preston,[9] in 1929 (alloys 4 and 6) and 1932 [10] (alloys 3 and 5), as well as data given by Kempf and Dean in the discussion of Gayler and Preston's second paper.[10]

From these results, obtained independently by a number of workers, it appears clear to the present author that Mg_2Si plays no part in the age-hardening at room temperature of Duralumin.

On the other hand, the properties of the alloys hardened at higher temperatures (alloys 2 and 3 of Table I, and alloys 3, 4, 5, 6, 7, 8, 9, and 10 of Table II) indicate the definite superiority of those containing silicon; this coincides with the view expressed by Archer to Meissner [30] in 1929. The properties of the silicon-free alloys are practically the same whether the ageing has taken place at ordinary or at elevated temperatures.

The Effects of Magnesium and Silicon on the Age-Hardening of 4 Per Cent. Copper–Aluminium Alloys.

The conviction held by the majority, but not by the present author and several others mentioned above, that when magnesium and silicon

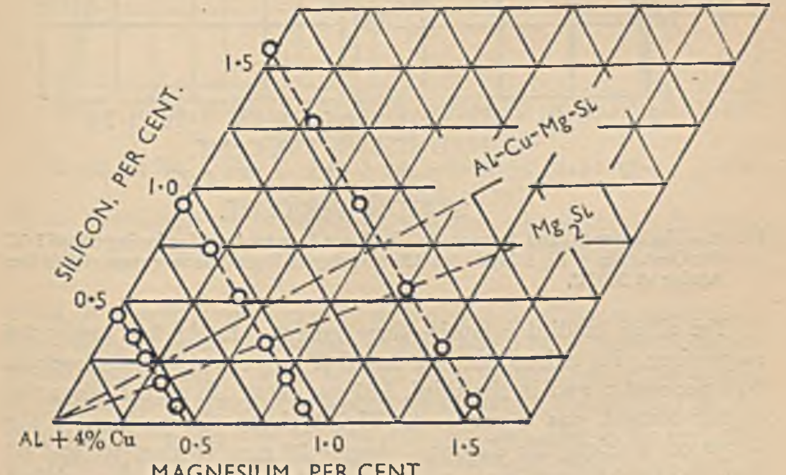


Fig. 1.—Location of Copper–Magnesium–Silicon–Aluminium Alloys Studied.

are present in a copper–aluminium alloy their effect on the age-hardening at room temperature is due to the formation of Mg_2Si, has led to the neglect of the investigation of the age-hardening of alloys in which magnesium or silicon is present in an amount in excess of that required just to form the compound. The present author has carried out such an investigation, and the results proved very instructive.

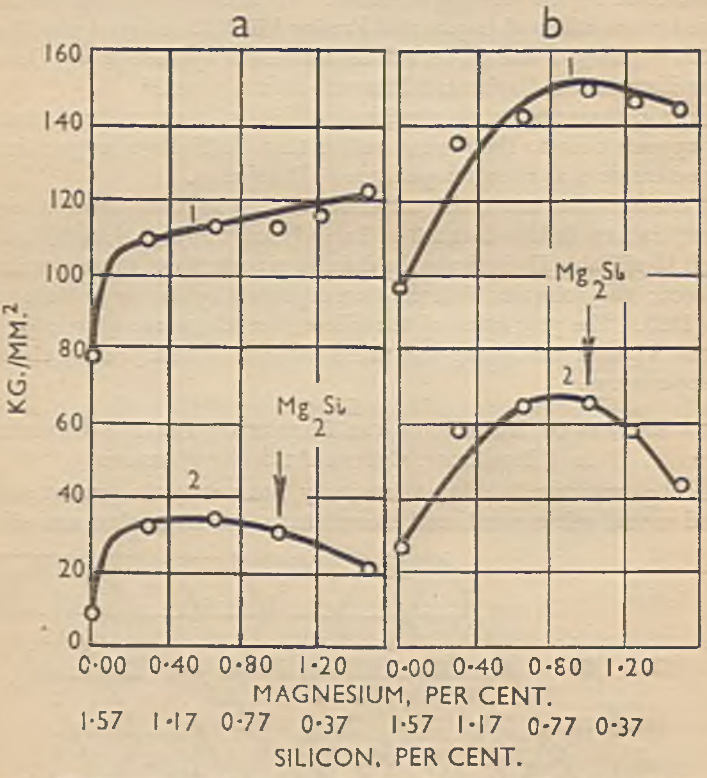


Fig. 2.—Hardness (1) and Increase in Hardness Due to Age-Hardening (2) of 1·57 Per Cent. (Mg + Si) Alloys: (*a*) After Ageing at Room Temperature; (*b*) After Ageing at 200° C.

The alloys studied comprise three groups. In the first group the magnesium plus silicon content was 0·47 per cent.; in the second, 0·94 per cent.; and in the third, 1·57 per cent. In all the alloys the copper content was 4 per cent. Fig. 1 shows the position of the alloys on a triangular diagram. Ingots 30 mm. in diameter and 60 mm. in height were prepared, forged to a quarter the original height, and maintained for 2 hrs. at 510° C. in a saltpetre bath before quenching. Two ageing treatments were employed : (*a*) 6 days at room temperature, and (*b*) 6 hrs. at 200° C. immediately after quenching.

The Brinell hardness values resulting from these ageing treatments are given in Figs. 2, 3, and 4, together with curves showing the increase in hardness due to age-hardening. From Figs. 2*a*, 3*a*, and 4*a* it will be seen that no singularity is exhibited by alloys in which there is no excess of either magnesium or silicon over the quantity required by the formula Mg_2Si, when aged at room temperature. The curves of hardness increment due to ageing for the alloys containing 1·57 per cent. (Mg + Si) (see Fig. 2*a*) and 0·94 per cent. (Mg + Si) (see Fig. 3*a*) pass through maxima at about 0·6 per cent. magnesium, but in the curve for alloys containing 0·47 per cent. (Mg + Si) (see Fig. 4*a*) no

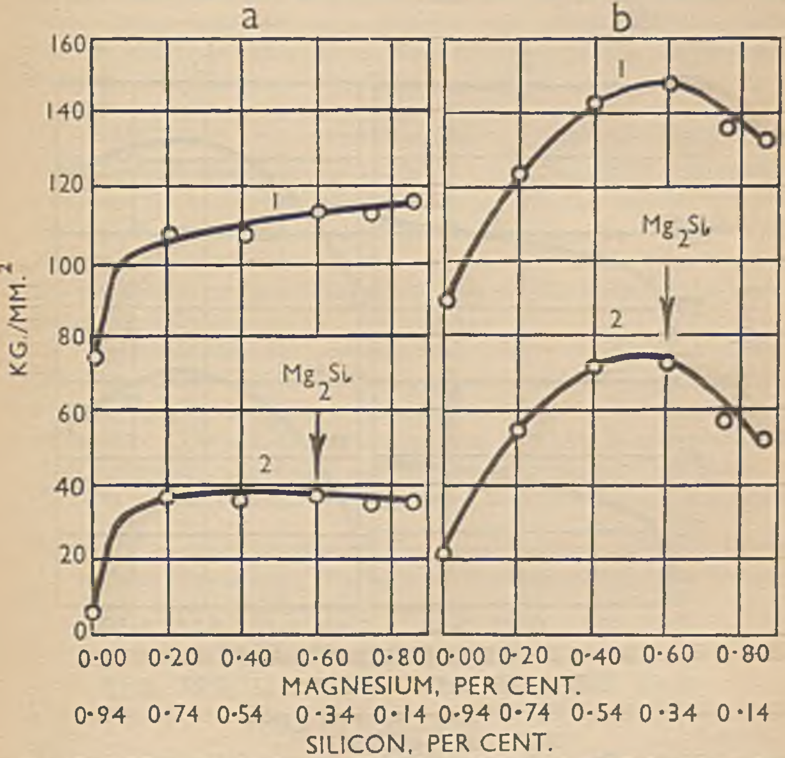


Fig. 3.—Hardness (1) and Increase in Hardness Due to Age-Hardening (2) of 0·94 Per Cent. (Mg + Si) Alloys : (*a*) After Ageing at Room Temperature; (*b*) After Ageing at 200° C.

maximum appears. The curves for age-hardening at elevated temperatures are quite different in character (see Figs. 2*b*, 3*b*, and 4*b*), and on both the hardness curves and the hardness increment curves a definite maximum always appears, slightly to the left of the alloy in which there is no excess of either magnesium or silicon over the quantity required by the formula Mg_2Si. This displacement may result from the combination of part of the silicon with the iron present as an impurity in the alloys, so that a small excess of silicon over the amount theoretically required to satisfy the formula Mg_2Si is necessary.

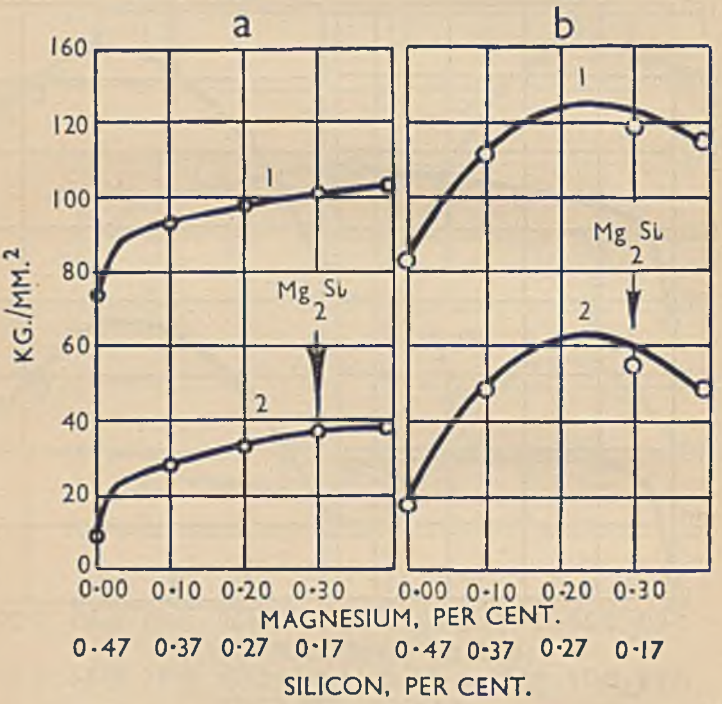


Fig. 4.—Hardness (1) and Increase in Hardness Due to Age-Hardening (2) of 0·47 Per Cent. (Mg + Si) Alloys: (*a*) After Ageing at Room Temperature; (*b*) After Ageing at 200° C.

It is difficult as yet to make any definite statement regarding the rôle played in these alloys by the quaternary aluminium–copper–magnesium–silicon compound discovered by Dix, Sager, and Sager.[15] This compound [16] contains less magnesium than does Mg_2Si, as is indicated by the Al–Cu–Mg–Si line drawn in Fig. 1.

The present results are regarded as confirming beyond all doubt that a phase containing silicon enters into the age-hardening at elevated temperatures of copper–magnesium–silicon–aluminium alloys, but they give no support to the view [4–10] that silicon participates in the age-hardening of these alloys at room temperature.

The question now arises as to why the age-hardening of copper–magnesium–aluminium alloys is greater at room temperature than that of magnesium-free copper–aluminium alloys (see Table III). The answer will be sought, in the first instance, in the copper–magnesium–aluminium ternary equilibrium diagram.

CONSTITUTION OF COPPER–MAGNESIUM–ALUMINIUM ALLOYS.

A detailed study of the Al–$CuAl_2$–Al_3Mg_4 region of this system was made by Vogel.[19, 20] Gayler [8] also investigated these alloys, but introduced no essential changes in Vogel's diagram. The work of Bastien [21] is not relevant here, as the area considered by him lies in the magnesium corner of the system, beyond the range of the alloys now being discussed.

Vogel established the existence of a ternary compound Al_6CuMg_4 (see Fig. 5), and indicated also a region of solid solubility extending from $CuAl_2$ towards Al_3Mg_4 (or Al_2Mg_3) and, to a lesser extent, towards aluminium. The solution of magnesium in $CuAl_2$ is represented as continuing until magnesium and copper are present in the phase in the ratio by weight of about 1 : 3. From Vogel's work it is concluded

TABLE III.—*Age-Hardening of Copper–Aluminium Alloys with and without Magnesium: Changes in Hardness and Tensile Strength due to Ageing at Room Temperature.*

Alloy* No.	Chemical Composition, Per Cent.				Brinell Hardness.			Tensile Strength, Kg./mm.².			Reference.
	Cu.	Mg.	Fe.	Si.	Directly After Quenching from 500° C.	After Ageing.	Increase, Per Cent.	Directly After Quenching from 500° C.	After Ageing.	Increase, Per Cent.	
1 (C_4)	4·12	...	0·01	0·01	60·0	84·2	40·3	...	...	...	Gayler and Preston [16]
2 (C_4M_1)	3·99	0·54	0·01	0·01	60·0	99·3	65·5	...	...	...	
3	4·00	...	†	†	51·4	66·1	28·6	...	...	...	Fraenkel [17]
4	4·00	0·50	†	†	56·0	94·9	69·5	...	...	...	
5	4·50	...	0·03	0·07	...	...	...	25·9	33·6	29·7	Schmid and Wassermann [18]
6	4·51	0·51	0·04	0·01	...	...	...	28·1	39·3	39·8	

* The designations of the alloys in the original papers are given in parentheses.

† The iron and silicon contents are not indicated; the alloys were prepared from the purest aluminium.

that Al_3Mg_4 (or Al_2Mg_3) is not precipitated from alloys of the Duralumin type, and Archer[14] points out that the precipitation of Al_6CuMg_4 is also improbable. From Vogel's diagram it would be expected that, when an alloy containing 4 per cent. copper and up to 1 per cent. magnesium age-hardens and the α-solid solution breaks down, the magnesium would be precipitated in the form of the solid solution in $CuAl_2$.

Laves and Witte,[23] however, in a recent investigation, have not confirmed Vogel's view that large proportions of magnesium dissolve in $CuAl_2$, and express the opinion that the solubility is in reality very small, but state that when magnesium is added to $CuAl_2$ a new ternary compound is formed (to which is ascribed the formula $Al_5Cu_2Mg_2$). This ternary compound lies very near to the solubility limit given in Vogel's diagram, and was evidently mistaken by him for a solid solution of Al_3Mg_4 in $CuAl_2$. Two other compounds are also indicated in Fig. 5 : $Al_{10}Cu_7Mg_3$ discovered by Laves and Witte,[23] and AlCuMg discovered earlier by Laves and Löhberg.[22] Laves and his collaborators unfortunately do not state the extent of the new fields, and give no metallographic data relating to them, but nevertheless their conclusions facilitate an explanation of the rôle of magnesium in the age-hardening of copper–magnesium–aluminium alloys.

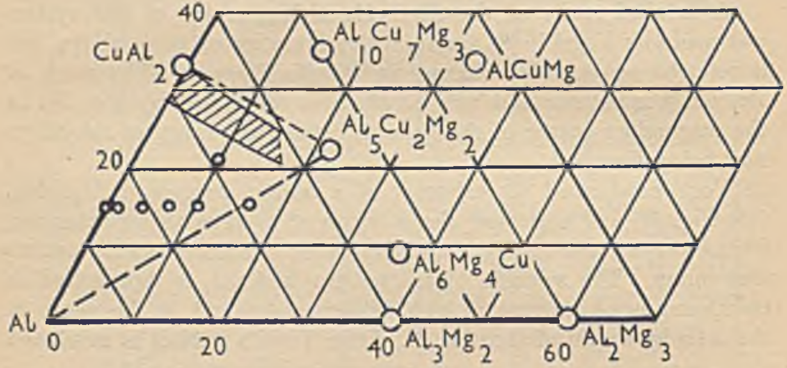


Fig. 5.—Location of Phases in Copper–Magnesium–Aluminium System; Compositions in Atomic Per Cent. (The small circles indicate the location of alloys photomicrographs of which are given in Figs. 11–15 (Plate I).)

Figs. 11–15 (Plate I) are photomicrographs of chill-cast copper–magnesium–aluminium alloys containing usually 30 per cent. copper and various amounts of magnesium, after etching in a warm (70° C.) 10 per cent. solution of NaOH. In the alloy with 1 per cent. magnesium (Fig. 11) only primary α crystals and the (α + $CuAl_2$) eutectic are present, though the $CuAl_2$ differs somewhat in appearance from that in a binary copper–aluminium alloy with 30 per cent. copper. In the alloy containing 3 per cent. magnesium (Fig. 12) a third phase, the compound $Al_5Cu_2Mg_2$, appears in the eutectic; this phase is also referred to as γ. Its absence from Fig. 11 may be due to the solubility of γ either in $CuAl_2$ or in the aluminium-rich α solid solution. The γ phase again appears, this time as primary crystals, in the alloy containing 7·2 per cent. magnesium and 40 per cent. copper (Fig. 13), which lies on the Al–$Al_{10}Cu_7Mg_3$ line (Fig. 5). The 8 per cent. magnesium alloy (Fig. 14) contains both the binary (α + γ) eutectic and the ternary (α + γ + $CuAl_2$) eutectic. Finally, $CuAl_2$ is absent from the alloy containing 12·5 per cent. magnesium, in which primary crystals of the γ phase are accompanied by the binary (α + γ) eutectic: this alloy lies on the Al–$Al_5Cu_2Mg_2$ line (Fig. 5). An additional phase appears in alloys of higher magnesium content. From the microscopical evidence it is concluded that the Al–$Al_5Cu_2Mg_2$ section is pseudo-binary; and the same presumably applies to the $CuAl_2$–$Al_5Cu_2Mg_2$ section.

The alloys which form the basis of commercial Duralumin lie within the triangle Al–$CuAl_2$–$Al_5Cu_2Mg_2$, the alloys lying to the right of the Al–$Al_5Cu_2Mg_2$ line being of no practical interest. This triangular zone alone, therefore, need be considered in explaining the age-hardening mechanism of Duralumin.

So far as age-hardening at room temperature is concerned, magnesium has two main effects: (1) it restores the hardening capacity of iron-containing commercial copper–aluminium alloys (this the present author has shown elsewhere [24] to be effected by as little as 0·03 per cent. magnesium), and (2) it produces additional hardening in high-purity copper–aluminium alloys. The second effect, which is connected, no doubt, with the formation of the compound $Al_5Cu_2Mg_2$, has been observed by all those who have studied the age-hardening of high-purity copper–aluminium alloys (see Table III). The formation of the ternary compound in the copper–magnesium–aluminium alloys also accounts for Gayler and Preston's [10] observation that an alloy of high-purity aluminium with 1 per cent. copper and 0·5 per cent. magnesium hardens considerably at room temperature, although binary alloys made from high-purity aluminium with either 1 per cent. copper [17] or 0·5 per cent. magnesium [18] do not age-harden at either room temperature or more elevated temperatures. In the ternary alloy the copper may all be present as $Al_5Cu_2Mg_2$, leaving about 0·12 per cent. magnesium in excess.

There seems to be no doubt that the room-temperature age-hardening of Duralumin is caused by $Al_5Cu_2Mg_2$ and $CuAl_2$, but that at higher temperatures the compound $Al_5Cu_2Mg_2$ breaks down and that the magnesium combines with silicon. From the general point of view of age-hardening theory there seems to be nothing improbable in this suggestion, and in fact a similar opinion in a more generalized form has previously been advanced by Kempf and Dean, in the discussion of Gayler and Preston's paper.[10] It is suggested now by the present author that in the first stage of ageing, *i.e.* prior to the decomposition of the solid solution, the collecting together of solute atoms gives rise to $Al_5Cu_2Mg_2$ groupings in the lattice proper (*cf.* the theories of Kokubo and Honda,[25] and Tammann[26]) or as nuclei associated with the blocks of a mosaic structure (*cf.* Dehlinger[27]). At more elevated ageing temperatures, the compound $Al_5Cu_2Mg_2$ proves to be unstable and breaks down, Mg_2Si or (Al–Cu–Mg–Si) complex groupings being formed instead. It is further suggested that the temporary decrease in hardness which occurs when copper–magnesium–aluminium alloys[6, 10, 31] are brought to an elevated ageing temperature after age-hardening at room temperature, is associated with this rearrangement of the groupings within the solid solution.

The $Al_5Cu_2Mg_2$ phase may therefore be expected to occur both in annealed Duralumin free from silicon and copper–magnesium–aluminium alloys free from silicon, and in commercial copper–magnesium–aluminium alloys with a high magnesium content (where it appears, after annealing, accompanied by silicon-containing constituents), but not in annealed Duralumin of moderate silicon content.

AGE-HARDENING OF HIGH-PURITY COPPER–MAGNESIUM–ALUMINIUM ALLOYS.

The author succeeded in confirming this last statement experimentally with a series of alloys made from high-purity aluminium (0·03 per cent. silicon, 0·03 per cent. iron) in the form of small cylinders 20 mm. in diameter and 40 mm. in height; these were annealed for 24 hrs. at 400° C., forged to twice the original diameter, prepared for hardness tests, and quenched from 500° C. after being held for 2 hrs. at that temperature. The compositions of the alloys are given in Table IV and plotted in Fig. 6, in which the dotted line runs from the aluminium corner towards the compound $Al_5Cu_2Mg_2$.

Table IV contains the results of Brinell hardness tests made directly after quenching, after 6 days' ageing at room temperature, and after further annealing for 24 hrs. at 350° C., followed by cooling in the furnace. Table V contains, for comparison, results obtained with alloys of similar compositions made from commercial

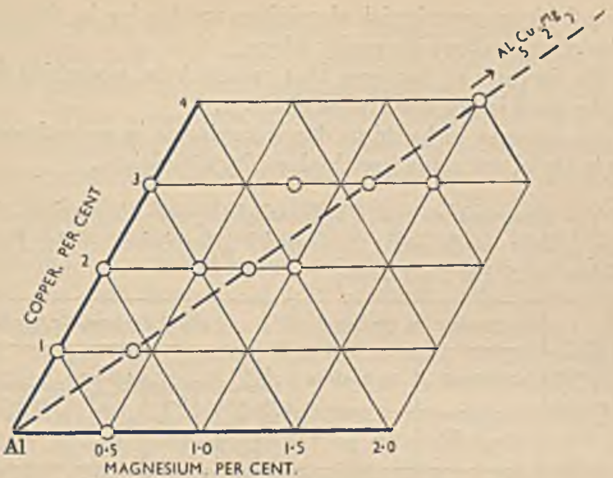


FIG. 6.—Location of Pure Copper–Magnesium–Aluminium Alloys.

aluminium having a considerable silicon content; these results have been discussed in detail elsewhere.[16] A comparison of Tables IV and V shows that:

(1) as a result of the presence of iron and silicon as impurities, the

TABLE IV.—*Composition* and Hardness of Copper–Magnesium–Aluminium Alloys made with High-Purity Aluminium* (0·03 *Per Cent. Silicon,* 0·03 *Per Cent. Iron*).

Alloy No.	Composition, Per Cent.		Brinell Hardness, Kg./mm.².				
	Cu.	Mg.	After Annealing at 350° C. for 24 hrs.	Directly After Quenching.	After 6 days' Age-Hardening at Room Temperature.	Increase Due to Quenching.	Increase Due to Age-Hardening.
1	...	0·5	22·4	22·6	22·7	0·2	0·1
2	1·0	...	25·8	26·4	27·8	0·6	1·4
3	2·0	...	29·6	37·6	39·6	8·0	2·0
4	3·0	...	30·1	47·7	52·0	17·6	4·3
5	3·0	0·75	36·6	60·7	97·0	24·1	36·3
6	3·0	1·15	38·1	71·7	104·5	33·6	32·8
7	3·0	1·5	37·4	76·7	104·0	39·3	27·3
8	2·0	0·5	...	45·7	80·4	...	34·7
9	2·0	0·74	...	47·5	84·6	...	37·1
10	2·0	1·0	...	51·0	86·8	...	35·8
11	1·0	0·4	...	33·5	51·2	...	17·7
20	4·0	1.53	...	99·4	123·5	...	24·1

* The calculated composition of the alloys is given. Check analyses showed only small deviations.

alloys made from commercial aluminium are harder in the annealed condition than are the high-purity alloys,

(2) the increase of hardness that results from quenching is practically the same in the two groups of alloys,

(3) the increase in hardness due to ageing is in general somewhat greater in the alloys made from high-purity aluminium.

Table V.—*Composition and Hardness of Copper–Magnesium–Aluminium Alloys made with Commercial Aluminium* (0·24 *Per Cent. Silicon*, 0·12 *Per Cent. Iron*).

Alloy No.	No. of Alloy of Similar Composition in Table IV.	Composition, Per Cent.				Brinell Hardness, Kg./mm.²				
		Calculated.		By Analysis.		After Annealing at 350° C. for 24 hrs.	Directly After Quenching.	After 6 Days' Age-Hardening.	Increase Due to Quenching.	Increase Due to Age-Hardening.
		Cu.	Mg.	Fe.	Si.					
47–3	1	...	0·60	0·12	0·24	24·8	32·1	42·5	7·3	10·4
48–1	2	1·00	...	0·16	0·26	31·9	33·3	35·0	3·4	— 0·3
38–1	3	2·00	...	0·15	0·29	34·2	44·9	46·1	10·7	1·2
40–1	4	3·00	...	0·14	0·31	37·4	52·6	57·1	15·2	4·5
46–3	5	3·00	0·60	0·15	0·26	38·7	62·2	98·6	23·5	36·4
46–4	5	3·00	0·90	0·15	0·26	40·7	67·1	104·2	26·4	37·1
46–5	6	3·00	1·20	0·14	0·25	42·7	72·4	105·2	29·7	32·8
38–3	8	2·00	0·40	0·15	0·29	34·6	50·8	80·1	16·2	29·3
38–4	8	2·00	0·60	0·15	0·29	34·3	52·9	85·3	18·6	32·4
38–5	9	2·00	0·80	0·15	0·29	35·8	56·5	90·2	20·7	33·7
38–6	10	2·00	1·00	0·12	0·31	38·3	60·7	91·7	22·4	31·0
48–5	11	1·00	0·30	0·16	0·27	34·6	38·5	48·4	3·9	9·9
48–6	11	1·00	0·60	0·16	0·27	34·5	42·3	61·3	7·8	19·0
27–10	20	4·00	1·80	0·17	0·28	56·5	100·0	127·2	43·5	27·2
27–11	20	4·00	2·20	0·16	0·28	53·6	104·2	123·2	50·6	19·0

It may be pointed out that the more marked quenching and ageing changes that occur in the first alloy of Table V (47–3), compared with the first alloy of Table IV (1), result from the formation of Mg_2Si, which is present only in very small quantities in alloy 1. These results for the copper–magnesium–aluminium alloys confirm the results of previous investigations [10, 14, 17, 30] and what has been said above regarding these alloys, viz. that silicon is not necessary for age-hardening, as Mg_2Si is not the hardening constituent at room temperature.

MICROSTRUCTURE OF HIGH-PURITY COPPER–MAGNESIUM–ALUMINIUM ALLOYS.

Figs. 16–21 (Plate II) are photomicrographs of the high-purity alloys referred to in the previous section and show the microstructures developed by annealing at 500° C. for 10 days, followed by slow cooling to room temperature during 7 days. In each case the specimen was etched in a warm (70° C.) 10 per cent. sodium hydroxide solution, which etches $CuAl_2$ brown and outlines the compound

$Al_5Cu_2Mg_2$; etching was of 10 seconds' duration, except in the case of the alloy shown in Fig. 21, where it continued for 30 seconds.

The 3 per cent. copper–aluminium alloy contains α and $CuAl_2$ (Fig. 16). When magnesium is added, an additional phase appears (Fig. 17), which is identical with the γ phase seen in the chill-cast alloys previously examined (see Figs. 12–15, Plate I). The amount of γ increases with the magnesium content, as seen in Fig. 18, until, when 1·5 per cent. magnesium is present, $CuAl_2$ disappears from the microstructure (Fig. 19). It will be noted that *in equilibrium* an alloy containing 3 per cent. copper and 1·15 per cent. magnesium might be expected to contain no $CuAl_2$, whereas Fig. 14 shows some $CuAl_2$ still present. It may be pointed out that the formula ascribed to the compound $Al_5Cu_2Mg_2$ may not be exact.[23] The cause may also be that the annealing of our alloys was not sufficiently prolonged to result in the attainment of complete equilibrium. Fig. 20 shows another alloy (4 per cent. copper, 2 per cent. magnesium, and 0·08 per cent. silicon) which was subjected to the same heat-treatment; $CuAl_2$ is absent, the ternary phase occurring together with a small amount of Mg_2Si and presenting a more polygonal form than that shown in Fig. 19. In Fig. 21, which is another photomicrograph of the same alloy, both elongated and polygonal forms are present.

This microscopical evidence confirms the suggestions made above regarding the part played by $Al_5Cu_2Mg_2$ in the age-hardening of pure copper–magnesium–aluminium alloys. In the alloys of high magnesium content, *e.g.* 1·5 per cent. magnesium with 3 per cent. copper, $Al_5Cu_2Mg_2$ may be regarded as the sole hardening constituent.

THE DILATOMETRIC RESULTS OF IGARASI.[28]

The isothermal dilatometric curves obtained by Igarasi[28] during the ageing at room temperature of samples quenched from 500° C., supply additional evidence for the view now advanced. Fig. 7 gives the curves for magnesium–silicon–aluminium alloys and shows that the expansion of alloys containing 0·22 per cent. silicon is much reduced by the presence of 1 per cent. magnesium. This results from the decreased concentration of Mg_2Si in solid solution in the presence of excess magnesium, and one would anticipate a further reduction of the solubility of Mg_2Si when copper as well as excess magnesium is present in the alloy. The expansion which occurs in an alloy containing 4 per cent. copper and 2 per cent. magnesium is seen, however, from Fig. 9 to be several times greater than that occurring in the copper-free alloys, and it cannot therefore be attributed to Mg_2Si. Even more certainly it does not result from the presence of $CuAl_2$, since Fig. 8 shows the dilatometric effect in copper–aluminium alloys to be a contraction.

The curves for copper–magnesium–aluminium alloys are readily

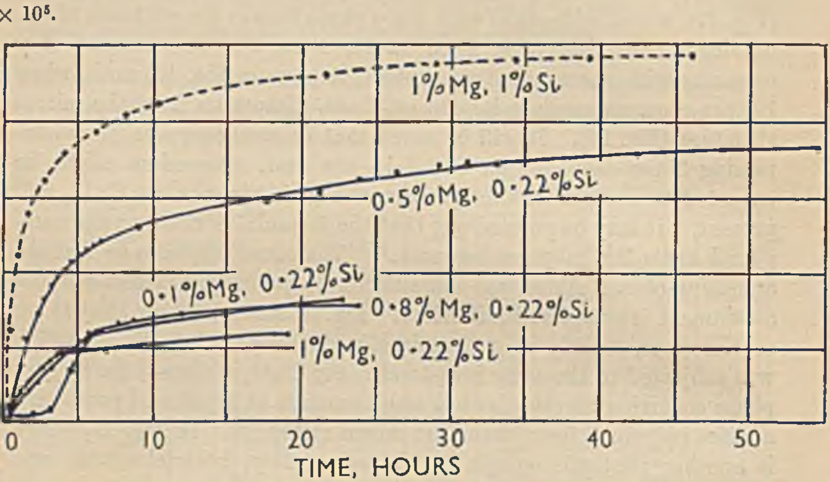


Fig. 7.—Changes in Length of Magnesium–Silicon–Aluminium Alloys During Age-Hardening at Room Temperature.

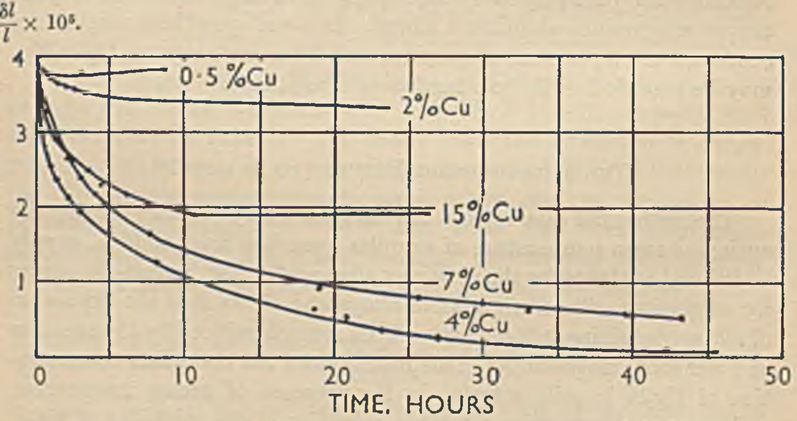


Fig. 8.—Changes in Length of Copper–Aluminium Alloys During Age-Hardening at Room Temperature.

interpreted, however, if the expansion be ascribed to the compound $Al_5Cu_2Mg_2$. From Fig. 9 it will be seen that for a copper content of 4 per cent., the expansion is slight when the magnesium content is only

0·5 per cent.; this alloy can contain only a comparatively small amount of the ternary compound and a large amount of $CuAl_2$ (see Table VI), which causes the initial expansion to be followed by contraction. In the alloy with 1 per cent. magnesium a greater amount of the ternary compound can be formed and the expansion is greater, though it is again followed by contraction as excess $CuAl_2$ is still present. $CuAl_2$ is absent from the 2 per cent. magnesium alloy, where the amount of ternary compound will be still greater; in this case the expansion reaches a maximum and the alloy suffers practically no subsequent contraction. In the alloys containing 3 and 5 per cent. magnesium there is a considerable excess of magnesium over the amount called for

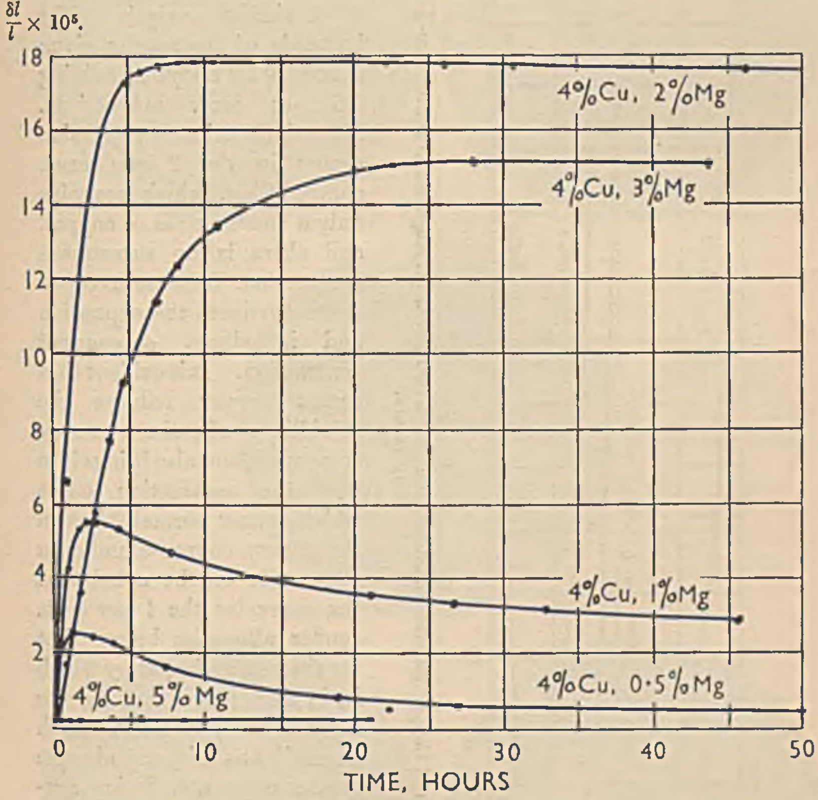


FIG. 9.—Changes in Length of Copper–Magnesium–Aluminium Alloys (4 Per Cent. Copper) During Age-Hardening at Room Temperature.

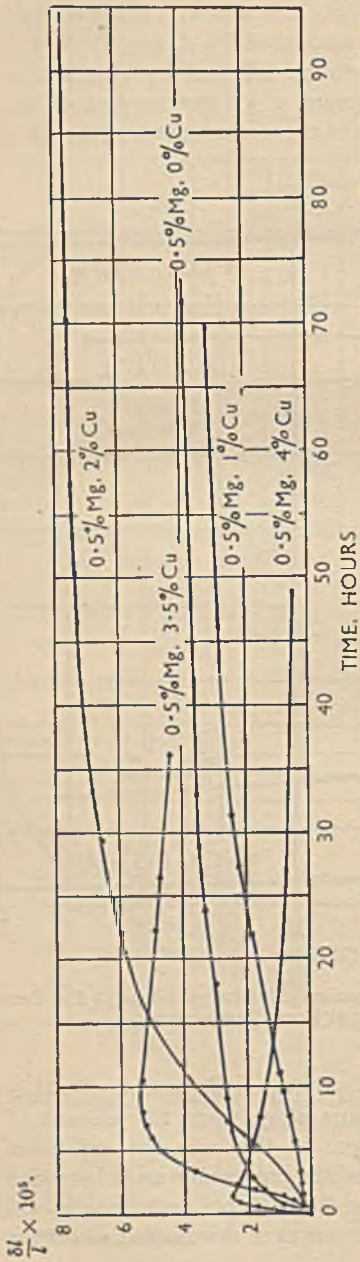
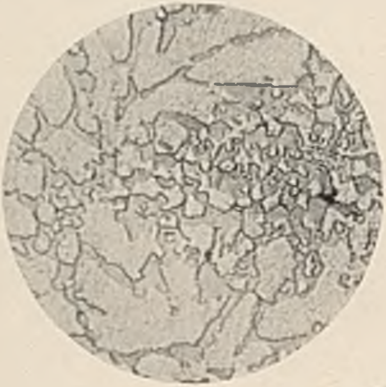


Fig. 10.—Changes in Length of Copper-Magnesium-Aluminium Alloys (0·5 Per Cent. Magnesium) During Age-Hardening at Room Temperature.

by the formula $Al_5Cu_2Mg_2$, so that the solubility of the ternary compound is reduced and the expansion becomes less; in the 5 per cent. magnesium alloy the expansion is very small.

A similar analysis might be made of the results given in Fig. 10 for alloys containing 0·5 per cent. magnesium. Here the maximum expansion occurs in the 2 per cent. copper alloy, which contains only a small excess of copper, and there is no subsequent contraction. Increase in copper content reduces the expansion and introduces subsequent contraction. It is evident that excess copper reduces the solubility of the ternary compound, and also brings into play the contraction effect which copper normally has in the binary copper–aluminium alloys. It will be noted that the curve for the 1 per cent. copper alloy lies below that for the copper-free alloy which is, in turn, below that for the 2 per cent. copper alloy. Such anomalies as this, and also the greater expansion during age-hardening of copper–magnesium–aluminium alloys than of magnesium–silicon–aluminium alloys, are difficult to explain on the basis of the earlier theory put forward by Botschvar[29] for the interpretation of Igarasi's dilatometric curves.

PLATE I.

11


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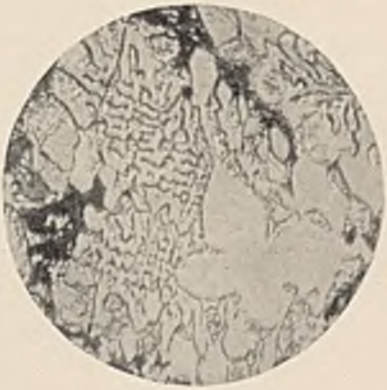

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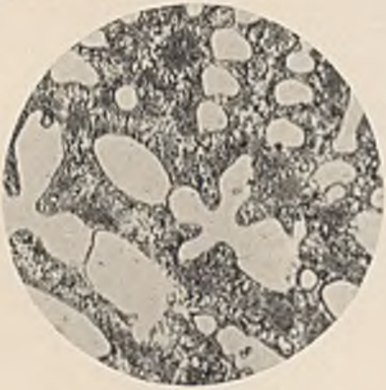


FIG. 11.—Cu 30, Mg 1%.

FIG. 12.—Cu 30, Mg 3%.

FIG. 13.—Cu 40, Mg 7·2%.

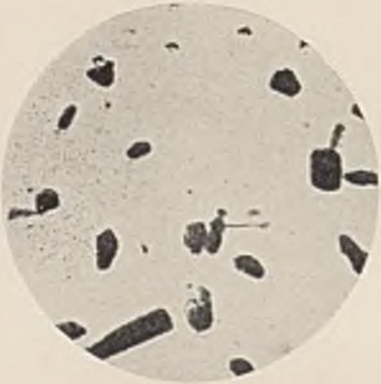
FIG. 14.—Cu 30, Mg 8%.

FIG. 15.—Cu 30, Mg 12·5%.

CHILL-CAST Cu–Mg–Al ALLOYS, ETCHED 10% NaOH. × 500.

PLATE II.

16



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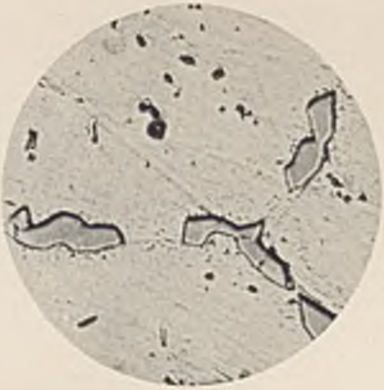

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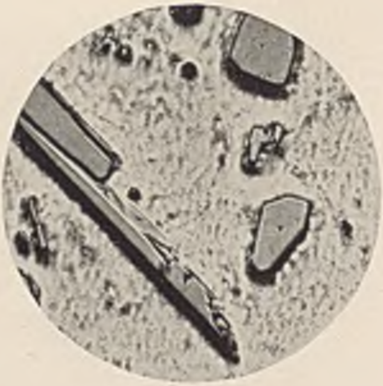

FIG. 16.—Cu 3%.
FIG. 18.—Cu 3, Mg 1·15%.
FIG. 20.—Cu 4, Mg 2%.

FIG. 17.—Cu 3, Mg 0·75%.
FIG. 19.—Cu 3, Mg 1·5%.
FIG. 21.—As Fig. 20.

SLOWLY-COOLED Cu–Mg–Al ALLOYS, ETCHED 10% NaOH. × 500.

Table VI.—*Composition of Igarasi's Alloys. (Calculated for the Maximum $Al_5Cu_2Mg_2$ Content.)*

Composition, Per Cent.		Copper + Magnesium in the Compound $Al_5Cu_2Mg_2$, Per Cent.	Excess of Copper, Per Cent.	Excess of Magnesium, Per Cent.
Cu.	Mg.			
4·00	0·5	1·81	2·69	...
4·00	1·0	3·62	1·38	...
4·00	2·0	5·53	...	0·47
4·00	3·0	5·53	...	1·47
4·00	5·0	5·53	...	3·47
0·00	0·5	...	...	0·50
1·00	0·5	1·38	...	0·12
2·00	0·5	1·81	0·69	...
3·50	0·5	1·81	2·19	...
4·00	0·5	1·81	2·69	...

Conclusions.

1. In agreement with the conclusions of some previous investigations, it has been established that silicon does not take part in the age-hardening of copper–magnesium–silicon–aluminium alloys at room temperature. At higher ageing temperatures, however, the compound Mg_2Si or a (Al–Cu–Mg–Si) complex is clearly involved in the hardening.

2. It has been established experimentally that, in addition to $CuAl_2$, the ternary compound $Al_5Cu_2Mg_2$ acts as a hardening constituent in the age-hardening at room temperature of high-purity copper–magnesium–aluminium alloys.

3. The compound $Al_5Cu_2Mg_2$ is regarded as behaving similarly as a hardening constituent in commercial Duralumin, where again Mg_2Si takes no part in the age-hardening at room temperature.

References.

[1] A. Wilm, *Metallurgie*, 1911, **8**, 225–227.
[2] *Aluminium*, 1936, **18**, 366–367.
[3] P. D. Merica, R. G. Waltenberg, and H. Scott, *Sci. Papers (U.S.) Bur. Stand.*, 1919, **(347)**, 271–316.
[4] W. Rosenhain, S. L. Archbutt, and D. Hanson, *11th Rep. Alloys Res. Cttee. Inst. Mech. Eng.*, 1921.
[5] D. Hanson and M. L. V. Gayler, *J. Inst. Metals*, 1921, **26**, 321–359.
[6] M. L. V. Gayler, *J. Inst. Metals*, 1922, **28**, 213–252.
[7] M. L. V. Gayler, *J. Inst. Metals*, 1923, **29**, 507–528.
[8] M. L. V. Gayler, *J. Inst. Metals*, 1923, **30**, 139–169.
[9] M. L. V. Gayler and G. D. Preston, *J. Inst. Metals*, 1929, **41**, 191–247.
[10] M. L. V. Gayler and G. D. Preston, *J. Inst. Metals*, 1932, **48**, 197–219.
[11] S. Konno, *Sci. Rep. Tôhoku Imp. Univ.*, 1922, [i], **11**, 269–294.
[12] W. Fraenkel and E. Scheuer, *Z. Metallkunde*, 1922, **14**, 49–58, 111–118.
[13] S. Kokubo, *Sci. Rep. Tôhoku Imp. Univ.*, 1931, [i], **20**, 268–298.
[14] R. S. Archer, *Trans. Amer. Soc. Steel Treat.*, 1926, **10**, 718–747.
[15] E. H. Dix, Jr., G. F. Sager, and B. P. Sager, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 119–131.
[16] D. A. Petrov, *Acta Physicochimica U.R.S.S.*, 1937, **6**, 505–512.

[17] W. Fraenkel, *Z. Metallkunde*, 1930, 22, 84–89.
[18] E. Schmid and G. Wassermann, *Metallwirtschaft*, 1928, 7, 1329–1355.
[19] R. Vogel, *Z. anorg. Chem.*, 1919, 107, 265–307.
[20] V. Fuss, "Metallographie des Aluminiums und seiner Legierungen," Berlin: 1934.
[21] P. Bastien, *Rev. Mét.*, 1933, 30, 478–501, 528–542.
[22] F. Laves and K. Löhberg, *Nachr. Gött. Ges. Wiss.*, 1934, [N.F.], 1, (6), 59 (Abstract in *Metallwirtschaft*, 1935, 14, 111).
[23] F. Laves and H. Witte, *Metallwirtschaft*, 1936, 15, 15–22.
[24] D. A. Petrov, *J. Inst. Metals*, this vol. p. 63.
[25] S. Kokubo and K. Honda, *Sci. Rep. Tôhoku Imp. Univ.*, 1930, [i], 19, 365–409.
[26] G. Tammann, *Z. Metallkunde*, 1930, 22, 365–368.
[27] U. Dehlinger, *Z. Metallkunde*, 1935, 27, 209–212.
[28] I. Igarasi, *Sci. Rep. Tôhoku Imp. Univ.*, 1923, 12, [i], 333–345.
[29] A. A. Botschvar, "The Heat-Treatment of Alloys" (in Russian), Moscow: 1934, 190–192.
[30] K. L. Meissner, *Z. Metallkunde*, 1929, 21, 328–332.
[31] M. L. V. Gayler, *J. Inst. Metals*, 1937, 60, 249–283.

CORRESPONDENCE.

DR. L. H. CALLENDAR * (Member): The author's statement that Mg_2Si is not a hardening constituent at room temperature seems to be contradicted by alloy 47–3, Table V, p. 92. There is here an increase in hardness of 10 per cent. due to age-hardening in an alloy containing no copper, but only magnesium, silicon, and iron.

The commercial alloys shown in Table V all contain an amount of silicon about double that of the iron present, whereas most British commercial metal contains nearly twice as much iron as silicon. Where in the process of manufacture does the Russian metal pick up this additional silicon?

It would appear that with this excess of silicon over iron, after the annealing treatment given of 24 hrs. at 350° C., only about 0·05 per cent. silicon (as the β constituent †) would be held by the iron, and the rest, 0·20 per cent., would be available to combine with the magnesium to form about 0·6 per cent. Mg_2Si, though possibly a small amount of free silicon might be left; the final separation of Mg_2Si would be the cause of the observed age-hardening at room temperatures. It would have been of interest and value if the author had determined the amount of free silicon in his various alloys after annealing and after ageing, using the soda gas-volumetric method,‡ as then he would have known more exactly what was happening during these processes.

Dr. MARIE L. V. GAYLER § (Member): The author remarks (p. 85), "From Figs. 2*a*, 3*a*, and 4*a*, it will be seen that no singularity is exhibited by alloys in which there is no excess of either magnesium or silicon over the quantity required by the formula Mg_2Si, when aged at room temperature," but he gives no reason why he should expect any "singularity," and from a consideration of the possible constitution of the alloys I do not see why any marked indication of Mg_2Si should be expected.

The changes in direction on the hardness–composition curves in Figs. 2*a*, 3*a*, and 4*a* indicate limits of solid solubility, as shown in Fig. A. The researches of Dix, Sager, and Sager || show that at 500° C. the constitution of an alloy

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* Research Laboratories, Chloride Electrical Storage Company, Ltd., Clifton Junction, Manchester.

† *J. Inst. Metals*, 1933, 51, 212.

‡ *Analyst*, 1933, 58, 580.

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

|| E. H. Dix, Jr., G. F. Sager, and B. P. Sager, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, 99, 119.

containing copper 4, Mg_2Si 1·38 per cent. consists most probably of the phases $\alpha + CuAl_2 +$ Al–Cu–Mg–Si, the last being a phase of unknown composition; while I have shown * that magnesium reduces the limits of the $\alpha + CuAl_2$ phase field considerably. It is evident also from these authors' results that the Al–Cu–Mg–Si phase is only formed after prolonged heat-treatment, and it is highly probable, therefore, that Mr. Petrov's specimens were far from being in a state of equilibrium. A possible representation of the constitution of these alloys in equilibrium is shown in Fig. A.

The author further remarks (p. 87), "The present results . . . give no support to the view [4–10] that silicon participates in the age-hardening of these alloys at room temperature." This statement rather misrepresents the view put forward, since it has not been maintained that silicon, as such, participates in age-hardening, but that the compound Mg_2Si plays a part, which is a very different matter. On the other hand, the formation of a quaternary phase containing Al–Cu–Mg–Si † indicates, again indirectly, that silicon must play an important part in the ageing of alloys of Duralumin composition.

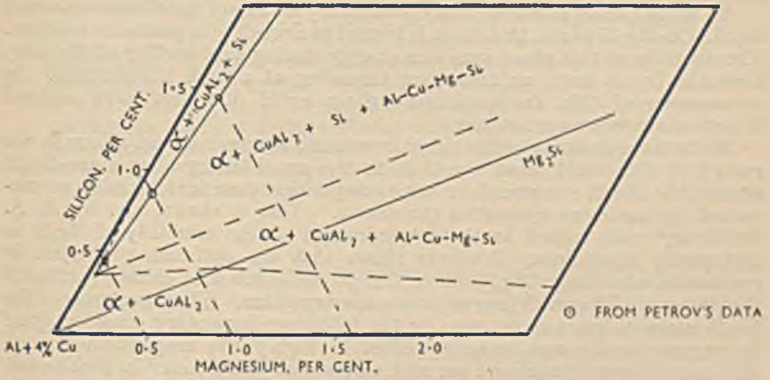

Fig. A.

The photomicrographs of slowly-cooled annealed alloys (Figs. 16—20) certainly are evidence in support of a phase other than $CuAl_2$ playing a rôle in the age-hardening of the ternary alloys. It would be more convincing, however, if the actual nature of the unknown phase could be determined. The author's own remark throws doubt on his conclusions, for he states, "There seems no doubt that the room-temperature age-hardening of Duralumin is caused by $Al_5Cu_2Mg_2$ and $CuAl_2$, but that at higher temperatures the compound $Al_5Cu_2Mg_2$ breaks down, and that the magnesium combines with the silicon." How is it possible for a compound, which is apparently formed as the product of a high-temperature reaction, to be responsible for age-hardening at room temperature, if it is unstable at an intermediate temperature?

Furthermore, in order to show that the phase $Al_5Cu_2Mg_2$ plays a part in the ageing of Duralumin alloys, the effect of the addition of silicon on the formation of the phase, etc., must be studied, since the former is a constituent of alloys of the Duralumin type.

The Author (*in reply*): I do not deny the part played by Mg_2Si in the age-hardening at room temperature of the aluminium–Mg_2Si alloys, and I am entirely of Dr. Callendar's opinion that Mg_2Si is a hardening constituent at

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* M. L. V. Gayler, *J. Inst. Metals*, 1923, 30, 139.

† Dix, Sager and Sager, *loc. cit.*

room temperature in alloy 47–3 (Table V). I have pointed this out in the text of my paper.

The comparatively large amount of silicon my alloys contained may be explained by the high silica content of the primary raw material (bauxites) used for the production of the aluminium used in our investigations.

It would be very interesting to endeavour to verify by the method of chemical analysis suggested by Dr. Callendar, the amount of silicon dissolved in the aluminium lattice at different stages of ageing, since this content must certainly change with the transformations taking place in the alloy.

I do not fully understand why Dr. Gayler thinks that changes in the direction of the hardness–composition curves in Figs. 2*a*, 3*a*, and 4*a* indicate the limits of solid solubility. I have established in my first paper (p. 63), that small additions of magnesium (of the order of 0·03 per cent.) restore the age-hardening capacity of copper–aluminium alloys at room temperature, and the sharp change of direction of the hardness–composition curves at this magnesium content in Figs. 2*a*, 3*a*, and 4*a* is connected only with this influence of magnesium, and does not indicate the limits of solubility.

So far as I could establish in my preliminary studies of the alloys containing the Al–Cu–Mg–Si phase, this phase is formed as a result of a peritectic reaction. The quantity of this phase increases sharply during slow cooling of the alloy from the liquid state, or after long annealing at a high temperature. In consequence of this, the quaternary phase could doubtless have escaped detection in more recent studies.

As to the singularity of the alloys containing magnesium and silicon in the ratio 2 : 1 (Mg_2Si), I must say that, in the quasi-binary aluminium–Mg_2Si system, the Mg_2Si compound, or some composition close to it, must be accompanied by optimum properties (hardness). This is shown, *e.g.* by A. A. Botchvar,* with regard to the determination of the solubility of Mg_2Si in high-purity aluminium. Botchvar shows that the optimum properties in commercial aluminium–Mg_2Si alloys shift to the silicon side, since a portion of the silicon combines with iron to form a ternary phase. The singularity of the Mg_2Si composition is shown also by the following elementary consideration: let us measure the age-hardening effect in high-purity magnesium–silicon–aluminium alloys containing 1 per cent. magnesium plus silicon. In such a case, the aluminium alloy with 1 per cent. magnesium shows no age-hardening at all. The alloy with 1 per cent. silicon shows age-hardening to a very small extent. Following gradually the 1 per cent. magnesium plus silicon section from 1 per cent. magnesium to 1 per cent. silicon, we arrive at the maximum age-hardening effect, which most probably coincides with the intersection of the section with the aluminium–Mg_2Si line. That the same is true also for the quasi-ternary systems is partly confirmed by the maximum on the hardness curves in Figs. 2*b*, 3*b*, and 4*b* for age-hardening at 200° C.

My remark on p. 87, referred to by Dr. Gayler, should be interpreted in such a way that not silicon as such (this is quite a separate question), but its compound with magnesium (Mg_2Si, Al–Cu–Mg–Si, or some other) does not take part in the age-hardening of silicon–magnesium–copper-aluminium alloys at room temperature.

I am in agreement with Dr. Gayler's opinion that the statement regarding the interaction of $Al_5Cu_2Mg_2$ and silicon at elevated age-hardening temperatures demands conclusive experimental proof, and that an investigation should be carried out of the exact composition of this phase, and of the influence of silicon on the limits of existence of this phase. Only these further investigations can dispel the doubts which arise naturally at the present time. But at all events I contend that the part played by $Al_5Cu_2Mg_2$ in the age-hardening of high-purity magnesium–copper–aluminium alloys is quite indisputable.

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* *Science of Metals*, 1935, p. 247 (in Russian).

THE INFLUENCE OF ALLOYING ELEMENTS ON THE CRYSTALLIZATION OF COPPER. PART I.—SMALL ADDITIONS AND THE EFFECT OF ATOMIC STRUCTURE.*

79

By L. NORTHCOTT,† Ph.D., M.Sc., F.I.C., Member.

Synopsis.

The influence has been determined of additions of from 0·1 to 2 per cent. by weight of alloying elements on the size of columnar crystals of copper cast into moulds specially designed to ensure uni-directional solidification. Different elements produced widely different effects on the crystallization of the copper. The results are discussed from the points of view of composition gradient and adsorption effects. The temperature gradients in the ingot during and after solidification have been measured. An examination of the valency and atomic structure of the added elements shows a correspondence between these and what has been termed the "crystal growth-restriction factor."

Introduction.

In a general way, it is known that the properties of metals and alloys are influenced by the size and shape of the crystals composing them. The effect of crystal size on the mechanical properties of metals and alloys, especially of worked and heat-treated steels, has been discussed in a number of isolated papers, but no systematic work has yet been carried out on the influence of alloying elements on the crystal size of the cast material.

Some control over crystal size may be obtained by modifying the conditions of casting, such as the temperature at which the liquid metal enters the mould, the temperature and material of the mould, and so on, or else by the addition of alloying elements. Although the presence of alloying constituents is known to facilitate the formation of equi-axial crystals in the cast ingot, this is usually explained as being due simply to the alloy's having a range of temperature over which it freezes as compared with a single temperature in the case of a pure metal. Unfortunately, there appears to be no information either on the fundamental factors affecting restriction of crystal growth or even on the relative effects of different alloying additions in this direction. An

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* Manuscript received October 1, 1937. Presented at the Annual General Meeting, London, March 9, 1938.

† Research Department, Woolwich.

investigation was therefore initiated to obtain information on these points, and the present paper describes the results of an attempt to assess the relative influence of small quantities of added elements in reducing the columnar growth of cast copper, and to determine the fundamental factors on which such influence depends. It was considered advisable, in the first instance, to investigate the crystallization of copper containing small amounts of different elements, as the properties of such alloys usually lend themselves more easily to generalizations less likely to be complicated by such features as irregularities in freezing range, limited liquid solubility, or the formation of metallic compounds. The effect of large additions and the influence of crystal size on the properties of the alloys will be discussed in later papers.

It will be assumed at the outset that when a pure metal is poured into a mould the crystals in the resulting ingot will be wholly columnar, provided that the temperature of the liquid metal is sufficiently above the melting point to avoid the formation of solid nuclei in the liquid stream entering the mould, and that the temperature of the mould is below the melting point of the metal entering it. The argument for this has been discussed by a number of writers.

EXPERIMENTAL.

When a pure metal is cast into the usual rectangular form of ingot mould, the columnar crystals grow inwards from the mould walls, and crystals from opposite faces meet along the axis of the ingot so that the length of the crystals is only half the thickness of the ingot. With an ingot of medium size, this means that the maximum crystal length is comparatively small. It was thought that, although such a mould might serve for comparing alloys solidifying wholly in columnar or in equi-axial form, it would not be satisfactory for differentiating between alloys having only slightly different growth tendencies. A special mould was therefore constructed, arranged for uni-directional cooling of the ingot. The base of the mould consisted of a water-cooled copper block, and the circular side was formed by refractory material, which was heated before casting. In order to reduce turbulence and splashing of the liquid metal, the Durville rotatory method of casting was adopted. A sketch of the apparatus in the final casting position is given in Fig. 1.

A round ingot, about 7 lb. in weight, 3 in. in diameter at the base, and nearly 3 in. high, was obtained. An axial slice was cut, and the axial face was polished and etched to determine the crystal structure. Owing to the uni-directional cooling, ingots of copper and of those alloys which tend towards columnar growth were composed wholly of columnar crystals growing from the bottom to the top of the ingot. The structure of ingots of other alloys consisted of columnar crystals at the bottom of the ingot and equi-axial crystals above. In such instances the lengths of the different columnar crystals were the same in any one ingot, the tops of the columnar crystals forming a line parallel to the base of the ingot. Under constant casting conditions, the length of the columnar crystals was taken as a measure of the tendency of any alloy to solidify in columnar form.

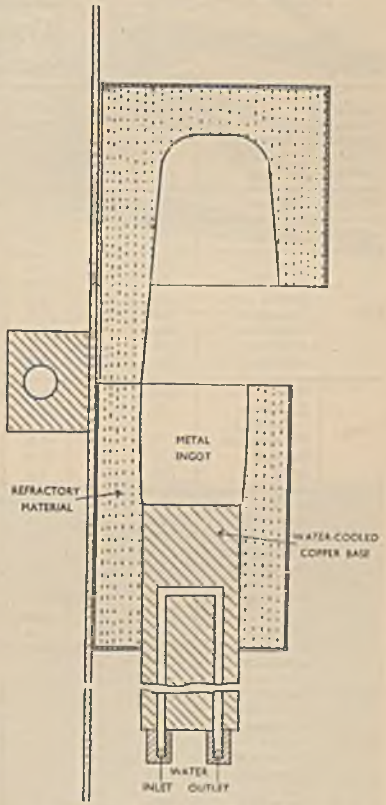


Fig. 1.—Sketch of Metal-Casting Apparatus.

The elements were added in amounts ranging from 0·1 to 2 per cent. by weight, but in most cases the amounts were 0·5 or 1 per cent. The temperature of the liquid metal was determined immediately before casting, and the difference between this and the liquidus temperature of the particular alloy is referred to as the superheat. In general, a constant superheat was adopted, although occasionally an alloy was cast at different temperatures to determine the effect of casting temperature. Particulars of all the castings are given in Table I, the elements being arranged for each percentage in order of increasing effect on the restriction of columnar growth. The effect of some of the elements is considerable, and indeed appears remarkable when the small quantity of the addition is taken into account. Structures representative of alloys of different growth tendencies are illustrated in Figs. 4–7 (Plates IV and V). The experimental results are given in another form in Table II, where the elements are listed in four ranges of atomic percentage.

From an examination of all the data, the relative influence of the different elements in restricting columnar growth was determined. In Table III the elements have been listed in the order of increasing power of restricting growth, those at the top of the list having least effect on the normal tendency of pure copper to form wholly columnar crystals, and those at the bottom showing the greatest effect in restricting growth ; some physical constants of the added elements are included.

TABLE I.—*Influence of Added Elements on Length of Columnar Crystals.*

Height of Ingots 2·8 in.

Addition, Weight Per Cent.	Element.	Superheat, ° C.	Freezing Range, ° C.	Crystal Length, In.
~0·005	Oxygen	115	...	2·5
~0·04	Oxygen	110	17	0·9
0·1	Iron	130	< 1	2·5
	Phosphorus	150	30	1·1
	Nickel	130	< 1	1·0
	Tellurium	115	200	0·9
	Titanium	130	4	0·8
	Arsenic	120	4	0·8
	Oxygen	120	14	0·3
0·2	Zinc	120	< 1	2·5
	Platinum (0·25%)	90	< 1	0·9
	Phosphorus	120	60	0·9
	Sulphur	120	11	0·6
	Lead	120	750	0·3
0·5	Bismuth	130	800	2·5
	Zinc	120	1	2·5
	Aluminium	130	< 1	2·5
	Chromium	130	< 1	2·4
	Manganese	130	<10	2·2
	Iron	160	< 1	2·1
	Calcium	130	170	1·8
	Silicon	110	9	1·4
	Lithium	120	800	1·4
	Cerium	130	200	1·2
	Beryllium	100	40	1·1
	Magnesium	110	60	1·0
	Silver	120	5	1·0
	Molybdenum	130	...	1·0
	Antimony	80	20	0·9
	Boron	100	...	0·9
	Phosphorus	130	150	0·85
	Titanium	140	18	0·8
	Tin	200	15	0·8
	Cadmium	120	300	0·7
	Sulphur	130	6	0·6
	Selenium	90	15	0·5
	Tin	100	15	0·5
	Lead	110	750	0·3
	Platinum	120	2	0·3
1·0	Zinc	100	2	2·4
	Vanadium	120	...	2·4
	Chromium	180	< 2	2·2
	Manganese	130	15	2·1
	Tantalum	130	...	2·0
	Barium	130	...	2·0
	Tungsten*	150	...	1·9
	Magnesium	130	120	1·3
	Molybdenum	150	...	1·3
	Zirconium	150	110	1·1
	Cobalt	100	< 2	1·0
	Beryllium	120	80	0·9
	Silver	100	10	0·9
	Phosphorus	180	300	0·9
	Calcium	10	~150	0·4
	Calcium	140	~150	0·8
	Cadmium	100	430	0·7
	Antimony	120	40	0·7
	Tellurium	115	200	0·6
	Nickel	120	5	0·6
	Silicon	100	18	0·6
	Arsenic	130	45	0·4
	Thallium	130	775	0·3
	Tin	130	35	0·3
	Lead	130	750	0·25
2·0	Bismuth	140	810	2·3
	Aluminium	140	2	2·3
	Iron	160	3	1·4
	Magnesium	120	230	0·9
	Antimony	100	100	0·8
	Calcium	110	140	0·7
	Silicon	110	35	0·7
	Titanium	115	70	0·7
	Tin	200	70	0·5

* Incomplete solution in liquid state.

Temperature Gradient Determination.

In order to obtain some information on the temperatures existing in the ingot during and after solidification, tests were carried out using four thermocouples suspended along the centre line of the ingot at 1 in.

PLATE III.

FIG. 2.—Assembly of Four Thermocouples.

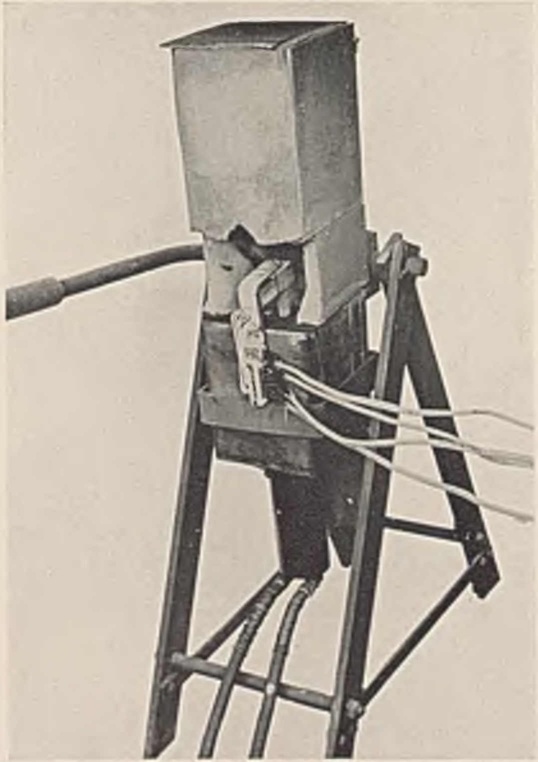


FIG. 3.—Thermocouples and Casting Apparatus.

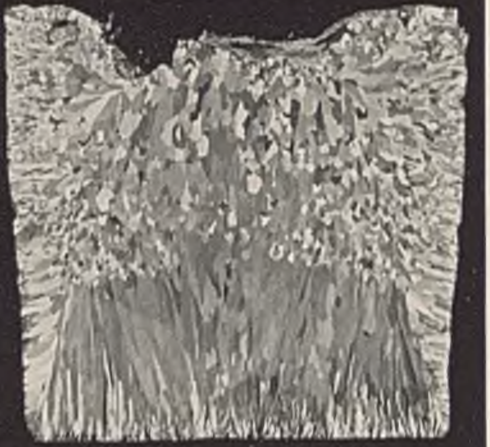
[*To face p.* 104.

PLATE IV.

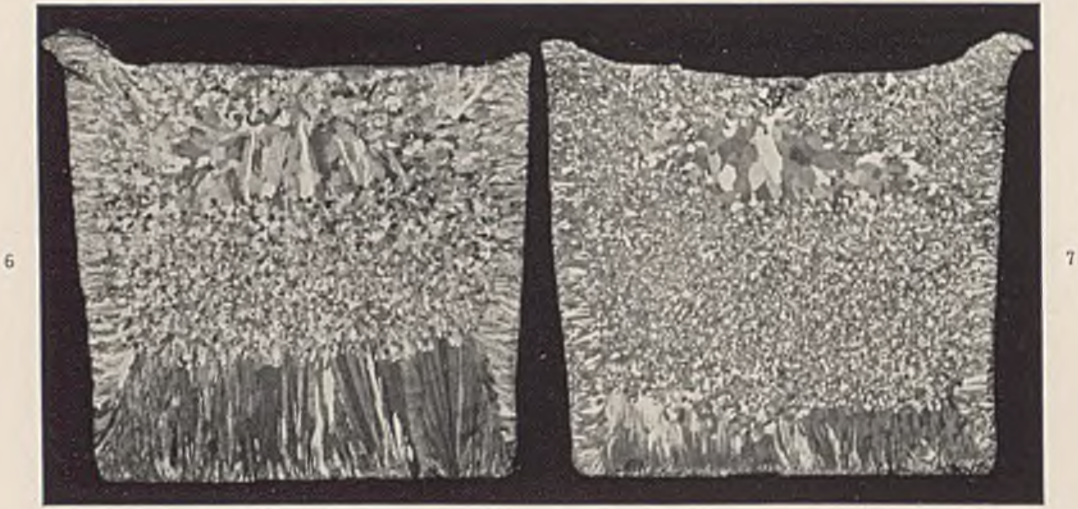
4

1% Zinc.

5



1% Molybdenum.



0·1% Titanium. 0·5% Selenium.

FIGS. 4-7.—Crystal Structures of Copper Alloy Ingots showing Columnar Crystals of Different Length Growing from Base of Ingot. × $\frac{2}{3}$.

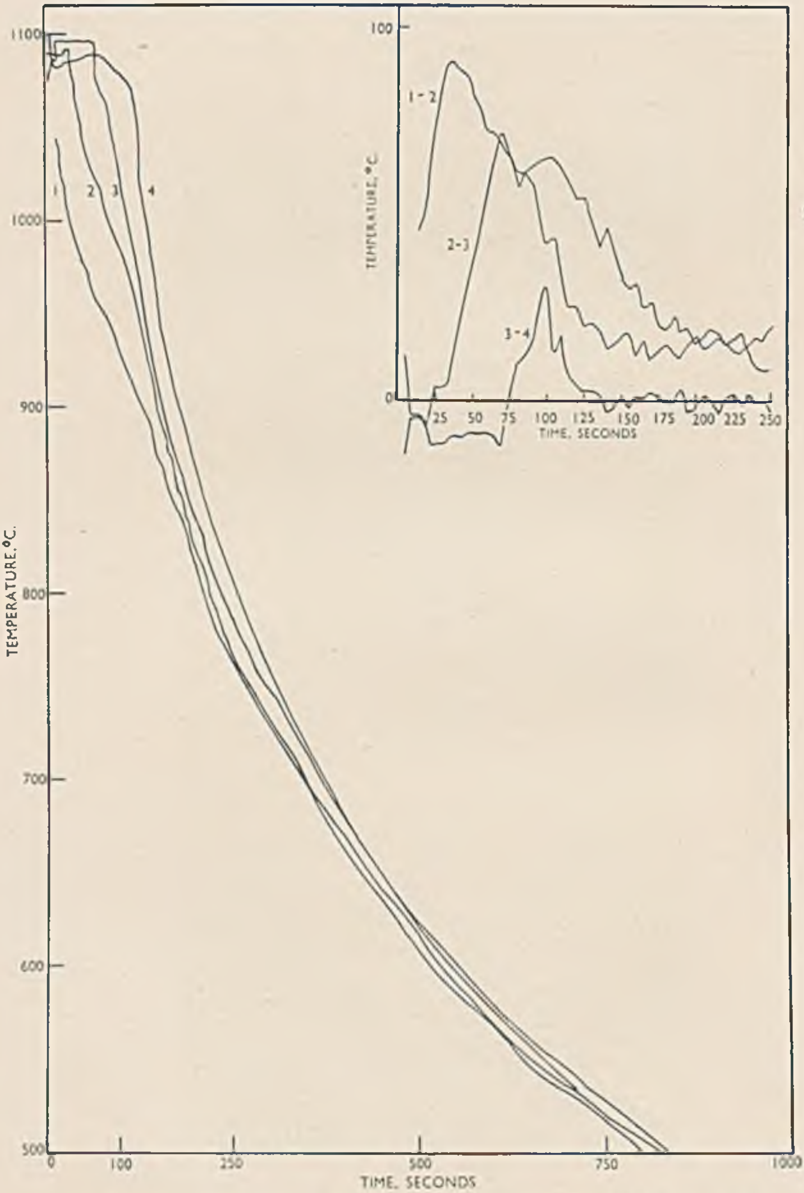


FIG. 8.—Time–Temperature Curves from Four Thermocouples, No. 1 near Ingot Base.

FIG. 9 (inset).—Temperature Gradient–Time Curves.

intervals from the water-cooled copper base. The thermocouple assembly is shown in Fig. 2 (Plate III), and the apparatus immediately

TABLE II.—*Influence of Added Elements on Length of Columnar Crystals.*

Additions in Atomic Per Cent.

Addition, Atomic Per Cent.	Element.	Crystal Length, In.	Addition, Atomic Per Cent.	Element.	Crystal Length, In.
<0·4			0·78–1·6		
0·15	Bismuth	2·5	1·18	Aluminium	2·5
0·20	Zinc	2·5	1·25	Vanadium	2·4
0·12	Iron	2·5	0·97	Zinc	2·4
0·35	Tantalum	2·0	1·24	Chromium	2·2
0·23	Cerium	1·2	1·16	Manganese	2·1
0·33	Molybdenum	1·0	0·78	Calcium	1·8
0·20	Phosphorus	1·1	1·53	Calcium	0·8
0·30	Silver	1·0	1·14	Silicon	1·4
0·26	Antimony	0·9	1·31	Magnesium	1·0
0·28	Cadmium	0·7	1·08	Cobalt	1·0
0·11	Nickel	1·0	1·05	Antimony	0·8
0·16	Oxygen	0·9	1·03	Phosphorus	0·9
0·13	Titanium	0·8	1·08	Nickel	0·6
0·08	Platinum	0·9	1·0	Sulphur	0·6
0·085	Arsenic	0·8	0·85	Arsenic	0·4
0·05	Tellurium	0·9	1·08	Tin (200°)	0·5
0·27	Tin	0·5			
0·31	Thallium	0·3			
0·16	Platinum	0·3			
0·06–0·15	Lead	0·3			
0·31	Lead	0·25			
0·4–0·7			>2·0		
0·49	Zinc	2·5	4·72	Aluminium	2·3
0·61	Chromium	2·4	4·58	Lithium	1·4
0·61	Bismuth	2·3	2·28	Iron	1·4
0·58	Manganese	2·2	2·62	Magnesium	1·3
0·46	Barium	2·0	3·53	Beryllium	1·1
0·57	Iron	2·1	7·06	Beryllium	0·9
0·66	Molybdenum	1·3	2·95	Boron	0·9
0·70	Zirconium	1·1	2·05	Phosphorus (180°)	0·9
0·59	Silver	0·9			
0·41	Phosphorus	0·9	3·18	Calcium	0·7
0·66	Titanium	0·8	4·54	Silicon	0·7
0·57	Cadmium	0·7	2·27	Silicon (100°)	0·6
0·53	Antimony	0·7	2·64	Titanium	0·7
0·50	Tellurium	0·6			
0·41	Selenium	0·5			
0·54	Tin	0·3			
0·40	Oxygen	0·3			

after casting in Fig. 3 (Plate III). The hot-junctions were protected by a thin wash of carborundum cement so that, although the first couple was placed as near as possible to the chill base of the mould, metal-to-metal contact was prevented by the carborundum insulation. Readings of the four indicators were taken by four observers at 5-second intervals during and after casting, and were then plotted in the form of time–temperature curves, one example of which is shown in Fig. 8 (Plate VI), the alloy concerned being that of copper with 0·2 per cent. phosphorus; the three curves given in Fig. 9 (Plate VI) show the differences in temperature between couples 1 and 2, 2 and 3, and 3 and 4, plotted against time. Although the mass and cooling effect of the thermocouples and their thin refractory insulators would lead to some difference between the temperature gradient thus determined and that normally existing in the absence of the thermocouples, the difference is probably small, and the values at least give some idea of the order of the temperature gradient existing in the ingot.

The curves in Fig. 9 show that the temperature gradient in the lowest 1 in. of the ingot reaches a maximum of about 90° C. per in. in 35 seconds and then falls; that the gradient becomes smaller with increasing distance from the base of the ingot; and that for a period of about 1¼ minutes there is a reverse gradient at the top of the ingot, due, presumably, to the cooling of the top surface by the air above it. The effect of this reverse gradient is shown in the ingot structure by crystals growing down for a short distance from the top of the ingot.

CONSIDERATION OF RESULTS IN RELATION TO ATOMIC STRUCTURE OF ADDED ELEMENTS.

In seeking an explanation of the very different effects exerted by different elements on the crystallization of copper, it was natural to examine the properties of the various elements in order to correlate one or more of these properties with that under review. It was expected that lattice type, atomic volume, inter-atomic distance, degree of solid solubility, tendency to form metallic compounds, freezing range, or effects due to surface tension might play a part in influencing the growth of the crystal. As will be observed from the values of some of these properties given in Tables I and III, it is clear that their effect, if any, is small and is completely outweighed by that of some major property; thus the effect on crystal size would appear to be a characteristic property of each individual element. The apparent absence of any effect due to difference in lattice type or dimensions is in agreement with the results obtained by Hothersall [1] on the continuation in electrodeposits of the crystal structure of the basis metal. Certain of the properties referred to above may, however, exert some effect in any one metallic system when the proportion of the added element is varied. It would appear from Table I that the crystallization is

TABLE III.—*Influence of Added Elements on Crystal Length. Relative Growth-Restricting Factor and Some Physical Constants.*

Element.	Atomic Number.	Atomic Weight.	Atomic Volume, cm.^{3}/grm.-atom.	Atomic Radius, cm. × 10^8.	Crystal Structure.	Inter-atomic Distance, A.	Specific Heat.	Maximum Solid Solubility in Cu at Solidus, Atomic-%.	$R = \frac{\sqrt{N}}{r'c}$ (see p. 113).	Growth-Restriction Factor.
Bismuth	83	209·00	21·33	2·03	rhom.	3·105, 3·474	0·0303	~ 0	1·33	1
Aluminium	13	26·97	10·03	1·58	f.-c. cube	2·856	0·217	17	1·33	2
Zinc	30	65·38	9·16	1·53	c.-p. hex.	2·659, 2·906	0·0924	32	2·35	3
Vanadium	23	50·95	8·92	1·52	b.-c. cube	2·60	0·1153	...	0·908	4
Chromium	24	52·01	7·32	1·42	α—b.-c. cube	2·492	0·110	1+	1·285	5
					β—c.-p. hex.	2·709, 2·717				
Manganese	25	54·93	7·52	1·43	cubic (complicated)	2·24–2·96	0·11	~80	1·572	6
Tantalum	73	181·45	11·2	1·64	b.-c. cube	2·856	0·036	...	0·908	7
Barium	56	137·36	38·2	2·10	b.-c. cube	4·34	0·068	...	1·588	8
Tungsten	74	184·0	9·63	1·56	b.-c. cube	2·735	0·034	~ 0	1·285	9
Iron	26	55·84	7·1	1·40	α—b.-c. cube	2·477	0·113	4	1·815	10
					γ—f.-c. cube	2·52				
Lithium	3	6·94	13·0	1·72	b.-c. cube	3·04	0·0795	< 1	1·666	11
Cerium	58	140·13	...	...	α—c.-p. hex.	3·63, 3·65	0·0448	< 5	1·778	12
					β—f.-c. cube	3·63		v. small		
Magnesium	12	24·32	14·0	1·76	c.-p. hex.	3·190, 3·202	0·248	7	2·35	13
Molybdenum	42	96·0	9·42	1·55	b.-c. cube	2·719	0·072	< 2	2·105	14
Cobalt	27	58·94	6·70	1·38	α—c.-p. hex.	2·49, 2·507	0·104	4	2·03	15
					β—f.-c. cube	2·507				
Zirconium	40	91·22	13·97	1·71	α—c.-p. hex.	3·16, 3·22	0·068	~ 0	2·42	16
					β—b.-c. cube	3·12				
Silver	47	107·88	10·27	1·59	f.-c. cube	2·883	0·050	5	2·38	17
Antimony	51	121·76	18·20	1·93	rhom.	2·89, 3·35	0·05625	5·5	1·905	18
Beryllium	4	9·02	4·90	1·24	c.-p. hex.	2·223, 2·267	0·425	17	2·35	19
Calcium	20	40·08	25·85	2·16	f.-c. cube	3·93	0·157	1·6	2·35	20
					hex. (>450° C.)	3·98, 3·99				
Silicon	14	28·06	...	...	diamond	2·34	0·179	12	2·85	21
Boron	5	10·82	...	...	...	...	0·307	~ 0	2·47	22
Phosphorus	15	31·02	...	...	rhom.	1·74, 3·01	0·19	3·4	3·19	23
Cadmium	48	112·41	13·01	1·73	c.-p. hex.	2·973, 3·286	0·0540	1·5	3·37	24
Nickel	28	58·69	6·67	1·38	α—c.-p. hex.	2·49	0·1089	100	2·23	25
					β—f.-c. cube	2·486				
Titanium	22	47·90	10·7	1·62	c.-p. hex.	2·91, 2·95	0·142	4	2·67	26
Tellurium	52	127·61	...	...	c.-p. hex.	2·858, 3·46	0·048	~ 0	2·69	27
Sulphur	16	32·06	...	...	...	...	0·1728	~ 0	3·5	28
Arsenic	33	74·91	13·11	1·73	rhom.	2·508, 3·146	0·082	6·2	3·19	29
Selenium	34	78·96	...	...	c.-p. hex.	2·316, 3·457	0·084	~ 0	3·5	30
Tin	50	118·7	16·30	1·86	diamond	2·797	0·055	7	4·08	31
					tetragonal	3·016, 3·175				
Oxygen	8	16·0	...	...	...	...	0·35 (liq.)	< 0·03	3·5	32
Platinum	78	195·23	9·12	1·53	f.-c. cube	2·768	0·032	100	2·23	33
Thallium	81	204·39	17·25	1·89	α—c.-p. hex.	3·4, 3·45	0·0326	<10	2·47	34
					β—f.-c. cube	3·42				
Lead	82	207·22	18·27	1·93	f.-c. cube	3·492	0·0305	~ 0·01	2·85	35
Copper	29	63·57	7·10	2·41	f.-c. cube	2·551	0·093	...	1·66	...

independent of, for example, the freezing range.* Now, the freezing range would be expected to play a part in the determination of crystal size in the freezing of any one alloy system, but it assumes much less importance when different alloying elements are compared. The influence of the freezing range will be discussed in more detail in a later paper.

Although the relative order of the influence of the different added elements varies slightly, depending on the proportions present, they have been given a number which, for want of a better term, has been termed the "growth-restriction factor": this appears in Table III, in the last column. This number has no real meaning as an absolute unit, of course, but is merely intended to denote the comparative effect of the different elements when added in small quantities, those with large factor numbers having greater effect than those with small numbers on the restriction of columnar growth of copper from the melt. It should be made clear that in this paper the actual numbers given to the different elements are intended to apply only to their effect on the crystallization of copper (or copper-rich alloys) from the melt. Whether the same or similar factors characterize the elements in their influence on the growth of, say, iron or any other metal from its melt is solely a matter for further experiment.

When the arrangement of the elements given in Table III is compared with that in the Periodic Table, it becomes evident that the effect of the elements on the crystallization of copper is a periodic one, and the periodicity becomes more pronounced when the elements in the long periods are considered to be arranged in groups of four instead of in groups of eight. Quite apart from its application in the present work, the division into two sections, each of four groups, is justified by the electro-negative or electro-positive characteristics of the elements. As it is known that in the metallic state metals are electro-positive, it is reasonable to divide the octet between group IV and group V and to consider the valency effect only in so far of course as it concerns the metals of groups I to IV and of groups V to VIII. This division is frequently made when classifying the elements for purposes of separating the electro-positive from the electro-negative ones as regards their maximum possible valencies. This sub-division applies particularly in the cases of the strongly-metallic metals in the A sub-groups of groups V and VI, but less in the B sub-groups. The difference in metallic nature between the elements in the A and B sub-groups decreases in the higher

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* This value represents the difference between the liquidus and solidus temperatures for the particular composition given. The temperatures were obtained from the published work on the equilibrium diagrams of the different systems and were not checked experimentally in the present investigation.

TABLE IV.—*Periodic Table, Showing Atomic Numbers and Growth-Restriction Factors.*

Period.	Zero Group.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.		
1	2 Helium	3 *Lithium* 11	4 *Beryllium* 19	5 *Boron* 22	6 Carbon	7 Nitrogen	8 *Oxygen* 32	9 Fluorine			
2	10 Neon	11 Sodium	12 *Magnesium* 13	13 *Aluminium* 2	14 *Silicon* 21	15 *Phosphorus* 23	16 *Sulphur* 28	17 Chlorine			
3	18 Argon	19 Potassium	20 *Calcium* 20	21 Scandium	22 *Titanium* 26	23 *Vanadium* 4	24 *Chromium* 5	25 *Manganese* 6	26 *Iron* 10	27 *Cobalt* 15	28 *Nickel* 25
		29 Copper	30 *Zinc* 3	31 Gallium	32 Germanium	33 *Arsenic* 29	34 *Selenium* 30	35 Bromine			
4	36 Krypton	37 Rubidium	38 Strontium	39 Yttrium	40 *Zirconium* 16	41 Niobium	42 *Molybdenum* 14	43 Masurium	44 Ruthenium	45 Rhodium	46 Palladium
		47 *Silver* 17	48 *Cadmium* 24	49 Indium	50 *Tin* 31	51 *Antimony* 18	52 *Tellurium* 27	53 Iodine			
5	54 Xenon	55 Cæsium	56 *Barium* 8	57 Lanthanum	58 *Cerium* 12 +Rare earths —72	73 *Tantalum* 7	74 *Tungsten* 9	75 Rhenium	76 Osmium	77 Iridium	78 *Platinum* 33
6		79 Gold	80 Mercury	81 *Thallium* 34	82 *Lead* 35	83 *Bismuth* 1	84 Polonium	85 ...			
7	86 Radon	87 ...	88 Radium	89 Actinium	90 Thorium	91 Protactinium	92 Uranium				

periods, and it is noticeable that in these the A and B elements show less differences in their effects on the crystallization of copper. Table IV

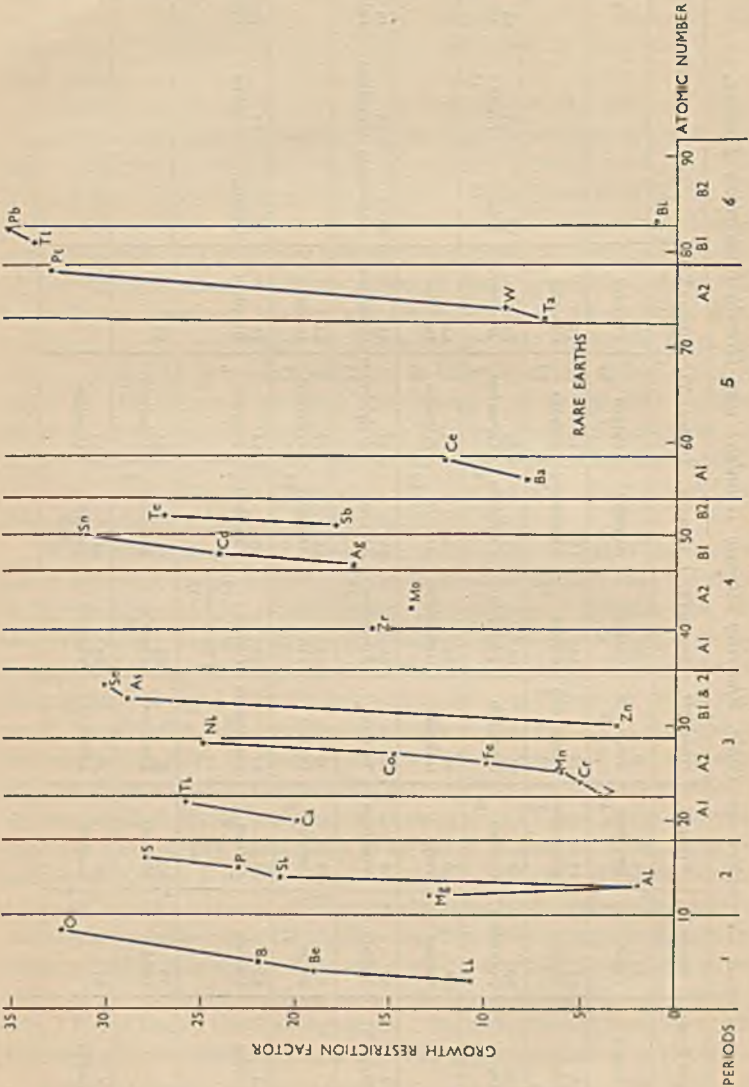

Fig. 10.

shows the usually accepted form of the Periodic Table; the elements given in italic type are those employed in the present work, the number before the element is its atomic number and the one after it the "growth-restriction factor." The periodic nature of the influence of the different elements is also illustrated in Fig. 10, in which the growth-restriction factors are plotted against the atomic numbers. The thin vertical lines represent the divisions between the different periods and between the quartets in the long periods. The thick sloping lines connect the values for the growth-restriction factors of the elements in any one section, and the similarity in the slope of these lines indicates the general periodic nature of the growth-restriction effect. The position of aluminium is discussed on p. 113.

It was natural, therefore, to connect the property of growth restriction with valency, but it was soon evident that, although as a general rule elements of low valency affected columnar crystallization less than those of high valency, elements having the same valency did not necessarily exert identical effects on the crystal growth. An examination of the electron structure as classified into the different quantum groups suggested a possible explanation of this point. Not only the number of electrons but also their sub-grouping appears to be important. In general, all those elements in which the effective electron sub-group (by effective electron sub-group is meant the sub-group of electrons which gives the element its characteristic properties) comes immediately after a fully-completed sub-group, and there are no electrons in a sub-group of higher quantum number, have a fairly pronounced influence in reducing the crystal size. Further, the effect rapidly increases with the number of electrons in any one of the short periods, or in a quarter period in the case of the long periods of the Periodic Table. To distinguish this grouping from others it is termed "open." Very open grouping is that in which there exists an unfilled sub-group of lower quantum number; elements having such a grouping exert a still more pronounced effect. On the other hand, a "screened" grouping is one in which there exists a sub-group of higher quantum number than the effective electron sub-group, and as a whole these elements have small effect on crystallization. In addition, the second quantum number of the sub-group appears to be important, since the effective sub-groups in which the second quantum number is low belong to elements having high growth-restriction factors.

The principle may be better understood from Table V, which shows the uncompleted electron grouping of the different elements. The last two columns give the effective electron sub-group and particulars of the "open" or "screened" nature of this sub-group for the elements here examined. Comparison with Table III, giving the order of the elements with respect to their growth-restricting power, shows that, in general, elements having low factor numbers have only one or two electrons in the effective sub-groups, and usually these latter are "screened," *e.g.* vanadium, tantalum, chromium, and barium. With a greater number

TABLE V.—*Atomic Structures.*

Elements in italics examined in the present work.
Earlier quantum levels to be taken as completed.

	L		Effective Sub-group.	Open or Screened.
	s	p		
3 *Li*	1		L_s	open
4 *Be*	2			
5 *B*	2	1	L_{s+p}	
6 C	2	2		
7 N	2	3		
8 *O*	2	4		
9 F	2	5		
10 Ne	2	6		

	M					N	Effective Sub-group.	Open or Screened.
	s	p_1	p_2	d_2	d_3	s		
11 Na	1						M_s	open
12 *Mg*	2							
13 *Al*	2	1					M_p	
14 *Si*	2	2					M_{s+p}	
15 *P*	2	2	1					
16 *S*	2	2	2					
17 Cl	2	2	3					
18 A	2	2	4					
19 K	2	2	4			1	M_d + N_s	open
20 *Ca*	2	2	4			2		
21 Sc	2	2	4	1		2		
22 *Ti*	2	2	4	2		2		
23 *V*	2	2	4	2	1	2	M_{d_3}	screened
24 *Cr*	2	2	4	2	2(3)	2(1)		
25 *Mn*	2	2	4	2	3	2		
26 *Fe*	2	2	4	2	4	2		
27 *Co*	2	2	4	2	5	2		
28 *Ni*	2	2	4	2	6	2		

	N			Effective Sub-group.	Open or Screened.
	s	p_1	p		
29 *Cu*	1			N_s	open
30 *Zn*	2				
31 Ga	2	1		N_{s+p}	
32 Ge	2	2			
33 *As*	2	2	1		
34 *Se*	2	2	2		
35 Br	2	2	3		
36 Kr	2	2	4		

	N					O				P	Effective Sub-group.	Open or Screened.
	s	p	d_2	d_3	f	s	p_1	p_2	d	s		
37 Rb	2	6				1					N_d + O_s	
38 Sr	2	6				2						
39 Y	2	6	1			2						
40 *Zr*	2	6	2			2						
41 Nb	2	6	2	2		1					N_{d_3}	screened
42 *Mo*	2	6	2	3		1						
43 Ma	2	6	2	4		1						
44 Ru	2	6	2	5		1						
45 Rh	2	6	2	6		1						
46 Pd	2	6	4	6		...						
47 *Ag*	2	6		10		1					O_s	very open
48 *Cd*	2	6		10		2						
49 In	2	6		10		2	1				O_{s+p}	
50 *Sn*	2	6		10		2	2					
51 *Sb*	2	6		10		2	2	1			O_{p_2}	
52 *Te*	2	6		10		2	2	2				
53 I	2	6		10		2	2	3				
54 Xe	2	6		10		2	2	4				
55 Cs	2	6		10		2	6			1	N_f + O_d + P_s	well screened
56 *Ba*	2	6		10		2	6			2		
57 La	2	6		10		2	6		1	2		
58 *Ce*	2	6		10		2	6		1	2		

Rare Earths.

	O				P	Effective Sub-group.	Open or Screened.
	s	p	d_2	d_3	s		
73 *Ta*	2	6	2	1	2	O_{d_3}	screened
74 *W*	2	6	2	2	2		
75 Re	2	6	2	3	2		
76 Os	2	6	2	4	2		
77 Ir	2	6	2	5	2		
78 *Pt*	2	6	2	6	2		

	P			Effective Sub-group.	Open or Screened.
	s	p_1	p_2		
79 Au	1			P_s	open
80 Hg	2				
81 *Tl*	2	1		P_{s+p}	
82 *Pb*	2	2			
83 *Bi*	2	2	1	P_{p_2}	
84 Po	2	2	2		
85 —	2	2	3		
86 Rn	2	2	4		

of electrons, particularly when the sub-group is "open," the growth-restriction factor is high, *e.g.* oxygen, sulphur, and selenium. With a "screened" sub-group it requires a large number of electrons for the element to have a high factor number, *e.g.* nickel or platinum (each with 6 electrons). On the other hand, elements having a "very open" sub-group have a high factor number, even when the number of electrons is small, although again the factor number increases with the number of electrons, see, for example, the elements silver to tellurium. Zinc, which has 2 electrons in an "open" sub-group, has a very low factor number and is thus an exception to the general rule; this may be due to the fact that zinc follows copper in the Periodic Table.

It does seem possible, therefore, to correlate the effect of the different elements of restricting columnar growth with the number and grouping of the electrons in their atoms. The relationship may be shown by a simple empirical formula of the type:

$$R = \frac{\sqrt{N}}{s'c}$$

where R is the relative growth-restricting power, s' is the screening factor to allow for variation in degree of binding, and termed s' to distinguish it from Pauling's screening constant, N is the number of effective electrons, and c is a constant, whose value depends on the second quantum number. Although it is probable that the screening constant s' will be different for similar terms in different K, L, M . . . levels, for the sake of simplicity single values have been given here as follows: 1 for an "open" sub-group, 0·7 for a "very-open" sub-group, 1·1 for a "screened" and 1·5 for a "well-screened" sub-group. c has been given the values: 0·6 for the s shell, 0·75 for the p shell, 0·7 where both s and p shells operate, 1·0 for the d or f shell, and 0·75 where both s and d shells operate.

The values of R for the different elements as computed from this formula are given in the last column but one of Table III, and it will be seen that the relative order of the elements according to these values approximates to that found by experiment. The value for copper is included, and it would appear that elements having the same or smaller R values show little effect in reducing the columnar crystal growth of the copper. It has been observed that aluminium has little effect on the structure; even when it is present in appreciable quantities, the resulting alloy shows a strong tendency to solidify in columnar form. This behaviour may be connected with the suggestion by Hume-Rothery [2] that aluminium is not fully-ionized in the metallic crystal. For this reason only the $1p$ electron has been considered in computing the value of R for aluminium in Table III. The agreement between the relative positions of aluminium as so calculated and as found by experiment may be considered to support Hume-Rothery's suggestion.

THEORETICAL DISCUSSION.

Since the attractive forces between atoms in metals are imperfectly understood, it is clearly impossible to put forward any complete explanation of the results of the experimental work. At the same time we are justified in attempting to obtain a picture of the mechanism controlling the growth of crystals from the melt, provided that our views do not conflict with those substantiated by experiment in other directions. The problem will be considered under the headings: 1. Effects due to a composition gradient; 2. Effects due to adsorption.

1. *Effects Due to a Composition Gradient.*

The first and most simple explanation of the formation of equi-axial crystals in place of columnar crystals depends on the formation of a composition gradient parallel to the direction of crystal growth. With a perfectly pure metal, the composition of the solid and liquid is the same throughout and, given the existence of a temperature gradient with the lower temperature below the solidifying temperature, wholly-columnar crystals must form. In the case of any alloy which solidifies over a range of temperature, the presence of a temperature gradient leads also to a composition gradient in which the higher melting point phase is in excess in the position corresponding to the lower temperature. This, of course, is the well-known phenomenon of differential solidification, which is shown by many cast alloys and which is liable to occur quite independently of the type of alloy formed, *i.e.* irrespective of whether one or more phases occur in the solid state or whether these are solid solutions, compounds, eutectics, &c. Differential solidification depends on the fact that where an alloy solidifies over a temperature range, the alloy first solidifying is of different composition from the liquid and diffusion in the solid crystal is alone able to produce homogenization. Therefore in the absence of complete diffusion the crystal is not uniform in composition and "cored" and "dendritic" structures, with which all metallurgists are familiar, are observed in the cast alloy.

A steep temperature gradient in an alloy in which the second constituent diffuses slowly may lead to an enrichment of the lower melting point constituent in the liquid layer adjacent to the solid so that the next layer in the liquid may reach the liquidus temperature of the alloy first and independent solid nuclei will appear and, since these will be of random orientation, equi-axial crystals will be formed. The process is shown diagrammatically in Fig. 11, in which the composition full line, and the temperature chain line, are plotted against position in the freezing alloy measured perpendicularly from the mould face, and the horizontal dotted line represents the average composition of the alloy. It is probable that there will be a slight kink in the temperature gradient curve, as shown in the diagram, at the solid-liquid interface, owing to the evolution of latent heat from the solidifying metal. This heat evolution will assist in delaying the solidification of the layer richest in low melting point constituent. As the heat conductivity of the liquid will be less than that of the solid, the two portions of the temperature gradient curve will have different slopes, but this does not affect the argument.

Now, the temperature gradient line is moving continuously downwards towards the abscissa as the temperature decreases and at some particular instant when the point on the temperature gradient curve corresponding with the liquidus temperature touches the mean composition line, crystallization will take place at the independent nuclei represented by the crosses in the diagram. With further decrease in temperature the liquid between these independent crystals and the earlier-formed solid will solidify, but by this time the continuity in direction of growth will be at least partly broken, so that the length of the columnar crystals will correspond to the distance between the row of independent crystals and the mould face. It has been shown in an earlier paper [3] that some such action may take place, and an explanation on these lines was put forward to account for the periodic structures found in a number of specially-prepared ferrous and non-ferrous alloy ingots in which the formation of a row of crystals of random orientation was repeated several times.

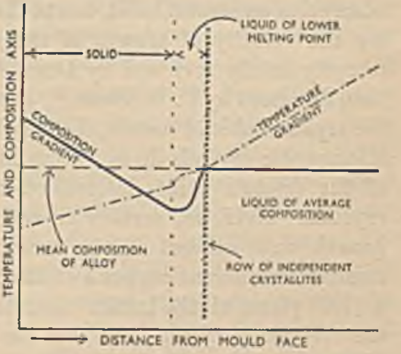

Fig. 11.

Although this effect may be in operation during the solidification of the ingots now considered, it is doubtful whether the explanation is wholly adequate. For one reason, if it be assumed that with the different elements present in solution in such small quantities, the heat conductivity of molten copper solutions is not vastly different, compared one with another, the rates of diffusion of the different elements in hot, solid copper do not follow the order of their effect upon crystal growth. Also, it was shown in the earlier paper that slight interference with columnar growth may occur several times within the length of the columnar crystal aggregates, and that with copper-rich alloys in particular, continuity in direction of growth may be maintained in spite of such interference. At the same time, the possibility of the occurrence of the action depicted in Fig. 11 should not be dismissed completely, since the effect may reach a maximum at the position corresponding with the limit of growth of the columnar crystals, and the increasing coarseness of the periodic lines away from the mould, as observed in the earlier work, lends support to this view. It is evident that another and more important phenomenon is in operation and this will now be considered.

2. *Effects Due to Adsorption.*

An alternative, and more complete, explanation is that the influence of the added elements is a result of adsorption. The effect of adsorption on crystal habit, due to the presence of foreign atoms modifying the velocity of growth of the different crystal planes, has been recently briefly reviewed by Desch,[4] and the theory of adsorption has been discussed by C. W. Bunn.[5] From the point of view of the effect on the crystal habit of metals, the problem is complicated by the fact that idiomorphic crystals do not occur in metal ingots, the external shapes of the crystals being determined by obstruction from neighbouring crystals. Even so, certain crystal planes have higher velocities of growth than others. X-ray examination of columnar crystals in a number of different copper α-solid solution alloy ingots has shown that a (100) plane of the lattice coincides with the direction of growth of the columnar crystals, but that the orientations normal to this plane differ in adjacent crystals. As would be expected, the equi-axial crystals above were differently oriented in all three planes. Without direct observation, such as by the growth of crystals direct from the vapour phase, it is clearly a difficult matter to prove that in metal ingots changes in crystal habit are due to preferential growth of one plane, owing to obstruction of others by adsorption of the solute atoms.

Since it appears most likely, however, that adsorption is at least partly responsible for the phenomenon now being discussed, fresh light may be thrown on the theory of adsorption by an examination of the results of the present work. Bunn [5] has discussed the similarity between adsorption and the formation of mixed crystals, and considers that in adsorption the amount of impurity taken up depends in a highly specific way on the nature of the face, whereas in mixed crystal formation it does not. The similarity which Bunn proposes is not at all clear, however. He gives examples in which there are little or no solubility ranges, and states that if the equilibrium solubilities are zero, adsorption bodies should be described as " unstable mixed crystals." In the present instance, however, even if solid solubility is considered as essential for adsorption, it is unlikely that any objection would be valid which was raised on the score that existing equilibrium diagrams of some of the copper alloys examined show the added element to have no solid solubility in copper. Firstly, there is no certainty that there is such a thing as absolute insolubility, especially when referring to an element in copper at its solidifying temperature. It is characteristic of a large number of metallic solid solutions that the solubility increases with temperature and it is now being appreciated that even in instances where the solid solubility of one metal in another is very small indeed at atmospheric temperatures, it may be appreciable at temperatures approaching the melting point. Even where the solubility is too small at atmospheric temperature to be conveniently determined by chemical analysis, the fact that there is some at higher temperatures may be shown by microscopical means, as has been done in the case of metallic oxides in metals.[6] Secondly, as Bunn himself has pointed out, some adsorption bodies in the dry state later separate into two solid phases although they appear first to crystallize as a solid solution. Since atom migration leading to such separation can occur in the solid crystal at atmospheric temperature, it is likely to occur much more readily in metals at temperatures in the neighbourhood of their melting points.

As to the precise nature of the effect of adsorption on crystal growth in the case of copper solidifying from the melt, the following theory is put forward. In the early stages of crystal growth the copper atoms arrange themselves in a lattice to form the crystal and at some stage the foreign atoms become adsorbed on the face of the growing crystal. The degree of adsorption will depend on the number of foreign atoms in the melt and on the binding power between the parent and foreign atoms. The greater the degree of adsorption the greater will be the resistance offered to the attachment of more copper atoms to the lattice, and presumably also the greater will be the distortion or irregularity at the surface of the growing crystal, so that when, finally, groups of atoms in the liquid have their mobility arrested by decrease in temperature such that they " solidify," they will not adopt the same orientation as the already solid copper on account of the " screening " action of the adsorbed layer.

Although the number of layers in any adsorbed film is in dispute, it is generally agreed to be very small. Whipp,[7] in an examination of the adsorption of iodine by potassium iodide, concluded that there exists a strongly adsorbed layer of molecules which attracts to itself a second layer by the action of much weaker fields, and that the forces binding the molecules in the second layer are much less than those binding the molecules in the first. The present results indicate that some such effect is in operation in the adsorption of foreign atoms on copper crystals growing from the melt. Since adsorption is a surface phenomenon, it seems that the attractive forces exerted by the solid surface are satisfied by the process of adsorption so that an adsorbed surface then offers little attraction to the attachment of further atoms, *i.e.* the effective range of the new surface forces of the adsorbed layer is extremely small. This effect of the adsorbed layer is analogous to that observed in the condensation of hydrogen on metal surfaces, where a much greater number of hydrogen molecules condenses on an absolutely clean surface than on one already covered with an adsorbed hydrogen layer.

There is some similarity between this explanation of the results of the present work, and the usually-accepted view of the effect of adsorbed foreign matter in reducing the crystal size of metals deposited electrolytically from aqueous solutions of their salts. Practical application is made of this phenomenon in industry in refining the crystal structure and improving the quality of electrodeposits.

It may be considered that there is some similarity between the present explanation and that put forward in the previous section, but, whereas in the composition gradient hypothesis the screening action is due to a liquid layer, in this case it is a solid layer which is effective. The difference may possibly only be one of degree.

The correspondence between valency and growth-restriction factor suggests that the binding power between the atoms is in some way responsible, and that it is not the size factors of the atoms, nor indeed their arrangement, since, as pointed out by Mott,[8] this is not much less regular in the liquid than it is in the solid.

In the present instance, the binding power of the adsorbed atom will be of the utmost importance, since a lightly-bound atom will have small stability and may easily be rejected by the growing crystal. Two cases may be considered, one in which the foreign atom is readily soluble in the solid copper and the other in which there is little or no solid solubility. The results show that the lightly-bound atoms have little effect on the structure, which means that they are more readily removed from the sphere of operations. The method of their removal will depend on their solubility relationships with copper. In the first case, where they are readily soluble, it would appear that sufficient diffusion takes place to allow many of the atoms to penetrate beneath the growing surface, and in the second case, the lightly-bound atoms having small solid solubility will be easily rejected by the growing crystal, or will separate as a second phase, as has been shown to occur in the manner previously described. In this connection it is of interest to note that the lower valency elements which are appreciably soluble and which have the smallest growth-restriction factors are those which most readily diffuse in copper. Looking at the problem in another way, a row of strongly-bound adsorbed foreign atoms offers less attraction to copper atoms in the liquid than do lightly-bound foreign atoms or the copper atoms in the solid crystal. The results of the present investigation show that the problem is not one of solid solubility, but principally of binding power of the adsorbed foreign atoms. This appears to be a more concrete hypothesis than the suggestion by Bunn that in adsorption the amount of impurity taken up depends in a highly specific way on the nature of the face.

The chemical nature of adsorption has been discussed on many occasions. Langmuir [9] has stated that there is every reason for the existence of very strong, attractive forces within a short distance of the surface of solid bodies, and that the phenomena of adsorption may be looked upon as a result of unsaturated chemical forces. There is no need, however, to differentiate, as Langmuir does,[10] between the chemical and physical aspects of the question; we consider it simply as being connected with the effective electrons of the adsorbed element. On the lines of Langmuir's adsorption theory, the degree of adsorption would depend upon the primary valence forces. There is probably some analogy with the mechanism of the condensation of metallic vapours, in which Langmuir [11] concluded "free electrons" play an important part.

The important feature brought out by the present work is that, if it be granted that adsorption affects columnar growth, the power of adsorption or binding power of the adsorbed atoms of the different elements, does in fact appear to depend upon their number of effective electrons. That this is so clearly evident from the present work is due to the fact that there has been studied the effect of foreign substances in their elementary form in which the valency conditions are fairly well known.

CONCLUSIONS.

The influence of small additions of alloying elements on the crystal size of copper solidified from the molten state has been determined. The effect is considered to be due to the adsorption of foreign atoms on the surface of the growing crystals. An examination of the valency and atomic structure of the added elements has shown a relationship between these and what has been termed the "crystal growth-restriction factor." Elements of high valency have a greater effect in reducing crystal size than have those of low valency, but the arrangement of the valency electrons is also important. Although the relationship must be looked upon at present as being purely an empirical one, it is too general to be without scientific value, and it is put forward here not only in view of its importance in connection with the crystal structure of metals, but also since it appears to throw some light upon the theory of adsorption. One advantage of the correspondence here submitted is that it includes all the elements examined, and it has not been found necessary to limit it to certain elements depending on solid solubility, atomic size factors, or other relationships.

REFERENCES.

[1] A. W. Hothersall, *Trans. Faraday Soc.*, 1935, 31, 1242.
[2] W. Hume-Rothery, *Phil. Mag.*, 1930, [vii], 10, 217.
[3] L. Northcott, *J. Iron Steel Inst.*, 1934, 129, 171.
[4] C. H. Desch, " The Chemistry of Solids," 1934, p. 43.
[5] C. W. Bunn, *Proc. Roy. Soc.*, 1933, [A], 141, 567.
[6] L. Northcott, *J. Inst. Metals*, 1936, 59, 225.
[7] B. Whipp, *Proc. Roy. Soc.*, 1933, [A], 141, 217.
[8] N. F. Mott, *Proc. Roy. Soc.*, 1934, [A], 146, 465.
[9] I. Langmuir, *Phys. Rev.*, 1916, [ii], 8, 165.
[10] I. Langmuir, *J. Amer. Chem. Soc.*, 1918, 40, 1361.
[11] I. Langmuir, *Phys. Rev.*, 1916, [ii], 8, 173.

APPENDIX.

Since the original publication of this paper, experiments have been carried out with two other alloying elements, indium and gold. Particulars of the castings are given in Table VI.

TABLE VI.

Addition.		Element.	Superheat, ° C.	Crystal Length, In.
Weight, Per Cent.	Atomic, Per Cent.			
1	0·32	Gold	120	2·0
0·5	0·28	Indium	120	0·6
1	0·56	Indium	120	0·4

These results are fully in accord with the positions of gold and indium in the Periodic Table, page 109, and with their R values of 1·666 and 3·53 respectively. It would thus appear that the approximate values of the growth-restriction numbers are : gold 7 and indium 28.

DISCUSSION.

(*Condensed.*)

Dr. W. Hume-Rothery,* M.A., F.R.S. (Member): I expect that a large number of members of the Institute would have said that if there was any subject on which it was hopeless to expect to find a simple valency relation it was that on which the author has experimented. On the experimental side the author's results are highly suggestive, and if they can be carried further they should lead to all sorts of applications.

On the theoretical side, it seems that the explanation is rather unsatisfactory. First of all, in so far as the author discusses his general theories of adsorption and so on, the explanation of the simple valency effect depends on the assumption made, on p. 119, that the adsorption can be regarded as associated with particular individual electrons, which seems to be a highly arbitrary assumption. The idea of effective electrons seems distinctly unsatisfactory, because Table V gives essentially the electron structures of the isolated atoms. The finer details of the table do not hold for the atoms when they are in solid solution or liquid solution. To take a specific example, a transitional metal such as nickel, in the free state, has the structure shown in Table V, in which there are 16 electrons in the M shell and 2 in the N. On the other hand, in the solid element itself the distribution is no longer 16/2; it is an average distribution, which is something like 0·6 N electrons to each atom and 17·4 M electrons. In the case of a nickel atom in solid solution in copper, the distribution is shifted still further, for there are no N electrons and 18 M electrons. That is a very general statement, due to the fact that the atoms are being drawn closer and closer together, and it holds equally for an atom in a liquid solution as for one in a solid. The finer details of the distribution depend on the particular structure. The general phenomenon is a simple characteristic of the closing of the atoms together from the free state, so that it seems to me that the atomic structures given in Table V do not apply to the experimental conditions.

I have discussed this matter with two leading physicists, who certainly understand far more about it than I do, and they confirm that the general principle of taking the structures of the free atoms and suggesting that they hold in the alloy is highly improbable. It seems to me, therefore, that a suggestion on these lines is scarcely likely.

On the other hand, I think that if Fig. 10 is examined more closely, it will show certain general tendencies. It is naturally very dangerous to speculate on this kind of thing, and so these suggestions may be looked on as very tentative until established explanations are forthcoming.

In general, Fig. 10 is a kind of combination of two or three different effects which are superimposed on each other. First of all one should perhaps say that the whole of the work on alloy structures suggests that the elements of the first short period are abnormal, so that on the whole I should be inclined to ignore the first two elements which the author has included in his figure. Otherwise, it seems to me that there are probably three distinct factors, and in the diagram it will be seen that among the elements which exert high effects there are oxygen, phosphorus, sulphur, arsenic, and selenium, but when one gets to the last two long periods that effect seems to stop, and the effects of antimony and bismuth are low. That suggests that the high effects connected with the first group of elements are essentially connected with the formation of stable compounds.

That, therefore, rather separates this series of elements. To go further is not quite so easy, but I think that one can see a general tendency which may

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be summarized by saying that if the elements of *any one particular sub-group* are considered, the author's effect increases with increasing difference between the size of the atom and the size of the atom of copper. Starting with Group II, the element which has an atomic diameter nearest to that of copper is zinc, and it will be seen from Fig. 10 that zinc has a comparatively small effect. Of the other elements of Group II, cadmium and magnesium have larger atoms than copper. In Group III, aluminium seems to have a very small effect, contrary to the author's general valency principle, and that is exactly the same thing that is found in the freezing point relations. Aluminium is quite anomalous, and seems to behave as a univalent rather than as a trivalent element in that connection. It will also be noticed among the elements in Group III that thallium has a very high effect. If it is regarded as a univalent, incompletely-ionized element, and compared with the other univalent element, silver, thallium is found to have a relatively very large effect, and there again is an example of the same general principle; the silver atom is larger than the copper atom, but the thallium atom is still larger. In Group IV there is the same effect; silicon has an atom which is somewhat smaller than the copper atom; tin, on the other hand, has an atom which is very much larger, and there the same principle applies, in that tin has a larger effect. I think that in general that characteristic can be seen. In the case of the transitional elements of the *A* group, however, it is more dangerous to attempt to draw conclusions about atomic diameters, because a definite atomic diameter cannot be assigned, but even there I think that the same principle holds. Comparison shows that nickel, which has very nearly the same atomic diameter as copper, has a smaller effect than platinum, which is in the same family but has a larger atomic diameter. Further back in the table, chromium, which has an atomic diameter more or less the same as that of copper, has a smaller effect than molybdenum and tungsten, which have larger atomic diameters. The principle fails, however, with zirconium and titanium. If the facts as a whole are surveyed, it may be said that, with one or two exceptions, the relation of size and effect *in any one family* is very clear, and that is the second principle which emerges from this table.

The third principle is that, apart from atomic diameters, there is a general valency effect such that increasing valency produces an increasing effect. The question of exactly how that occurs is naturally a much more speculative matter. The essential problem seems to be the tendency to form a new nucleus, and although one is on very dangerous ground in arguing from conditions of stable equilibrium to conditions such as the formation of a nucleus, I think that one can perhaps argue that, other things being equal, one may expect an increased tendency to form a nucleus with increasing difference in the energy between the liquid and the solid phases. It has been shown by Jones, in his theory of freezing points, that in a series of elements such as silver and cadmium one may go along one horizontal row of the table with an increasing difference in the energy of the liquid and the solid phases, and in that way one seems to have a connection between the author's effect and the effect which one would expect, perhaps, from the energy relations, although that is speculation rather than sound theory.

Dr. C. J. SMITHELLS,* M.C. (Member of Council): I think that the author has gone too far in reaching conclusions regarding the relative effects of elements in giving them such a definite numerical order. For example, to take two elements quoted by Dr. Hume-Rothery, antimony is given a growth-restriction factor of 18 and oxygen that of 32, whereas the tables show that these elements have the same effect on the length of the crystals, namely 0·9 in. in both cases.

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I could not at first see how the author had arrived at the order given in Table IV, so I re-analyzed his results, placing the elements into six separate groups—those which produced crystal lengths of 2 to 2½ in., 1½ to 2 in., and so on. I obtained six groups which are approximately consistent with the author's arrangement, but individually not quite consistent; and if attention is paid only to Table IV there may be some false deductions made, which I am sure is not intended. It would be safer on the basis of such evidence as there is to give the elements qualitative numbers from 1 to 6, according to their effect.

Of the author's two explanations, I think that the adsorption one is the more acceptable, but that he has overlooked, or not emphasized, one of the strongest points in favour of the adsorption theory, namely, that the effect of concentration is practically nil. In Table II, in which there are three series containing atomic percentages from 0·1 to about 4 per cent. of added element, it will be seen that it makes very little difference whether 0·1 or 4 per cent. of the particular element is present; the length of the crystal is about the same. If the effect of the added element were a concentration effect one would expect to find considerable differences between concentrations of 0·1 and 4 per cent., whereas if it is an adsorption effect, it may not be necessary to have more than enough to produce a monoatomic layer of adsorbed atoms. This indicates an adsorption type of process rather than a process of the concentration gradient type.

Regarding the author's definition of adsorption, I cannot quite agree with his views, or that the picture which he gives is the accepted one. It is stated on p. 117 that "The greater the degree of adsorption the greater will be the resistance offered to the attachment of more copper atoms to the lattice"; almost the same thing is stated at the top of the next page. That may be true sometimes, but not always. On a nickel surface at 800° C. an atomic layer of barium atoms can be adsorbed, but no more. On top of that, however, it is possible to adsorb a layer of oxygen atoms, and then it is possible to adsorb more barium atoms. It is not possible to put barium atoms on barium atoms, but it is possible to have alternate layers of oxygen and barium atoms. It is not true to say, therefore, that a layer of foreign atoms will necessarily prevent the further adsorption of copper atoms.

My greatest difficulty in accepting the explanation that the effect is related to the electron grouping, is that the electron grouping is a fundamental property of the impurity, and therefore if the elements are placed in order according to their electron grouping their growth-restriction factors will always have that order, whatever be the metal to which they are added. I think that it is highly improbable—though without evidence—that the elements will come in the same order in restricting growth when added to different metals, and particularly so because adsorption is a selective process. With some other element than copper an entirely different order of growth-restriction factors will probably be obtained.

One other factor which probably has some importance and which I do not think that the author has mentioned, is the effect of viscosity of the liquid immediately in front of the growing boundary.

Dr. D. Stockdale,* M.A. (Member of Council): I have puzzled over this paper, but I have reached no definite conclusion, except that I cannot yet accept the author's valency theory. My criticism of the paper is that it contains too much theory; a fuller description of the experimental work would have been more welcome.

To me, as to Dr. Smithells, one of the most remarkable points about this

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restrictive effect, is its independence of the concentration. Data relating to eight elements, taken from Table II, are set out in Table A, which shows clearly that with many elements the effect is independent or almost independent of their concentration, but that with certain other elements, notably iron, nickel, platinum, calcium, silicon, tellurium, arsenic, oxygen (Table II, p. 105), the effect does depend on concentration.

TABLE A.

Atomic Per Cent. of Element.	Crystal Length, In.	Atomic Per Cent. of Element.	Crystal Length, In.
Bi.		Sb.	
0·15	2·5	0·26	0·9
0·61	2·3	0·53	0·7
		1·05	0·8
Al.		Be.	
1·18	2·5	3·53	1·1
4·72	2·3	7·06	0·9
Zn.		P.	
0·20	2·5	0·20	1·1
0·49	2·5	0·41	0·9
0·97	2·4	1·03	0·9
		2·05	0·9
Mg.		Pb.	
1·31	1·0	0·15	0·3
2·62	1·3	0·31	0·25

It is interesting to note that the three transition elements, iron, nickel, and platinum, about which there is evidence, are in the second group. I think that it is fairly obvious that quite small concentrations of certain elements are going to have a great influence on the size of the columnar crystals, and it is therefore the more surprising that no analysis of the copper used has been given.

I should like to ask whether, after all, if adsorption is the cause of the effect, the "size" of the atoms is not the controlling factor. The atomic radii given in Table III are unfamiliar. The correct co-ordination number presumably is not known, but it seems to me that the "size" of the copper atom ought to be taken at C.N.12, where the radius is 1·275 A., that given in the table being 2·41 A. In this connection I would point out that the radius of the bismuth atom appears to be $\sqrt{2}$ times that of the copper atom; this may be fortuitous, but, on the other hand, it may be that bismuth atoms can fit neatly on to a surface of a copper crystal in a way that other atoms cannot, so giving an explanation of the very small growth-restriction factor of bismuth.

The author seems to have looked entirely at the growing faces of the crystals; he does not seem to have considered what may be taking place in the liquid in front of these faces. In Germany, the effect of tellurium on lead has been explained on the classical lines of crystallization velocity and nucleus number.* It has been shown that at 315° C. two lead alloys, one containing 0·072, the other 0·213 atomic per cent. tellurium, have almost exactly the same crystallization velocity, a velocity not greatly different

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* E. Jenckel and C. Thierer, *Z. Metallkunde*, 1937, 29, 21.

PLATE VII.

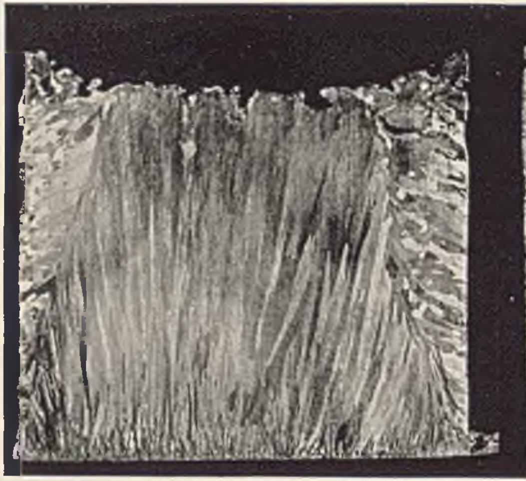

FIG. A.—Hydrogen about 0·0001%.

FIG. B.—Hydrogen about 0·0005%.

[*To face p.* 125.

from that of pure lead itself. The nucleus number of the alloy richer in tellurium, on the other hand, is about eleven times greater than that of the poorer alloy, and hence, other things being equal, it will have a substantially smaller grain-size. This example appears to be exactly parallel to those of the author, and I think that he is not justified in putting aside the views of Tammann without first giving them very serious consideration.

To return again to the adsorption theory. If foreign atoms are adsorbed on the crystal faces, they are presumably passing through, and diffusing in, the metal itself. Rhines and Mehl * have recently studied the effect of various elements on the self-diffusion coefficient of copper. They find that the elements are in the order zinc, aluminium, beryllium, silicon, and tin, zinc and aluminium having almost exactly the same effect, this being the smallest. That is, zinc and aluminium atoms should find it difficult to get away from the face, and should therefore have a large growth-restriction factor; tin atoms, which have a large effect on the coefficient, should find it easy, and should have a small effect on the factor. The contrary is the case.

Mr. R. CHADWICK,† M.A. (Member): I am interested in this paper because I have just been examining copper ingots with macrostructures very similar to those shown by the author. These ingots were about 100 lb. in weight and roughly cubic; they were cast in an open mould the bottom of which was of 2 in.-thick copper, bone ash dressed, and the sides of which were firebrick lined; the mould was heated by means of charcoal before pouring, the base being at about 100° C. and the walls at 500°–600° C. Solidification therefore proceeded almost entirely from the base upwards, the upper surface of the ingot being protected by an insulating charcoal cover. A number of ingots were cast under similar temperature conditions, the material being phosphorus-deoxidized copper, containing about 0·05 per cent. phosphorus. It was found that the length of columnar crystals was determined solely by the hydrogen content of the metal at the time of solidification, a copper of very low hydrogen content giving entirely columnar crystals. Two typical ingots are shown in Figs. A and B (Plate VII), and it will be seen that the hydrogen contents were extremely small; the actual amounts are approximate only, and were estimated partly from the method of preparation of the molten metal, and partly from the density of the ingots.

It was found, moreover, that various grades of commercial copper, ranging from a pure deoxidized cathode copper to a deoxidized arsenical copper, gave identical macrostructures, the length of columnar crystals being determined by the hydrogen content, and no restriction being noted as a result of the impurities present.

The author gives no indication of the melting conditions. It may be that the conditions were completely gas free, or it may be that dissolved hydrogen diffused away during melting and pouring owing to the small size of the heats employed. On the other hand, if hydrogen was absorbed during melting, it would be anticipated that the hydrogen content of the molten copper would vary with the alloying constituent used; for example, in Table I, some of the additions such as phosphorus and aluminium are definitely deoxidizing, whilst others such as oxygen and nickel may result in an oxygen–hydrogen reaction in the early stages of melting; other alloying additions, such as zinc, would tend to reduce the hydrogen content because of the internal vapour pressure; and, finally, additions such as aluminium and silicon would restrict the outward diffusion of hydrogen by reason of their skin-forming properties.

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* F. N. Rhines and R. F. Mehl, *Metals Technology*, 1938, 5, (1); *A.I.M.M.E. Tech. Publ.*, No. 883.

† Research Metallurgist, I.C.I. Metals Ltd., Birmingham.

Mr. E. H. Bucknall,* M.Sc. (Member): It is becoming recognized more and more that information is lacking on the crystallization characteristics of metals and alloys, and, if there are to be developments towards continuous casting, the sort of information which the author has given us is essential.

On the theoretical side, I associate myself with the remarks made by Dr. Hume-Rothery as to the complexity of the parameter measured and the unlikeliness of its being associated by a simple law with such a factor as valency. What is being measured seems to be the height of the columnar zone, which may not be simply related to the crystal length. Fig. 4, for example, representing the alloy containing zinc, shows new crystals arising high up in the columnar zone. In the case of the titanium alloy (Fig. 6), it would appear that the conditions for columnar growth, after ceasing at about 1 in. from the base of the ingot, re-establish themselves, so that there is a strong tendency to columnar nature in the patch of darker crystals above the small centre of the ingot.

One wonders whether the author's apparatus could be used also in a somewhat different manner, to find (by varying the rate of flow of cooling water or the temperature of the cooling water through the mould-base) what rate of extraction of heat yields single crystal ingots with various alloy compositions.

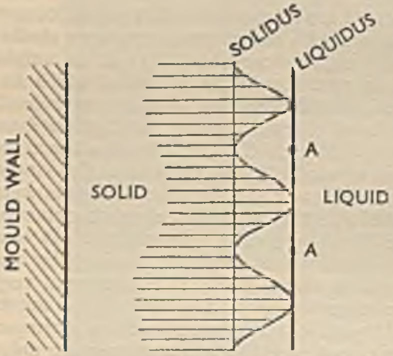

Fig. C.

Dr. R. Genders,† M.B.E. (Member of Council): I desire to refer to the presentation of the effects due to the composition gradient in the liquid near the solid face. It is obvious that if two lines are drawn representing the solidus and the liquidus isotherms, as in Fig. 11, solid metal must exist at all temperatures between the isotherms. That being so, the solid surface in any mass solidifying over a range of temperature must be of a form resembling that shown diagrammatically in Fig. C. That this is actually the type of solid surface formed has been confirmed by experiment. The distance to which the dendrites project into the liquid is affected by the temperature gradient and the concentration gradient in opposite directions. This method of illustrating the growing solid surface is suggested as a clearer picture of the actual conditions, and as a means of visualizing how, at points in the liquid between the projecting dendrites (as at *A* in the sketch) independent solidification may commence owing to fall of temperature to the liquidus in the intervening zone of highly concentrated liquid near the crystal surfaces.

Dr. Hume-Rothery: When I commented on the adsorption theory, I did not mean to say that I disagreed with a theory of adsorption. I think it highly probable that the effect is an adsorption effect. The general idea may be entirely sound; it was only the application of it in terms of individual electrons which I criticized.

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† Research Department, Woolwich.

Dr. E. Voce,* M.Sc. (Member): There seems to be no reference in the paper to the use of a protective atmosphere or other means of preventing oxidation during melting. Substances such as molybdenum, titanium, etc., which have an extraordinarily high affinity for oxygen, would simply disappear if added to copper molten in ordinary air. I should like to know what experimental precautions, if any, were taken against that kind of thing.

The President: I will ask the author to deal with the practical points now and to reply to the theoretical points in writing.

Dr. Northcott (*in reply*): Dr. Hume-Rothery has discussed the atomic size-factors of a number of elements, and suggests that a better theory would have resulted from applying the atomic size-factors to the results of the experimental work. I cannot agree with him there. I have spent much time in thinking over a satisfactory explanation on the lines which he suggests, and it was because I could not find one to cover the whole of the elements with which I have dealt, that I had to look for some other and better theory.

I disagree with Dr. Hume-Rothery's inference that the electron arrangement in the paper is wrong because in solid nickel, for example, the number of free electrons is 0·6 in the solid or liquid state. That is undoubtedly so, but if one atom of nickel is taken from a copper–nickel alloy not 0·6 of an electron but the whole of the electrons associated with that one nickel atom are taken away. Conversely, if a nickel atom is added, as many electrons are put in as are indicated in Table V.

I was glad of Dr. Hume-Rothery's and Dr. Smithells's confirmation of the adsorption theory; Dr. Smithells's remarks perhaps partly answer Dr. Stockdale's criticism as to whether the effects are dependent on, or independent of, the concentration. One reason for dealing with such small quantities in the present paper was to avoid, so far as possible, the effects of concentration. Larger quantities of addition elements will be dealt with later.

I investigated the viscosity effects, mentioned by Dr. Smithells, so far as the viscosity data were known, but I could obtain no very satisfactory explanation on these lines.

Mr. Chadwick and Dr. Voce referred to the casting conditions, the effect of gas, and so on. The alloys were normally melted with charcoal under flux in an injector furnace. Pre-solidification was adopted to get rid of gas so far as possible, and the effects in some ingots were checked by melting in a nitrogen atmosphere in an electric furnace. In the experimental work described in the paper, the ingots were comparatively small (7 lb.), and there was a steep temperature gradient. It is hoped to deal later with the effects of gas, and particularly of hydrogen. Ingots have been obtained in which gas was intentionally introduced, and, where there is columnar crystallization, columnar blow-holes reach from the bottom to the top of the ingot. In the case of an alloy which has a very strong tendency to crystallize in wholly columnar form, it will, in the presence of gas, under the conditions of the present experiment, still solidify in columnar form, but it will include columnar gas-holes.

In reply to Mr. Bucknall, the columnar crystals in the upper portion of the ingot are, of course, affected by the cooling from the top of the ingot.

Dr. Genders, in referring to the solidus and liquidus isotherms, showed the solidus and liquidus rather a large distance apart, but in the case of most of the additions discussed in the paper these two lines come extremely near together, and, though the effect is there, the point is covered by Fig. 11 of the paper.

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* Investigator, British Non-Ferrous Metals Research Association, London.

CORRESPONDENCE.

MR. R. GRIFFITHS,* M.Sc. (Member): This is a valuable contribution to the study of the crystallization of metals. I am interested in the subject from the point of view of scaling of metals, and have found † that, in the case of iron scale as well as copper scale, peculiarly straight-sided, equiaxed grains are formed under ordinary conditions of oxidation in air. In the iron scale, however, if the conditions of oxidation are changed by the addition of steam to the atmosphere, columnar grains are formed in the resulting scale. The effect of the presence of steam may be twofold: (*a*) the rate of grain formation may be increased, since the amount of scale produced is increased, and/or (*b*) the hydrogen liberated from the steam may act *per se* in some way not explainable at present. Disregarding the second possibility, the first effect implies that if the rate of grain formation at a particular temperature is a critical one, then columnar grains will be formed. Incidentally, it may be stated that increasing the rate of oxidation in air by raising the temperature is not effective in causing columnarization.

I have quoted this case to suggest the possibility that what occurs in the formation of a solid from solid and vapour (oxygen) phases, can be applied to the case of solid and liquid phases. There appears to be a critical rate of formation of solid in relation to the velocity of grain formation.

A possible contributory factor to the control of grain-size is the setting up of convection currents in the liquid. In the process of solidification, latent heat is evolved by the various grains as they are formed, and it is conceivable that local differences of temperature will be set up which will cause local convection currents. Now if these currents have sufficient velocity, they may disturb the tendency for regular deposition of the atoms on the crystal lattice, and cause a re-orientation of a set of atoms in the vicinity of an already-formed grain, with the consequent formation of a new grain.

BERGINGENIÖR HELGE LÖFQUIST: The great number of elements whose action on solidifying copper has been investigated gives a very good basis for the scientific interpretation of the results, and the new theoretical deductions made will no doubt greatly contribute to their explanation. In some investigations made by Benedicks and myself, the surface tension of crystal grains and the adsorption in the grain boundaries of dissolved elements caused thereby, have been discussed in relation to grain-growth in solid metals, especially steel.‡ It is of great interest, therefore, that similar principles have been applied by the author to the case of solidifying metals. In both cases the adsorption may be said to be due to the tendency towards an enrichment in the boundary surfaces of elements which have the power to lower the surface tension—a form of free energy—as further developed by Benedicks and myself.§

Regarding the effects due to a composition gradient, as described in Fig. 11, showing the formation inside the columnar crystals of a row of independent crystallites, a similar phenomenon has been investigated by Benedicks and myself in steel ingots.‖ A certain periodicity in freezing was explained as being due to an enrichment of dissolved impurities in front of the growing columnar crystals, giving a lowering of the freezing point there, which caused

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† *Carnegie Schol. Mem. Iron Steel Inst.*, 1937, **26**, 165.

‡ C. Benedicks and H. Löfquist, *J. Iron Steel Inst.*, 1936, **134**, 531.

§ *loc. cit.*

‖ C. Benedicks and H. Löfquist, "Non-Metallic Inclusions in Iron and Steel," London, 1930, p. 231.

freezing to start further in. This phenomenon was repeated, and thus gave the observed periodicity in freezing.

Regarding the slope of the "composition gradient" of Fig. 11, its starting point must evidently be at the outer (left) end of the line giving "mean composition of alloy," corresponding to the composition of the so-called chill layer. If, now, the alloying element decreases the melting point of the base metal, it is easily seen that from that point onwards the composition curve must fall more or less steeply, depending on the horizontal distance between the solidus and the liquidus curves of the alloy used, and the rate of diffusion during freezing. Diffusion may then cause the curve to assume a slight upwards slope. Finally, a distinct peak is formed just in front of the columnar crystals. For further details reference is made to the book cited. A very good experimental confirmation of this deduction of "periodicity in freezing" has appeared in a study by Swinden * of rimming steel ingots. As previously pointed out by the author, and later on by Benedicks and myself,† the heat evolved during crystallization may cause a certain periodicity on a smaller scale, in crystal growth, but this effect might certainly be of influence also in the case discussed here, as mentioned by the author.

Dr. **Mike A. Miller** ‡ (Member): There has seldom appeared in the technico-scientific literature a more important contribution to the vital problem of grain-size and grain shape than that presented by Dr. Northcott. Ever since the original experiments of Tammann,§ the problem of crystal size, shape, and distribution has been of paramount importance to the understanding of the performance of metals and alloys in service. Empirical thermal treatments, as pointed out by the author, have in isolated, and more often than not, secretive, cases, resulted in acceptable microscopic structure and mechanical properties. These procedures, however, seldom contribute to the knowledge of the fundamental character of the fluid–solid transformation, or more definitely, to the mechanism of the interaction of solvent *versus* foreign atoms at the crystal–melt interface.

The conclusions reached by the author, despite the apparent agreement between empirically-calculated values and experimental results, appear to be open to further discussion. The effect of foreign atoms is undoubtedly due to their specific interaction at the crystal–fluid interface; adsorption is a pre-requisite to such an interaction. It is not nearly as apparent why it is possible to disregard "solid solubility, atomic size-factors, or other relationships."

As pointed out by Goldschmidt,‖ crystal structure depends on the relative numbers, the relative size, and the polarization properties of atoms, atom groups, and ions. Likewise, the ionization energy of metals, *i.e.* the energy which is necessary to remove electrons from the neutral atom, varies with the radius of the metallic ion.¶ As for metalloid atoms, it is known that the electron affinity decreases with increasing ionic radius. Bernal ** has shown

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[*] T. Swinden, Iron and Steel Inst., "Seventh Report on the Heterogeneity of Steel Ingots," London, **1937**, p. 15; see also H. Löfquist, *J. Iron Steel Inst.*, 1937, **135**, 375.

[†] C. Benedicks and H. Löfquist, *Trans. Amer. Inst. Min. Met. Eng.*, 1937, **125**, 349.

[‡] Aluminium Research Laboratories, Aluminum Company of America, New Kensington, Pa., U.S.A.

[§] G. Tammann, "Aggregatzustände. Die Zustandsänderung der Materie in Abhängigkeit von Druck und Temperatur," Leipzig, **1932**.

[‖] V. M. Goldschmidt, *Trans. Faraday Soc.*, 1929, **25**, 281.

[¶] *loc. cit.*, p. 275.

[**] J. D. Bernal, *ibid.*, p. 378.

that the nuclear density *versus* the number of electrons beyond the last inert gas shell is a measure of the attractive force between atoms. If one accepts the equivalence principle of supernumerary shells, it is apparent that a minimum interaction energy exists before and after each inert gas. This likewise explains the large atomic volumes on the basis of the actual space distribution of supernumerary electrons; maximal interaction is reached with an incompleted eighteen shell.

Considering solubility, one can see at once that mutual solubility is not a reciprocal property; even solvent atoms might not be able to "dissolve" in an adsorbed layer of solute atoms. Obviously dissolving power is a function of the lattice of the solvent metal, *i.e.* the amount of lattice distortion permissible; solubility, on the other hand, is strictly a function of the metallic solute atom, *i.e.* the amount of distortion produced by the foreign atom. It is therefore difficult to understand how any "growth-restriction factor" can disregard atomic size and arrangement.

On this basis, it is interesting to note that Semenchenko * has attempted to correlate modification of certain alloys with the adsorption of foreign atoms at the crystal–fluid interface. He has shown that the "totalized moment" of metal ions, *i.e.* the ionic charge multiplied by valence and divided by ionic radius, determines such properties of metals as surface tension, surface activity or adsorption at interfaces, compressibility, thermal expansion, etc. Semenchenko and Pokrovskii † recently discussed the electron theory of surface tension in pure metals from the point of view of the thermodynamics of a two-dimensional electron gas and an ionic-force theory for the surface tension of alloys. The mutual effects of both ions and electrons were combined to give an equation for surface tension involving "generalized moments" and atomic volumes of solvent and solute atoms. It is a well-known principle that in the fluid state the constituents which have the lowest surface tensions tend to segregate at interfaces.

Lipman ‡ has discussed adsorption of foreign atoms in relation to modification of light metal alloys. McKenna § pointed out that for compounds of the same crystalline form, hardness appears to vary directly with a function involving the square of the valence divided by the two-thirds power of the atomic volume; that is to say, the atoms in a lattice are held together as the square of the valence and inversely as the square of the distance between them.

On the other hand, the screening factor used by Dr. Northcott, as well as the N-factor for number of free electrons, must certainly be related to atom size. Accordingly, such electronic factors must actually take atomic space into consideration; the agreement between the calculated R values and the experimental results for length of columnar zone would indicate this to be the case. This agreement is much more marked if the effect of concentration is taken into consideration. One has only to remember that the Gibbs adsorption equation involves concentration, as well as surface tension, in order to realize that columnarization would be expected to vary with the amount of foreign material available. If one plots Dr. Northcott's values for length of columnar zone against concentration of added element for those elements added in more than one concentration, and extrapolates to zero concentration, values are obtained for length of columnar zone which, with very few exceptions, fit the calculated R values much more satisfactorily

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* V. K. Semenchenko, *Zvetnye Metally*, **1936**, (6), 92–100.

† V. K. Semenchenko and N. L. Pokrovskii, *Uspehi Khim.*, 1937, **6**, 945–961.

‡ M. S. Lipman, *Zvetnye Metally*, **1937**, (7), 77–90; (8), 86–89.

§ P. M. McKenna, *Metals Technology*, 1938, **5**, (2); *A.I.M.M.E. Tech. Publ.* No. 897, 1938.

than the values assigned by Dr. Northcott. The exceptions mentioned above would probably vanish if some function of atomic size were considered.

Further, one has only to segregate the elements of a given crystal form and note the remarkable agreement between the growth-restriction factors, in order to recognize the importance of crystal form. Has Dr. Northcott considered such a relationship?

However, any growth-restriction factor involving atomic size is not at present obvious. That such a relationship must exist is indicated by the present discussion. It is hoped that the near future will bring forth a more complete explanation. It will likewise be necessary to consider the specific effect of copper, or of the particular solvent metal under consideration.

Dr. R. Schnurmann *: In an interesting attempt to explain the influence of small additions of alloying elements on the crystal size of copper solidified from the molten state, Dr. Northcott refers to a relationship between the valency and atomic structure of the added elements and "the crystal growth-restriction factor." According to Dr. Northcott, "elements of high valency have a greater effect in reducing crystal size than have those of low valency, but the arrangement of the valency electrons is also important."

The "growth-restriction factor"—I should like to refer to it as G for brevity—is empirical and "is merely intended to denote the comparative effect of the different elements when added in small quantities, those with large factor numbers having greater effect than those with small numbers on the restriction of columnar growth of copper from the melt." The author deals with 35 alloying elements having 35 different G values. These are compared with R values derived from the empirical formula $R = \frac{\sqrt{N}}{s'c}$, where R is "the relative growth-restrictive power," s' the screening factor to allow for variation in degree of binding, N the number of effective electrons, and c is a constant, whose value depends on the second quantum number. According to Dr. Northcott, elements having the same or smaller R values than copper show little effect in reducing the columnar crystal growth of copper.

As a result of the values chosen for the constants s' and c by Dr. Northcott, one might not expect more than a division of the alloying elements into two groups, a growth-restricting group (large G values) and a non-restricting group (small G values). The division line in Dr. Northcott's Table III would go between cerium and magnesium, the twelve first elements in the table with the exception of Zn ($R = 2{\cdot}35$, whereas for copper $R = 1{\cdot}66$) would not be growth-restricting ($G = 1$ to 12), whereas the remaining 23 plus Zn would be growth-restricting.

Splitting up Table III into two parts according to the R values of the elements, one sees that the mere consideration of the electron structure of an element is not sufficient for a prediction of its behaviour towards growth-restriction, even in the rough way of classifying into only two groups of elements, *i.e.* growth-restricting and non-growth-restricting.

Clearly, from the electron structures given in Tables B and C, which correspond exactly to the structures given in Table V, it does not yet seem possible to predict which elements will restrict growth and which will not. It might seem that aluminium *e.g.* would behave as not fully ionized when added to copper (as assumed in Table B), whereas it would behave trivalently when added to iron and thus contribute a factor $R = 2{\cdot}53$, instead of $1{\cdot}33$.

On the other hand, in the case of zinc there cannot be the slightest doubt about two s electrons being the valency electrons, the lower electron levels

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TABLE B.—*Elements Which Do Not Restrict the Growth of Copper Crystals.*

Element and Atomic Number.	Principal and Secondary Quantum Numbers.																Normal State of Atom.	Electron Structure.	*R.*	*G.*
n =	1	2		3			4				5			6						
l =	0	0	1	0	1	2	0	1	2	3	0	1	2	0	1	2				
83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	2	3		${}^4S_{3/2}$	open	1·33	1
13 Al	2	2	6	2	1												${}^2P_{1/2,3/2}$	open	1·33	2
23 V	2	2	6	2	6	3	2										${}^4F_{3/2,5/2,7/2,9/2}$	screened	0·908	4
24 Cr	2	2	6	2	6	5	1										${}^7S_3$	screened	1·285	5
25 Mn	2	2	6	2	6	5	2										${}^6S_{5/2}$	screened	1·572	6
73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3	2			${}^4F_{3/2,5/2,7/2,9/2}$	screened	0·908	7
56 Ba	2	2	6	2	6	10	2	6	10		2	6		2			${}^1S_0$	well screened	1·588	8
74 W	2	2	6	2	6	10	2	6	10	14	2	6	4	2			${}^5D_{0,1,2,3,4}$	screened	1·285	9
26 Fe	2	2	6	2	6	6	2										${}^5D_{4,3,2,1,0}$	screened	1·815	10
3 Li	2	1															${}^2S_{1/2}$	open	1·666	11
58 Co	2	2	6	2	6	10	2	6	10	1	2	6	1	2				well screened	1·778	12

Among these eleven elements are three with "open" electron shells, the other ones being "screened" or "well screened" in Dr. Northcott's meaning of these terms.

TABLE C.—*Elements Which Restrict the Growth of Copper Crystals.*

Element and Atomic Number.	Principal and Secondary Quantum Numbers.																Normal State of Atom.	Electron Structure.	*R.*	*G.*
n =	1	2		3			4				5			6						
l =	0	0	1	0	1	2	0	1	2	3	0	1	2	0	1	2				
30 Zn	2	2	6	2	6	10	2										${}^1S_0$	open	2·35	3
12 Mg	2	2	6	2													${}^1S_0$	open	2·35	13
42 Mo	2	2	6	2	6	10	2	6	5		1						${}^6D_{1/2,3/2,5/2,7/2,9/2}$	screened	2·105	14
27 Co	2	2	6	2	6	7	2										${}^4F_{9/2,7/2,5/2,3/2}$	screened	2·03	15
40 Zr	2	2	6	2	6	10	2	6	2		2						${}^3F_{2,3,4}$	screened	2·42	16
47 Ag	2	2	6	2	6	10	2	6	10		1						${}^2S_{1/2}$	very open	2·38	17
51 Sb	2	2	6	2	6	10	2	6	10		2	3					${}^4S_{3/2}$	very open	1·905	18
4 Be	2	2															${}^1S_0$	open	2·35	19
20 Ca	2	2	6	2	6		2										${}^1S_0$	open	2·35	20
14 Si	2	2	6	2	2												${}^3P_{0,1,2}$	open	2·85	21
5 B	2	2	1														${}^2P_{1/2,3/2}$	open	2·47	22
15 P	2	2	6	2	3												${}^4S_{3/2}$	open	3·19	23
48 Cd	2	2	6	2	6	10	2	6	10		2						${}^1S_0$	very open	3·37	24
28 Ni	2	2	6	2	6	8	2										${}^3F_{4,3,2}$	screened	2·23	25
22 Ti	2	2	6	2	6	2	2										${}^3F_{2,3,4}$	open	2·87	26
52 Te	2	2	6	2	6	10	2	6	10		2	4					${}^3P_{2,1,0}$	very open	2·69	27
16 S	2	2	6	2	4												${}^3P_{2,1,0}$	open	3·5	28
33 As	2	2	6	2	6	10	2	3									${}^4S_{3/2}$	open	3·19	29
34 Se	2	2	6	2	6	10	2	4									${}^3P_{2,1,0}$	open	3·5	30
50 Sn	2	2	6	2	6	10	2	6	10		2	2					${}^3P_{0,1,2}$	very open	4·08	31
8 O	2	2	4														${}^3P_{2,1,0}$	open	3·5	32
78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	3	2			${}^3F_{4,3,2}$	screened	2·23	33
81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10	2	1		${}^2P_{1/2,3/2}$	open	2·47	34
82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2		${}^3P_{0,1,2}$	open	2·85	35

being completely filled. The *R* value thus deduced classifies Zn as a growth-restricting element with respect to Cu. The experimental growth-restriction factor *G*, as found by Dr. Northcott, is, however, only 3.

In Table D the elements without gaps in their lower electron levels are summarized.

TABLE D.—*Elements With Completely Filled Lower Electron Levels.*

Element.	Quantum Numbers of Valency Electrons.		No. of Electrons in Effective Sub-Group.	G.
	Principal.	Secondary.		
Bi	6	1	1 (5 or 3)	1
Al	3	1 (0 + 1)	1 (3)	2
Li	2	0	1	11
Zn	4	0	2	3
Mg . . .	3	0	2	13
Be	2	0	2	19
Si	3	1	4	21
B	2	1	3	22
P	3	1	5	23
S	3	1	6	28
As	4	1	5	29
Se	4	1	6	30
O	2	1	6	32
Tl	6	1	3	34
Pb	6	1	4	35

It seems as if for this particular group the author might be justified in saying that with the exception of aluminium and bismuth these elements show a large growth-restriction factor for copper ($G > 20$), when the uncompleted valency electron level has the secondary quantum number $l = 1$.

It is quite likely that the added elements influence the velocity of formation of crystallization nuclei. But as long as no physical mechanism of such an effect can be offered for discussion it seems impossible to reach any conclusions from the Periodic Table.

Scheil * recently discussed the influence of crystallization nuclei on the growth of metal crystals and the formation of these nuclei in the case of homogeneous melts for various degrees of undercooling.

Dobinski † ventured to give a physical explanation of the accumulation of one constituent of an alloy on the surface. The free surface energy of a solution tends towards its minimum value by concentration of the constituent of the smallest surface tension in the surface. He assumes the values of the surface tension of solid metals to be roughly proportional to those of the molten metals in the neighbourhood of the melting point. Thus the surface tension of the following metals would increase in the order: antimony, bismuth, lead, mercury, tin, cadmium, zinc, silver, gold, copper. In any alloy the constituent preceding the others in this series should tend to accumulate in the surface.

Though this series is not parallel with that of the growth-restriction factor of alloying elements on copper, it might indicate the direction in which the formation of crystallization nuclei is influenced by the added metals. However, no experimental data which would allow this assumption to be checked exist so far.

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* E. Scheil, *Z. Metallkunde*, 1937, 29, 404.

† S. Dobinski, *Nature*, 1938, 141, 81.

Dr. C. S. Smith * (Member): The subject of primary crystallization and the influence of factors restricting grain-size is one of considerable practical importance and theoretical interest. There seems little doubt in view of the present work that adsorption is one of the most important factors in restricting grain growth, and that this in turn is associated in some way with the electronic structure of the atoms concerned.

The paper would be even more valuable were analyses of the final castings made available, so that the conclusions could be based on the actual amount of the elements present. The solubility of elements like molybdenum, tungsten, and tantalum in copper is supposedly quite small and several other elements are notoriously difficult to introduce into molten copper on account of oxidation. Unless a special technique was used, it seems unlikely that more than a fraction of the intended amount of some of the elements was retained. Beyond a certain minimum, however, this may not be important, since it can be seen from the data in Table I that the crystal length in most series of alloys is relatively independent of the amount of added element, beyond the smallest addition studied. (Exceptions to this, in a slight degree, are nickel, arsenic, and tellurium, and to a greater extent, calcium, iron, and particularly oxygen.) It is obvious that the curve of crystal length *versus* concentration for all alloys in which the restricting effect is large must slope downwards at small concentrations, and, indeed, the author's data for oxygen fall entirely in this range. In the case of elements of limited liquid solubility it seems likely that the figure reported is just the termination of the crystal length curve at the concentration corresponding to the liquid solubility of the element in question, which is hardly an appropriate figure to compare with the data from other elements considered and for which the reported figure is the value corresponding to the horizontal part of the curve. The initial slope of the curve would be the proper basis of comparison but, of course, the experimental difficulties in obtaining such data would be great.

The potency of oxygen, even in small quantities, is well shown by Dr. Northcott's data. Under certain conditions it is to be expected that the presence of oxygen, not only in solution but also in the form of insoluble inclusions in the liquid alloy, would have a considerable influence on grain-size, and it would be interesting to know what the oxygen and inclusion contents of the various melts were, and whether contact with the atmosphere was prevented either during the transfer of metal to the Durville crucible or during the actual casting operation. A further effect of oxidation might be the formation, by reaction, of an insoluble gas that would introduce local turbulence at the solid–liquid interface and upset the growth of the crystals.

It would also be interesting to know what effect the various elements have had on the spacing of the dendrite branches in the columnar crystals, and whether this bears any relation to the other factors considered.

Dr. E. Voce,† M.Sc. (Member): In reply to a question from me, the author admitted that no special precautions were taken to ensure that the more highly reactive of the elements added to copper were adequately protected from oxidation during casting. It is improbable, for instance, that tungsten or molybdenum (to name but two of many) would remain in the metallic state in molten copper for more than a minute fraction of time, even though the melt were "protected" with charcoal or a flux. A high vacuum or completely inert atmosphere is requisite.

In his description of the experimental procedure, the author does not suggest that the elements added were actually present in the castings, but merely

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* Research Metallurgist, American Brass Company, Waterbury, Conn., U.S.A.

† Investigator, British Non-Ferrous Metals Research Association, London.

that certain additions had certain effects upon the crystallization. In the more theoretical parts of the paper, however, it seems to be tacitly assumed that the elements added were actually present, and this impression is fostered by such phrases as ". . . the influence of the different added elements varies slightly, depending upon the proportions present . . ." (p. 108). Any discussion of the results from the point of view of valency and atomic constants is clearly futile until it be established beyond question that the additions were actually present in the metallic state at the moment of solidification. For this purpose ordinary chemical analysis of the castings is scarcely sufficiently discriminative between element and oxide. The surest method of establishing data for theoretical discussion would be to repeat the work in an atmosphere of purified hydrogen followed by purified nitrogen, or in a high vacuum. I have reason to think that very different results would then be obtained.

From a practical point of view, the paper provides useful information as to which elements added to copper under ordinary casting conditions may be expected to inhibit the growth of large columnar crystals. Even in this direction, however, it suffers from the omission to state whether or not the molten copper contained cuprous oxide prior to making the additions. As might have been expected, cuprous oxide itself was shown to have a marked inhibitive effect upon crystal growth, and the influence of such powerful deoxidants as aluminium, zinc, vanadium, chromium, manganese, tantalum, barium, tungsten, lithium, cerium, magnesium, molybdenum (to take those from the top of Table III) in permitting growth might be largely explained by their scavenging action.

The Author (*in reply*): The example of crystal formation in scale quoted by Mr. R. Griffiths is interesting, although there may be some uncertainty as to whether the mechanism suggested is the correct one. It is hoped, later, to study the question of rate of formation of the solid. In the small ingots dealt with in the present work, I think that any tendency towards convection currents in the liquid will be masked by motion due to turbulence in casting and solidification shrinkage.

Mr. Lofquist's agreement with my views on adsorption is appreciated. The conditions operating at the interface of two solid crystals, to which the first reference applies, may naturally differ from those at a solid–liquid interface. The position of the starting point of the "composition gradient" line in Fig. 11 is surely correct, since, according to the theory of the constitutional diagram, the first crystals to form in an alloy having a freezing range are *not* of the same composition as the original liquid; no account is taken of back diffusion or inverse segregation effects.

I read the contributions by Dr. Miller and Dr. Schnurmann with interest, and I am indebted to them for the suggestions put forward. It is not possible, on this occasion, to reply in detail to the various points raised, but they will be further considered when the subject is next offered for discussion, after the completion of additional experimental work.

I fully agree with Dr. Smith that the initial slope of the crystal length curve would be the proper basis of comparison. The accurate determination of such a slope, however, would require much work with each alloying element. It is hoped to offer, in the near future, results of work on these lines for the more important elements; the other suggestions will then be kept in mind.

I think that Dr. Voce paints an unnecessarily black picture as to the ability of an alloying element to remain in the metallic state when added to copper, and such pessimism is scarcely justified when one considers, for example, alloy steel manufacture, where the opportunities for loss of alloying constituents are far greater, on account of the higher temperatures and more oxidizing conditions, and yet compositions can be predicted with quite tolerable accuracy. Dr. Voce may rest assured that loss due to oxidation, in some instances quite a high loss, was not ignored, and that the Research Department, Woolwich, is not without experience of the subject. The percentages of the addition elements given in the tables do not necessarily refer to the quantity actually added to the melt; in many instances the additions were made by means of pure hardener alloys of known composition. Furthermore, as pointed out by Dr. Smith, over a range beyond a certain minimum the content of addition element is not important, since the crystal length is relatively independent of the proportion added; this is to be expected on the grounds of the adsorption theory. I completely disagree with the suggestion that the influence of certain elements in permitting growth may be largely explained by their scavenging action, for the reasons that: (i) certain of the elements quoted do not exert a scavenging action; (ii) many elements known to exert a strong scavenging action have a pronounced effect on reducing columnar growth; (iii) similar results have been obtained after the preliminary addition of a suitable scavenger. In any case, the statement as to the inability of tungsten or molybdenum to remain in the metallic state is contrary to the facts in the present instance.

Experimental work on the subject of columnar crystallization of metals is continuing, and it is thought that some of the questions raised in the oral and written discussions on the present paper will be better answered by a consideration of the results of that work.

X-RAY EXAMINATION OF A BRASS CARTRIDGE CASE.*

By Professor Dr.-Ing. L. LOSKIEWICZ,† Member.

Synopsis.

In order to ascertain the method of manufacture of certain 90 : 10 brass sporting cartridges, their X-ray structure was compared with that of a sheet from which they might have been made. Then the method of cold-rolling and annealing was found which would give the sheet the closest X-ray structure to that of the cartridge.

A short time ago we were asked to establish the method of manufacture of sporting cartridges of 90 : 10 brass from an examination of two specimen cases and a piece of strip metal from which more were to be made.

The problem could be resolved into three parts:

(1) The determination of the probable degree of cold-work to which the metal was subjected in the manufacture of the cases.
(2) The determination of the heat-treatment applied.
(3) Finding a suitable method of working for making similar cases from the strip supplied.

Since only a very small amount of metal was available for the tests, the Laue X-ray method was used for establishing the orientation of the structure of the cartridges.‡

The radiograms (Figs. 1 and 2, Plate IX) afford the following information: The presence of " nodes " along the circumferences of the circles shows that the metal was cold-worked during manufacture and that the crystals have a preferred orientation. On the other hand, the breaking up of the circles into points shows that the cases were annealed at a temperature and for a time sufficient to produce recrystallization but not to destroy orientation of the crystals. We then established the structure of the sheet. Fig. 3 (Plate IX) shows that the sheet is annealed, recrystal-

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* Manuscript received July 12, 1937.

† Professor of Metallography, High School of Mines, Krakow, Poland.

‡ For working details see: Loskiewicz, Guschlbauer and Nosowicz, *Prace nad mosiadzami*, 1934, 1; and the same authors with Hayto and Podczaski, *Congr. Internat. Mines, Met. Geol., Paris*, 1935, 2, 195–210.

lized, and without pronounced directionality; the crystals are larger than those of the cases. By cold-rolling, portions of the sheet were reduced in thickness by 5–80 per cent.* and the structure examined. (It should be noted that, for the same degree of reduction, the structure of cold-rolled sheet is not exactly analogous to that of metal deep-drawn into a cartridge case.) Figs. 4 and 5 (Plate IX) show the structure of the sheet after 15 and 35 per cent. reduction, respectively. The points of reflection have disappeared and are replaced by continuous circles. With increasing degree of reduction, nodes form on the circles, showing that the crystals are beginning to orient themselves in preferred directions. The structure, which in our opinion is the closest to that which existed in the cartridge cases before annealing, was obtained after an 80 per cent. reduction.

The next stage of the work was to find the temperature and time of anneal necessary to produce the structure with preferred orientation. Annealing at 250° C. for 1 hr. produced no satisfactory result in the cases of sheets reduced 60, 70, or 80 per cent. (see Figs. 6, 7, and 8, Plate X), the structure after annealing being the same as before.

Taking as our basis sheet reduced 80 per cent., we annealed this at 300° C. for 30 minutes without visible change in structure (Fig. 9, Plate X). A similar test at 350° C. produced a structure similar to that of the cases (Fig. 10, Plate X) as also did a third test at 375° C. (Fig. 11, Plate X). On repeating the last two tests for 2 hrs. instead of 30 minutes, it will be seen that the specimen annealed at 350° C. has still not lost its directionality (Fig. 12, Plate XI), whereas it has completely vanished in that annealed at 375° C.

Finally, it had to be proved that the cartridge cases had not been cold-worked after annealing. Specimens of the sheet which had been annealed for 30 minutes at 300° and 350° C. were cold-rolled to 10 per cent. reduction and their structure again examined (Figs. 14 and 15, Plate XI). It will be seen that the recrystallization structure has disappeared and that the radiograms resemble closely those given by severely cold-rolled sheets.

Tools were therefore made of such dimensions that cases made on them were cold-worked to about 80 per cent. reduction during manufacture. Cases made on these tools and then annealed for ½–2 hrs. at 350° C. were eminently satisfactory in all respects.

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* The degree of reduction was calculated from the expression $100(S - s)/S$, where S is the original and s the final thickness of the sheet.

PLATE VIII.

DESCRIPTIONS OF RADIOGRAMS.

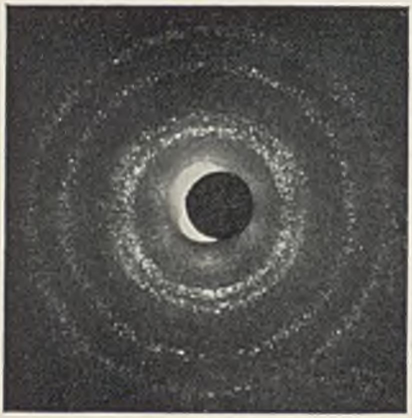
PLATE IX. FIG. 1.—Long cartridge case. FIG. 2.—Short cartridge case. FIG. 3.—Sheet as received. FIG. 4.—Sheet after 15% reduction. FIG. 5.—Sheet after 35% reduction.	All photos with X-rays from Mo rendered monochromatic by a Zr filter perpendicular to the surface of the specimens. Distance between specimen and film, 30 mm.; thickness of specimen 0·05 mm.; time of exposure, 6–8 hrs.

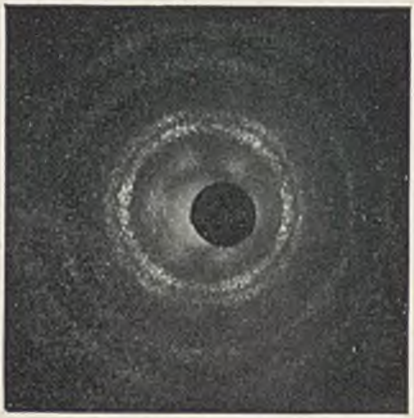
PLATE X. FIG. 6.—Sheet reduced 80%, annealed 1 hr. at 275° C.
FIG. 7.—Sheet reduced 70%, annealed 1 hr. at 275° C.
FIG. 8.—Sheet reduced 80%, annealed 1 hr. at 275° C.
FIG. 9.—Sheet reduced 80%, annealed 30 min. at 300° C.
FIG. 10.—Sheet reduced 80%, annealed 30 min. at 350° C.
FIG. 11.—Sheet reduced 80%, annealed 30 min. at 375° C.

PLATE XI. FIG. 12.—Sheet reduced 80%, annealed 2 hrs. at 350° C.
FIG. 13.—Sheet reduced 80%, annealed 2 hrs. at 375° C.
FIG. 14.—Sheet reduced 80%, annealed 30 min. at 300° C., cold-rolled to 10% reduction.
FIG. 15.—Sheet reduced 80%, annealed 30 min. at 375° C., cold-rolled to 10% reduction.

[*To face p.* 138.

PLATE IX.





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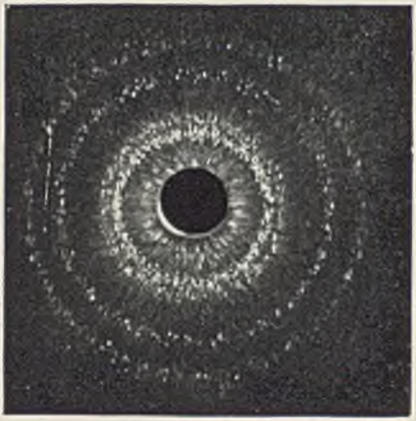

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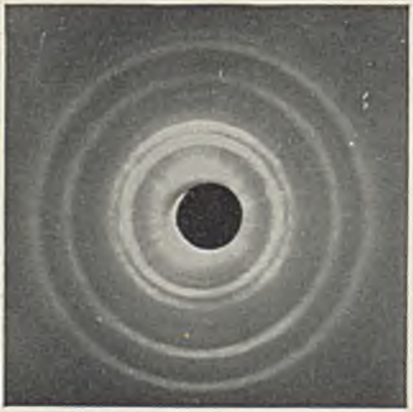

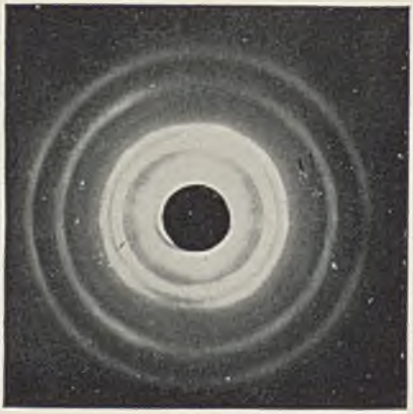

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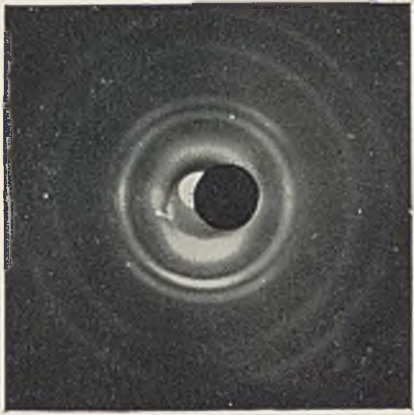
For Descriptions, see Plate VIII.



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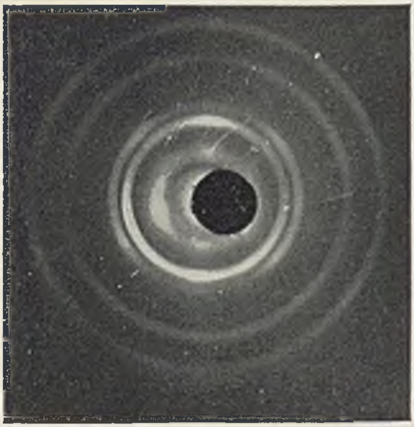

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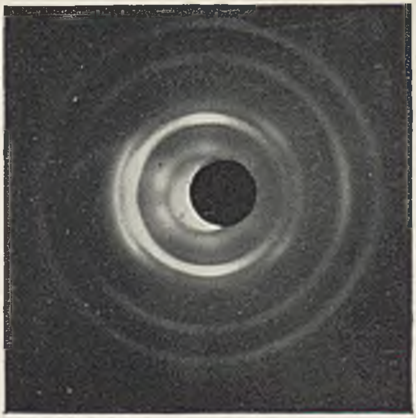

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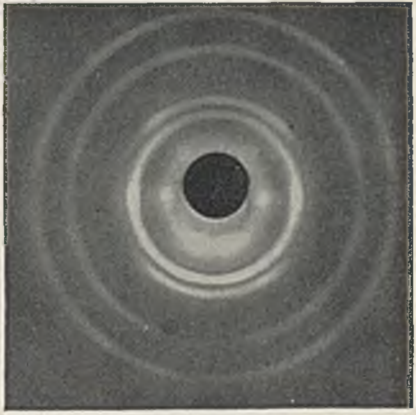

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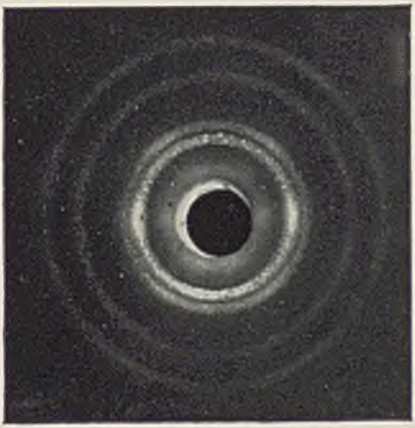

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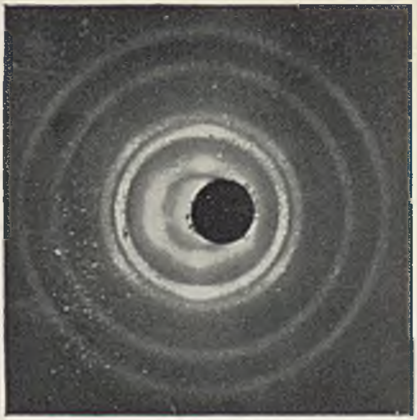

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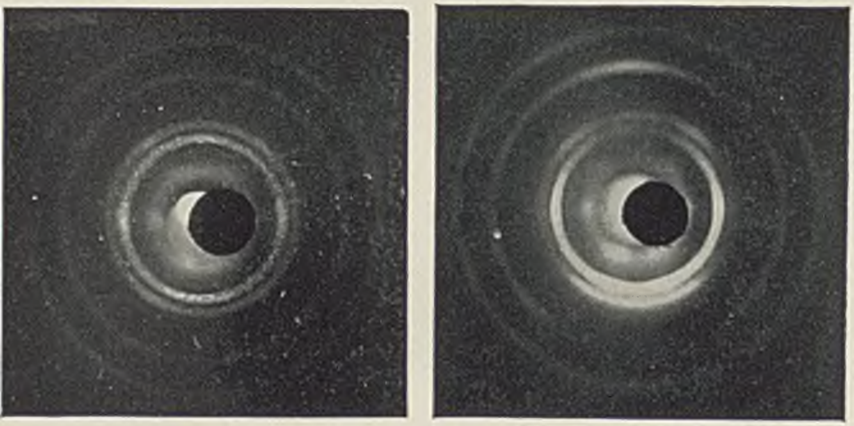
For Descriptions, see Plate VIII.

PLATE XI.



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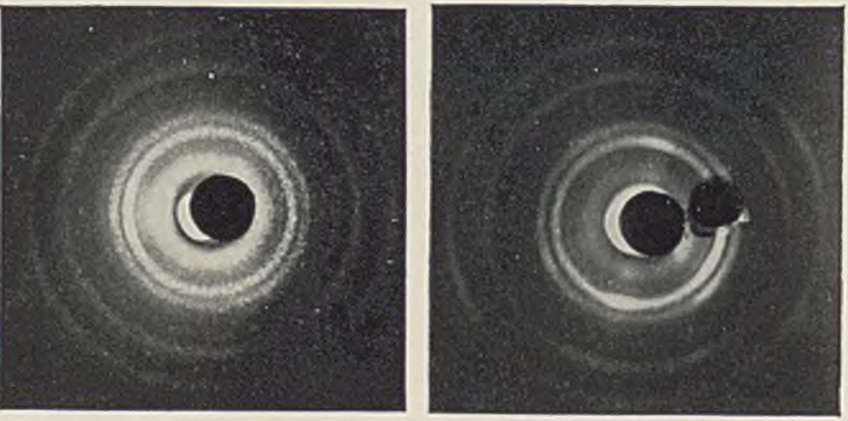

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For Descriptions, see Plate VIII.

THE PHYSICAL AND MECHANICAL PROPERTIES OF NICKEL–BRASSES.* 792

By MAURICE COOK,† M.Sc., Ph.D., Member.

SYNOPSIS.

After a preliminary study of the physical properties of alloys containing copper from 60 to 25, nickel 5 to 30, and zinc 30 to 55 per cent. in the chill-cast condition and in the form of bar, hot-forged from chill-castings, a more detailed examination has been made of the properties of a few selected alloys in the form of extruded rod, with and without small additions of alloying elements. In addition to determinations of the physical properties of the extruded materials, observations have been made on the microstructure, machinability, and hot-stamping characteristics of the alloys.

A VERY wide variety of copper-rich non-ferrous alloys containing nickel is now manufactured and used, the two most important groups being the straight copper–nickel alloys commonly known as cupro-nickels, and the ternary alloys with copper and zinc, known as nickel silvers or German silvers. The latter group covers a very wide range of compositions, with a nickel content of about 5 to 30 per cent., and with zinc ranging from about 5 to 30 per cent. These alloys may be subdivided into three principal classes, viz.: cold-working, hot-working, and casting alloys. Those that may be regarded as cold-working alloys generally contain from about 10 per cent., or rather less, to 30 per cent. nickel, and about 10 to 30 per cent. zinc. Structurally, these alloys resemble 70 : 30 brass, consisting of a single solid solution. Although they are commonly fabricated cold, there is, of course, no hard and fast line of demarcation between so-called cold-working and hot-working alloys, and many of the alloys in this range can, for example, under suitable conditions, be hot-rolled. Those regarded as essentially hot-working alloys contain about 38 to 45 per cent. zinc, and from about 6 to 16 per cent. nickel. Structurally, they consist of varying proportions of the α and β constituents. As in the case of the brasses, the β phase is more easily worked hot than cold, and the rough classification into hot- and cold-working alloys, according to the presence or absence of the β phase, is similar to that commonly used for brasses. The

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† Deputy Research Manager, I.C.I. Metals, Ltd., Witton, Birmingham.

casting alloys vary considerably in composition, and very commonly contain appreciable additions of lead and tin.

The characteristic hot-working alloys with a duplex structure, a relatively high zinc content, and a low or medium nickel content, are often known as nickel–brasses, and, in fact, they may be regarded as α–β brasses containing nickel additions. A typical alloy of this type is that containing 10 per cent. nickel and 45 per cent. each of copper and zinc. Comparatively little detailed information has been published regarding these alloys, and the work which forms the subject of this paper was carried out in order to obtain further information regarding the hot-working, physical, and mechanical properties of alloys of this type. The first part of the work, namely that on chill-castings and forgings, was of an exploratory character, to obtain an indication of the range of composition likely to provide alloys which may be of practical interest.

CHILL-CAST AND HOT-FORGED ALLOYS.

A series of alloys was made up under laboratory conditions from 70 : 30 brass of cartridge quality, 80 : 20 cupro-nickel, shot nickel, and electrolytic spelter. The alloys were melted in Salamander crucibles, in a gas-fired injector furnace. Each heat was adequately protected with a layer of charcoal, and no deoxidant was used. From each heat two chill-castings were made in iron moulds dressed with a mixture of graphite and linseed oil. One of the castings was a round bar ⅞ in. diameter × 8 in. long, and the other a rectangular bar measuring 6 in. × 1¾ in. × ¾ in., the former being reserved for tensile testing and micro-specimens, while the latter was used for hot-forging tests and chemical analysis. In several instances check tests were made on the chill-cast alloys.

Chill-Cast Alloys.

The results of tensile tests on the 26 alloys so prepared are given in Table I. In the 5, 10, 15, and 20 per cent. nickel alloys, the tensile strength values appear to reach a maximum near to 45 per cent. zinc, while, in a general way, the elongation in an alloy of given nickel content decreases with increasing zinc content, and the hardness increases. The sharp decrease in the elongation values between 40 and 45 per cent. zinc. is due to the largely increased proportion of β present in the 45 per cent. zinc alloy. Figs. 1 and 2 (Plate XII) show the differences in structure between alloys 2 and 3, which have elongation values of 46·5 and 15·5 per cent. on 2 in., respectively. No. 2 is composed of α and β, whereas No. 3 consists entirely of β. Fig. 3 (Plate XII) illustrates the structure of alloy No. 7, which consists largely of α with

TABLE I.

Alloy No.	Chemical Composition, Per Cent.						Physical Properties.						
	Nominal.			Analytical.			Chill-Cast.				Chill-Cast and Hot-Forged.		
	Cu.	Ni.	Zn.	Cu.	Ni.	Zn (Diff.).	Tensile Strength, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Diamond Pyramid Hardness No. (10 Kg. Load).	Microstructure.	Tensile Strength, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Diamond Pyramid Hardness No. (10 Kg. Load).
1	60	5	35	60·2	4·8	35·0	19·6	50·2	95	Cored α (trace β)	24·0	37·0	92
2	55	5	40	56·7	4·9	38·4	23·9	46·5	115	Cored α and β	29·9	33·0	122
3	50	5	45	49·5	5·3	45·2	30·0	15·5	163	β	26·8	9·0	153
4	45	5	50	46·2	4·9	48·9	25·2	10·5	179	β	3·3	0	151
5	60	10	30	59·5	10·1	30·4	18·0	45·5	79	Cored α	27·3	56·0	114
6	55	10	35	54·9	9·8	35·3	18·3	43·0	105	Cored α	27·2	53·0	109
7	50	10	40	50·1	9·9	40·0	24·3	37·5	130	Cored α (and β)	30·5	55·0	120
8	45	10	45	45·0	10·2	44·8	30·9	9·0	183	β (trace α)	37·0	22·0	134
9	55	15	30	54·4	15·7	29·9	18·6	25·0	105		29·6	47·5	126
10	50	15	35	50·1	15·5	34·4	19·6	26·7	120	Cored α	30·5	56·5	122
11	45	15	40	45·6	15·5	38·9	23·0	18·5	138	Cored α (trace β)	33·5	47·0	137
12	40	15	45	40·2	14·7	45·1	27·8	5·0	208	β (and α)	36·0	7·0	159
13	35	15	50	35·5	14·9	49·6	12·9	1·0	218	β	Cracked when hot-forged.		
14	30	15	55	30·6	14·8	54·6	4·0	0·5	246	β and γ	Cracked when hot-forged.		
15	50	20	30	50·3	20·2	29·5	20·9	15·5	117	Cored α	31·4	47·0	120
16	45	20	35	44·0	21·5	34·5	26·1	9·0	165	Cored α (trace β)	34·0	34·5	130
17	40	20	40	41·7	21·0	37·3	33·2	3·0	221	Cored α (and β)	38·0	29·0	164
18	35	20	45	35·8	20·9	43·3	36·8	1·0	270	Cored α and β	...	...	231
19	30	20	50	30·8	20·5	48·7	9·5	0·5	258	β (trace α)	Broke in pieces when hot-forged.		
20	25	20	55	24·6	19·7	55·7	6·3	0	284	β and γ	Broke in pieces when hot-forged.		
21	45	25	30	44·6	27·2	28·2	25·9	19·0	134	Cored α	34·8	36·5	150
22	40	25	35	39·8	26·1	34·1	31·0	5·5	181		35·5	11·5	162
23	35	25	40	34·3	25·5	40·2	33·1	0·5	317	Cored α (and β)	Broke in pieces when hot-forged.		
24	40	30	30	41·3	30·3	28·4	29·1	20·2	143	Cored α (trace β)	Cracked when hot-forged.		
25	35	30	35	35·2	31·3	33·5	30·5	3·5	230	Cored α (and β)	Cracked when hot-forged.		
26	30	30	40	32·5	32·6	34·9	33·6	0·5	250	Cored α (and β)	Cracked when hot-forged.		

only a little β. This alloy has an elongation of 37·5 per cent., but alloy No. 8, which has a similar nickel content but contains 44·8 per cent. zinc, has an elongation of only 9 per cent. It is composed largely of β and contains only very little α (Fig. 4, Plate XII).

With the higher nickel series, the mechanical properties are poorer, even when the copper is sufficiently high and the zinc sufficiently low for the alloys to be composed of the α solid solution. The alloys containing the γ constituent are very weak and brittle. The structure of one of these alloys—No. 20—at magnifications of 50 and 250 diameters, is shown in Figs. 5 and 6 (Plate XIII).

When the results of tensile tests are considered in relation to increasing nickel at a given zinc content, the values show a very definite increase after 15 per cent. nickel is exceeded, except in the case of the alloys of highest zinc content—50 and 55 per cent.—which are composed of γ or β and γ. Between the limits 30 and 45 per cent. zinc, the tensile strength increases with the zinc content for a given nickel content. With a constant zinc content, the elongation values decrease progressively with increasing nickel contents. The hardnesses in all cases increase with increasing nickel and zinc contents.

Hot-Forged Alloys.

In the hot-forging test, the 1¾ in. × ¾ in. rectangular bars were heated to about 800° C. in a gas-fired muffle furnace, and then forged under a power hammer until they were approximately round in shape, and about 1 in. in diameter. The ease with which the alloy could be hot-forged was noted, and also whether it withstood the test without cracking. In so far as the forging operation itself was concerned, it was found that the difficulty in forging increased with increasing nickel content. With low nickel contents the forging became easier as the zinc content was increased. All the alloys listed in Table I containing 5 per cent. nickel hot-forged very easily. The alloys containing 10 per cent. nickel also forged without cracking, or any great difficulty, but not so easily as the alloys containing 5 per cent. nickel. The alloys containing 15 per cent. forged satisfactorily up to 45 per cent. zinc, but when the zinc exceeded this value the metal cracked under the hammer. Of the alloys containing 20 per cent. nickel, only those containing less than 45 per cent. zinc forged without cracking, but even these deformed much less rapidly than alloys with a smaller nickel content. The alloys with 25 and 30 per cent. nickel were still more difficult to hot-forge, and of the three alloys of the former nickel content, only two, *i.e.* those containing 30 and 35 per cent. zinc, forged without cracking, but the three alloys containing 30 per cent. nickel cracked on forging.

Test-pieces were machined from the hot-forged bars, and the results of tensile tests are detailed in Table I. Generally, when an alloy is capable of being hot-forged satisfactorily, its physical properties in that condition are superior, as would be expected, to those of the corresponding alloy in the chill-cast state. This is associated, at least to some extent, with structural change, that in the case of alloy No. 17 being illustrated in Figs. 7 and 8 (Plate XIII). The best combination of strength and ductility is shown by the 10 and 15 per cent. nickel series.

EXTRUDED ALLOYS.

Preparation and Physical Properties.

After consideration of the results obtained in tensile tests on chill-cast alloys, hot-forging tests on alloys of similar compositions, and tensile tests on the hot-forged alloys themselves, a limited number were chosen for large-scale experiments, to obtain further data regarding the properties of those alloys of the most promising compositions. The compositions selected were:

Alloy No.	Copper, Per Cent.	Nickel, Per Cent.	Zinc, Per Cent.
E1	45	10	45
E2	45	12½	42½
E3	55	15	30
E4	45	15	40
E5	40	20	40

A 160-lb. billet, 5 in. in diameter, of each of these compositions was cast and extruded through a two-hole die, on a 5-in. direct-action press, into ¾-in. diameter round rod. The heats were made up from 18 per cent. nickel silver scrap, H.C. copper, electrolytic spelter, and nickel shot, and were deoxidized with 70 : 30 cupro-manganese. The extrusion was carried out at 800°–850° C., and, of the five selected alloys, Nos. E3 and E5 would not extrude under these conditions. Nos. E1 and E2 extruded without difficulty, but No. E4 was slightly difficult to extrude, although the whole of the billet was extruded into rod.

The chemical compositions and physical properties of samples cut from the front and back ends of rod of alloys Nos. E1, E2, and E4 are given in the first section of Table II. The analytical figures for copper, nickel, and zinc only are given. A number of complete analyses, however, have been made, and the impurities are all very similar, as would be expected, since the same raw materials were used in all cases for making up the alloys. In each alloy about 0·20 per cent. manganese and 0·07 per cent. iron were present. Except where specially added, lead was absent, and the only other elements detected were those which were deliberately added, namely, phosphorus and silicon, in certain of the alloys. In the column on microstructures in Table II, the brackets indicate that the constituent named within is present to a less extent than the other.

The physical properties need no detailed comment. The 10 per cent. nickel alloy (E1) which has the greatest zinc content has the greatest tensile strength and smallest elongation values of the three. The greatest elongation values and intermediate values for tensile strength are shown by E2, which, in respect of composition, lies between alloys E1 and E4. Izod impact values were determined on three notch British Standard test-pieces (B.S.I. Report, No. 131, 1920) with 2 mm. deep notches having a root radius of 0·25 mm.

Since of the various compositions tried, the 45 : 10 : 45 alloy appeared to be the easiest to extrude, a further series of alloys of this major composition was prepared, to which no cupro-manganese deoxidant was added, but to which additions of varying amounts of phosphorus and silicon were made. An alloy of this composition without any deoxidant was also prepared. These alloys, E6 to E10, were made and extruded under conditions identical with those for the production of Nos. E1 to E5; the chemical compositions and physical properties are detailed in Table II. Small quantities of phosphorus increase the tensile strength and decrease the elongation; silicon, which was added in larger amounts, also increases the tensile strength and reduces the elongation to a very marked degree.

In preparing extruded brass for applications in which free-cutting qualities are essential, it is common practice to add appreciable quantities of lead. This is also done with nickel–brasses, and to obtain data on the effect of increasing amounts of lead on the machining properties of extruded rod, three alloys, E11, E12, and E13, of the 45 : 10 : 45 composition and containing 0·5, 1·5, and 3 per cent. lead were prepared. These were made under similar conditions to those for the other " E " series of alloys, previously referred to, and were deoxidized with cupro-manganese. The compositions of these rods, and the results of tensile tests on specimens cut from the front and back ends of extruded rod, are given in Table II, in which details of alloy No. E1 are quoted to facilitate comparison.

Increasing amounts of lead tend to reduce the tensile strength slightly, but the effect does not appear to be very marked. The elongation, however, decreases progressively with increasing lead content.

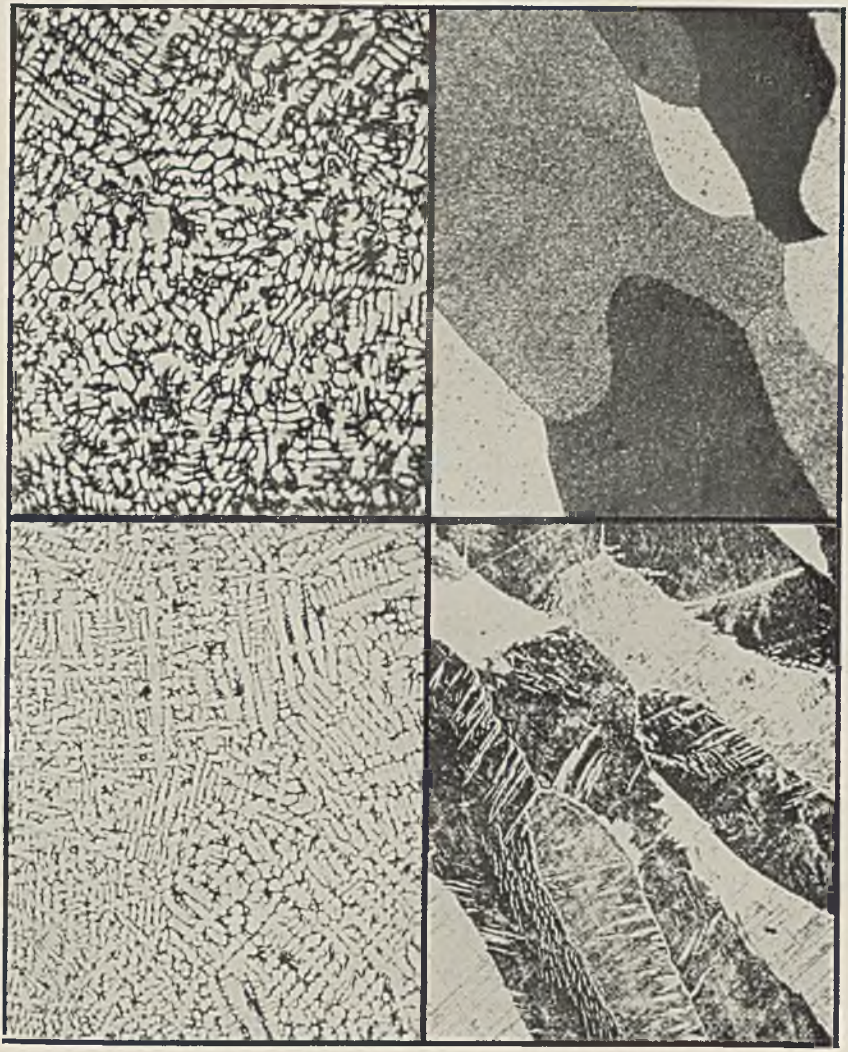

FIG. 1.—Cu 55, Ni 5, Zn 40%. (Alloy No. 2.) Chill-Cast. × 50.
FIG. 2.—Cu 50, Ni 5, Zn 45%. (Alloy No. 3.) Chill-Cast. × 50.
FIG. 3.—Cu 50, Ni 10, Zn 40%. (Alloy No. 7.) Chill-Cast. × 50.
FIG. 4.—Cu 45, Ni 10, Zn 45%. (Alloy No. 8.) Chill-Cast. × 50.

[*To face p.* 141.

PLATE XIII.

FIG. 5.—Cu 25, Ni 20, Zn 55%. (Alloy No. 20.) Chill-Cast. × 50.
FIG. 6.—Cu 25, Ni 20, Zn 55%. (Alloy No. 20.) Chill-Cast. × 250.
FIG. 7.—Cu 40, Ni 20, Zn 40%. (Alloy No. 17.) Chill-Cast. × 50.
FIG. 8.—Cu 40, Ni 20, Zn 40%. (Alloy No. 17.) Chill-Cast and Hot-Forged. × 50.

PLATE XIV.

FIG. 9.—Cu 45, Ni 15, Zn 40%. (Alloy No. E4.) Front End. × 100.
FIG. 10.—Cu 45, Ni 15, Zn 40%. (Alloy No. E4.) Back End. × 100.
FIG. 11.—Cu 45, Ni 12½, Zn 42½%. (Alloy No. E2.) Front End. × 100.
FIG. 12.—Cu 45, Ni 12½, Zn 42½%. (Alloy No. E2.) Back End. × 100.

PLATE XV.

13

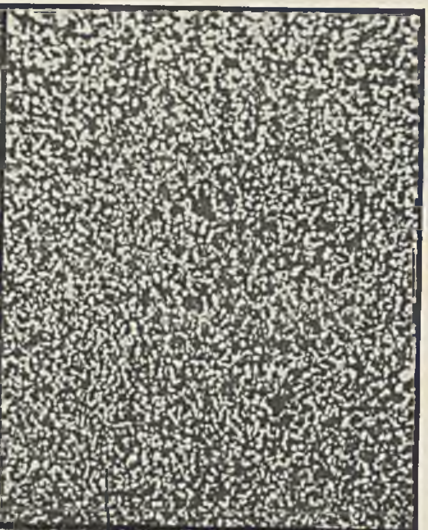

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FIG. 13.—Cu 45, Ni 10, Zn 45%. (Alloy No. E1.) Front End. × 100.
FIG. 14.—Cu 45, Ni 10, Zn 45%. (Alloy No. E1.) Back End. × 100.
FIG. 15.—Cu 45, Ni 10, Zn 45%. Pb 2·88%. (Alloy No. E13.) Front end. Unetched. × 100.
FIG. 16.—Cu 45, Ni 10, Zn 45%. Pb 2·88%. (Alloy No. E13.) Front end. Etched. × 100.

TABLE II.—*Extruded Nickel–Brasses.*

Alloy No.	Chemical Composition, Per Cent.							Physical Properties.					Micro-structure.
	Nominal.			Analytical.				Tensile Strength, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	D.P. Hardness No. (10 Kg. Load).	Izod Value, Ft.-lb.	Machinability.	
	Cu.	Ni.	Zn.	Cu.	Ni.	Zn (Diff.).	Other Additions.						
E1	45	10	45	44·8	10·1	45·1	Deoxidized with Cu–Mn	F 41·0 B 43·4	28·0 26·0	155 166	27 29	60	β (and α) β (and α)
E2	45	12½	42½	44·6	12·6	42·8		F 35·2 B 39·8	41·9 37·0	132 144	47 54	52	α and β α and β
E4	45	15	40	43·8	16·1	40·1		F 35·8 B 37·8	40·5 34·0	168 171	20 48	40	α (and β)
E6	45	10	45	44·5	10·2	45·3	No deoxidant	F 38·3 B 39·2	... 28·5	157 161	29 32	56	β (and α) β (and α)
E7	45	10	45	44·8	9·9	45·3	0·02% P	F 41·6 B 45·8	25·3 ...	157 175	27 28	55	β (and α) β (and α)
E8	45	10	45	44·9	10·2	44·8	0·08% P	F 44·1 B 45·7	21·0 15·5	162 166	22 25	60	β (trace α) β (and α)
E9	45	10	45	44·7	10·5	44·7	0·11% Si	F 38·2 B 39·3	10·5 9·5	172 170	20 28	63	β (trace α) β (trace α)
E10	45	10	45	44·6	10·1	45·0	0·26% Si	F 45·3 B 46·5	14·0 12·5	198 196	19 14	53	β β
E1	45	10	45	44·8	10·1	45·1	Deoxidized with Cu–Mn	F 41·0 B 43·4	28·0 26·0	155 166	27 29	60	β (and α) β (and α)
E11	45	10	45	44·9	9·7	44·8	0·56% Pb	F 42·4 B 42·3	28·7 18·5	177 164	28 23	57	β (and α) β (and α)
E12	45	10	45	44·6	9·4	44·4	1·55% Pb	F 40·5 B 40·4	27·2 17·0	150 151	28 20	77	β (and α) β (and α)
E13	45	10	45	44·1	9·1	43·9	2·88% Pb	F 40·5 B 35·8	25·0 12·0	154 161	22 16	80	β and α β and α

PLATE XIII.

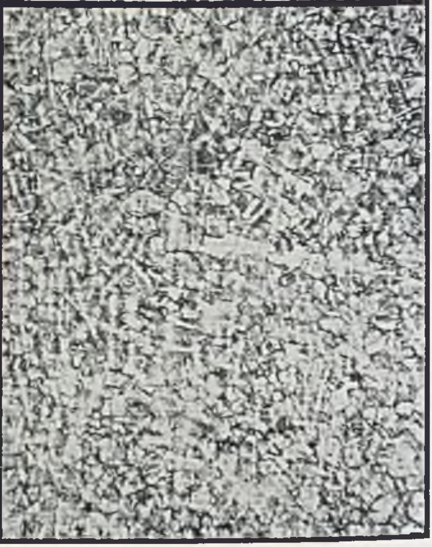
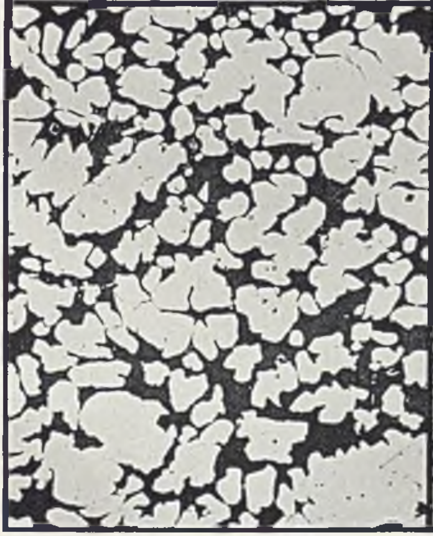


FIG. 5.—Cu 25, Ni 20, Zn 55%. (Alloy No. 20.) Chill-Cast. × 50.
FIG. 6.—Cu 25, Ni 20, Zn 55%. (Alloy No. 20.) Chill-Cast. × 250.
FIG. 7.—Cu 40, Ni 20, Zn 40%. (Alloy No. 17.) Chill-Cast. × 50.
FIG. 8.—Cu 40, Ni 20, Zn 40%. (Alloy No. 17.) Chill-Cast and Hot-Forged. × 50.

PLATE XIV.



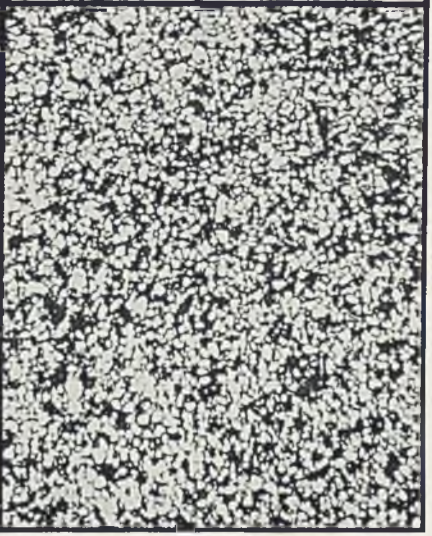


FIG. 9.—Cu 45, Ni 15, Zn 40%. (Alloy No. E4.) Front End. × 100.
FIG. 10.—Cu 45, Ni 15, Zn 40%. (Alloy No. E4.) Back End. × 100.
FIG. 11.—Cu 45, Ni 12½, Zn 42½%. (Alloy No. E2.) Front End. × 100.
FIG. 12.—Cu 45, Ni 12½, Zn 42½%. (Alloy No. E2.) Back End. × 100.

PLATE XV.

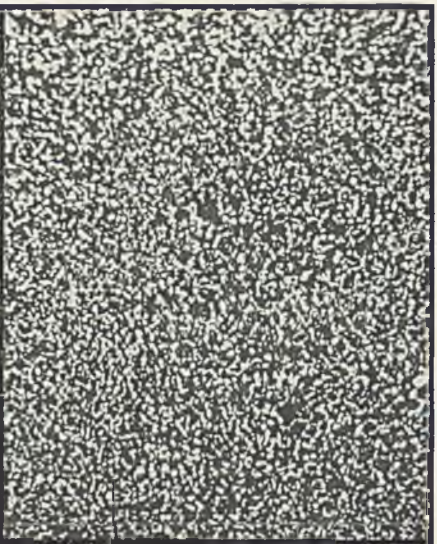


FIG. 13.—Cu 45, Ni 10, Zn 45%. (Alloy No. E1.) Front End. × 100.

FIG. 14.—Cu 45, Ni 10, Zn 45%. (Alloy No. E1.) Back End. × 100.

FIG. 15.—Cu 45, Ni 10, Zn 45%. Pb 2·88%. (Alloy No. E13.) Front end. Unetched. × 100.

FIG. 16.—Cu 45, Ni 10, Zn 45%. Pb 2·88%. (Alloy No. E13.) Front end. Etched. × 100.

TABLE II.—*Extruded Nickel–Brasses.*

Alloy No.	Chemical Composition, Per Cent.							Physical Properties.					Micro-structure.
	Nominal.			Analytical.									
	Cu.	Ni.	Zn.	Cu.	Ni.	Zn (Diff.).	Other Additions.	Tensile Strength, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	D.P. Hardness No. (10 Kg. Load).	Izod Value, Ft.-lb.	Machinability.	
E1	45	10	45	44·8	10·1	45·1	Deoxidized with Cu–Mn	F 41·0 B 43·4	28·0 26·0	155 166	27 29	60	β (and α) β (and α)
E3	45	12½	42½	44·6	12·6	42·8		F 35·2 B 39·8	41·9 37·0	132 144	47 51	52	α and β α and β
E4	45	15	40	43·8	16·1	40·1		F 35·8 B 37·8	40·5 34·0	168 171	20 48	40	α (and β)
E6	45	10	45	44·5	10·2	45·3	No deoxidant	F 38·3 B 39·2	... 28·5	157 161	29 32	56	β (and α) β (and α)
E7	45	10	45	44·8	9·9	45·3	0·02% P	F 41·6 B 45·8	25·3 ...	157 175	27 28	55	β (and α) β (and α)
E8	45	10	45	44·9	10·2	44·8	0·08% P	F 44·1 B 45·7	21·0 15·5	162 166	22 25	60	β (trace α) β (and α)
E9	45	10	45	44·7	10·5	44·7	0·11% Si	F 38·2 B 39·3	10·5 9·5	172 170	20 28	63	β (trace α) β (trace α)
E10	45	10	45	44·6	10·1	45·0	0·26% Si	F 45·3 B 46·5	14·0 12·5	198 196	19 14	53	β β
E1	45	10	45	44·8	10·1	45·1	Deoxidized with Cu–Mn	F 41·0 B 43·4	28·0 26·0	155 166	27 29	60	β (and α) β (and α)
E11	45	10	45	44·9	9·7	44·8	0·56% Pb	F 42·4 B 42·3	28·7 18·5	177 164	28 23	57	β (and α) β (and α)
E12	45	10	45	44·6	9·4	44·4	1·55% Pb	F 40·5 B 40·4	27·2 17·0	150 151	28 20	77	β (and α) β (and α)
E13	45	10	45	44·1	9·1	43·9	2·88% Pb	F 40·5 B 35·8	25·0 12·0	154 161	22 16	80	β and α β and α

Machinability Test.

The machinability values of specimens from different extruded rods were determined by comparison with a brass of the 60 : 40 type, containing approximately 3 per cent. lead (free-turning quality). Machinability values given in Table II are percentages representing the depth of penetration of a standard $\frac{1}{8}$-in. diameter twist drill, rotated at 1000 r.p.m., and applied under a known load for 15 seconds, referred to the free-turning brass taken as 100 per cent. Between each test, samples of the standard brass rod were also tested, and the values in the table are the average of 4 or 5 tests. They show quite clearly the improving effect of appreciable lead additions on machinability. With 2·88 per cent. lead present, the machining properties of the alloy are not so good as those of brass containing about this amount of lead.

Season-Cracking Tests.

It is a well-known fact that brasses left in a stressed condition are very susceptible to season-cracking, and extruded brasses may be prone to season-cracking, but this can be largely overcome by such operations as reeling or low-temperature annealing. In order to test the susceptibility of the alloys to season-cracking, samples 4 in. long of the 10 per cent. nickel alloy to which no deoxidant had been added during melting, and also of alloys Nos. 1, 6, 7, 8, 9, and 10, containing manganese, phosphorus, and silicon, were subjected to a mercurous nitrate test. A 1 per cent. solution of the salt was used, and the specimens, which were in the extruded condition, were examined at intervals for cracks. Even after immersion for 1 week no cracks were found in any of the materials.

Hot-Stamping Tests.

A considerable amount of extruded brass rod, usually of round section, is used for the manufacture of hot-stampings and forgings. The behaviour of the alloy in such operations is affected by variations in the major composition, and also by the amount and nature of impurities or alloying elements specially added. Tests have been carried out to obtain some idea of the hot-working properties of the alloys under consideration; these took the form of the hot-stamping test included in B.S.I. Specification No. 218 for hot-working brass. In this test a cylindrical test-piece of a length equal to the diameter is reduced to 20 per cent. of its original height by one blow from a drop hammer. The test was carried out at six different temperatures, at 50° intervals, over the range 600° to 850° C. The specimens were heated in a small muffle furnace, adjacent to the hammer so that it was possible to transfer the specimen from the pyrometrically-controlled furnace to the anvil, and to flatten it within a few seconds. The edges of the flattened specimens were examined for cracks, and only those which were absolutely free from cracks were regarded as satisfactory. It is obvious, of course, that the extent of cracking varies over a considerable range from those specimens which show only one or two cracks to those which show a badly shattered periphery. The results of the hot-stamping tests are given in Table III.

TABLE III.—*Extruded Nickel–Brass Rod—Hot-Stamping Test.*

O indicates satisfactory stamping.
X indicates cracked stamping.

Alloy No. as in Table II.		Temperature Range, ° C.					
		600.	650.	700.	750.	800.	850.
E1	Front end .	O	O	O	O	O	O
	Back end .	O	O	O	O	O	O
E2	Front end .	X	X	X	X	X	O
	Back end .	X	X	X	X	X	O
E4	Front end .	X	X	X	X	X	X
	Back end .	X	X	X	X	X	X
E6	Front end .	X	O	O	O	O	O
	Back end .	X	O	O	O	O	O
E7	Front end .	O	O	O	O	O	O
	Back end .	X	O	O	O	O	O
E8	Front end .	O	O	O	X	X	X
	Back end .	X	X	O	X	X	X
E9	Front end .	X	O	O	O	O	O
	Back end .	O	O	O	O	O	O
E10	Front end .	O	O	O	O	O	O
	Back end .	O	O	O	O	O	O
E11	Front end .	X	X	O	O	X	X
	Back end .	X	X	O	X	X	X
E12	Front end .	X	X	X	O	O	X
	Back end .	X	X	X	O	X	X
E13	Front end .	X	X	X	X	X	X
	Back end .	X	X	X	X	X	X

It will be seen from these results that the straight 45 : 10 : 45 alloy (E1) hot-stamps satisfactorily over the range 600° to 850° C., inclusive, an increase in the nickel content, when the copper content is maintained constant, quickly reducing the hot-stamping range, until with the

45 : 15 : 40 alloy (E4) no satisfactory results are obtained within the temperature range considered.

The 45 : 10 : 45 alloy, melted and cast without the use of any deoxidant (E6), hot-stamps from 650° C. upwards, and so also does the alloy of the same major composition containing 0·02 per cent. phosphorus (E7). When the phosphorus content is increased to 0·08 per cent. (E8), the satisfactory hot-stamping range is limited on either side to the region of 700° C. The presence of silicon (E9 and E10) in the amounts considered, *i.e.* up to 0·26 per cent., does not appear to have any injurious effect on the hot-working properties of the material. The results for alloys E11, E12, and E13, given in Table III, show clearly the injurious effect of increasing amounts of lead on the hot-working properties of the alloy.

Microstructure of Extruded Alloys.

Figs. 9 to 14 (Plates XIV–XV) show the microstructures (× 100) of samples cut from the front and back ends of rods of alloys with 45 per cent. copper, 15, 12½, and 10 per cent. nickel. In all three pairs of photographs the pronounced difference of structure between the front and back ends of the rod is very clearly shown. Alloy E4, containing 15 per cent. nickel, consists at the front end largely of α with a little interstitial β, and at the back entirely of α (Figs. 9 and 10, Plate XIV). In the alloy containing 12½ per cent. nickel, more β is present, and this constituent is also present in the back end of the rod (Figs. 11 and 12, Plate XIV), and a further reduction of the nickel content to 10 per cent. (alloy E1) results in an appreciable increase in the amount of β (Figs. 13 and 14, Plate XV).

This change in structure with nickel content is reflected in the machining and hot-stamping properties of the alloys. Figs. 15 and 16 (Plate XV) illustrate (× 100) alloy E13, which contains 2·88 per cent. lead. The lead is fairly evenly distributed, as will be seen in the photograph of the unetched sample, and the α–β structure of the alloy is similar to that of alloy E1, but is much finer, although the corresponding back ends of these two rods were not very dissimilar.

All the specimens illustrated were etched with a mixture of ferric chloride and hydrochloric acid solution.

SUMMARY.

Tensile tests, hardness tests, and observations on the microstructure have been made on a range of nickel–brasses containing copper 60 to 25, nickel 5 to 30, and zinc 30 to 55 per cent., in the form of chill-castings and hot-forged bars prepared from chill-castings.

More extended observations, including the determination of machinability values and hot-stamping properties, have been made on three alloys, in the form of extruded rod, with a copper content of 45 per cent. and nickel contents of 10, 12½, and 15 per cent., respectively, and on the 10 per cent. alloy, with and without the use of cupro-manganese as deoxidant, and with additions of lead, phosphorus, and silicon. The differences in physical properties of these three alloys of varying nickel content were not very marked, but the alloy containing 10 per cent. nickel gave superior machinability values, and, moreover, gave satisfactory results in the hot-stamping tests over the range of 600° to 850° C.; the other two alloys compared very unfavourably with it in this respect.

The addition of lead to the 10 per cent. nickel alloy improves the machinability, but adversely affects its hot-stamping properties, and it also tends to reduce the tensile strength and elongation values.

ACKNOWLEDGMENTS.

The author's thanks are due to Messrs. Imperial Chemical Industries, Limited, for permission to publish the results contained in this paper, and to Dr. H. W. Brownsdon for his interest and helpful advice. He also gratefully acknowledges the help which he has received in the experimental part of the work from Messrs. E. W. Tremayne, B.A., and A. Fletcher.

DISCUSSION.

(*Condensed.*)

Professor W. R. D. Jones,* D.Sc. (Member): This paper is very useful, since the data available on the effect of nickel on the high-tensile brasses are not altogether conclusive, mainly because the effect of the nickel has been obscured by its effect on the relative proportion of α and β in the microstructure, and the correlated effect on the mechanical properties.

The casting of these alloys requires care, owing to the deleterious effects of oxygen, carbon, and sulphur. Experience has shown that it is good practice to preheat the crucible to a high temperature before charging, and to try to obtain as rapid a melting as possible in a forced-draught crucible furnace, using a high grade of hard coke. The cupro-nickel is first melted under charcoal, but using no flux, and then the other ingredients, such as brass, are added; otherwise there is a tendency for nickel to be concentrated at the bottom of the pot. The casting temperature is important in sand-castings, and as high a temperature as possible should be used, while avoiding overheating and stewing. The alloy must be very fluid when teeming, and a temperature of 1250°–1300° C. can be used. Can the author state at what temperature his alloys were cast?

With regard to the mechanical properties given in Table I, those alloys which failed to withstand hot-forging—*i.e.* Nos. 13, 14, 19, 20, and 26—are really alloys of zinc rather than nickel–brasses. Assuming a zinc equivalence of 1·2, these alloys should consist mainly of the δ constituent, with, in some cases,

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* Department of Metallurgy and Fuel Technology, University College, Cardiff.

the ε phase. Taking alloy No. 20, the fictitious zinc content is 76 per cent., which from the usually accepted equilibrium diagram for brass is in the $\gamma + \varepsilon$ region. Is it to be assumed that in Figs. 5 and 6 the structure is $\beta + \delta$?

Is there any particular reason why the cast blanks should be $1\frac{3}{4} \times \frac{3}{4}$ in. before forging down to 1 in. under the hammer? We generally use round, chill-cast ingots and swage down to size, constantly turning the bar round. By this method the forging is carried out evenly, and bars which are sometimes difficult to forge by hammering on the flat and then forging round to finish, seem to withstand deformation better.

Would the 0·2 per cent. manganese present in the extruded billets account for the higher Izod values in Table II, or is the effect due entirely to the higher proportion of nickel and the lower zinc content (cf. E2, E1, and E6)? It certainly seems that the manganese has an effect at least equal to that of the phosphorus, and more beneficial than that of the silicon added.

The results given regarding the effect of lead are interesting. Nickel increases considerably the solubility of lead in copper. With an addition of 2–3 per cent., the liquid copper and lead are completely miscible. This is borne out by Fig. 15 (Plate XV), in which, for the amount of lead present in the alloy, the amount not in solution seems low when compared with a free-machining straight brass of similar lead content. The machinability of this alloy No. E13 is not so good as the standard, for that reason. The hot-working properties are decreased, but not appreciably, by reason of the solubility of lead in the α and/or β constituents.

The paragraph dealing with the season-cracking tests is of little value for comparative purposes. The mercurous test is by no means infallible, and as ordinarily carried out, the specimen is first cleaned in dilute nitric acid and the mercurous nitrate is used as an aqueous solution containing 1 per cent., which is acidified with 1 per cent. concentrated nitric acid. Although the test seems a simple one, considerable misunderstanding has arisen as to its interpretation. Cases are known in which articles have easily passed this test but still failed by season-cracking after the lapse of some months, the number of failures increasing with the length of time in storage. Can the author give any information on this point obtained during his experience?

Dr. L. B. Pfeil,* A.R.S.M. (Member): The author has dealt primarily with nickel-brasses which are of high zinc content relative to the more familiar nickel silvers. A large proportion of the alloys studied were of the $\alpha + \beta$ type at room temperature, and this fact should be kept clearly in mind in considering the statements regarding extrusion. There is no doubt that normal α nickel silvers at all nickel contents can be extruded commercially without difficulty. A good furnace is necessary, so that the billet may be heated under accurate control to the desired temperature, which is, in general, higher the greater the nickel content of the alloy. There seems to be no difficulty in extruding even a 30 per cent. nickel alloy of the α type, provided that the correct billet temperature is employed. I do not suggest that the $\alpha + \beta$ alloys are not, as a class, more easy to extrude than the α type, but only that the α alloys may be extruded satisfactorily, though requiring a little more pressure than the $\alpha + \beta$ type. In introducing his paper, the author stated that the alloys of higher nickel content can be extruded, but that they require higher pressures. In my view the position can be explained in another way, namely, that they require higher extrusion temperatures to extrude satisfactorily.

Regarding the machinability tests, a material having satisfactory free-machining characteristics under one set of conditions, *e.g.* high-speed automatic lathe work, sometimes proves unsuitable in machining characteristics

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* The Mond Nickel Company, Ltd., Birmingham.

under other conditions. I wonder, therefore, whether the type of test which the author employed gives a correct impression of the situation. The matter is important, because machining characteristics determine largely the production costs in many cases, and a material may be employed because it is free-machining as much as because it has other good properties.

Mr. J. E. Newson,* M.Met. (Member): The title of this paper promises more than the paper contains, as it is essentially an exploratory study of the hot-working properties of only some of the commercially-produced nickel brasses. Since the object of the paper was to study alloys "which may be of practical interest," it would have been helpful if the author had indicated more clearly the scope of this interest, and whether high mechanical strength, resistance to atmospheric and other forms of corrosion, or colour for decorative work was in view. Nickel additions, which are costly, are not usually made to commercial brasses unless some special properties, unobtainable by cheaper alloy additions, are required, and of these colour is frequently quite important. Higher mechanical strength, in the cold at any rate, can be obtained by suitable additions to $\alpha + \beta$ brasses, of iron, aluminium, and manganese, whilst the pressure required to extrude certain of the high-nickel brasses suggests that they may possess useful strength at temperatures above normal. For resisting some types of corrosion, the high-nickel brasses may be superior to aluminium bronze, but one of their chief attractions at present lies in the non-tarnishing silvery whiteness of the alloy for architectural decoration and household, automobile, and sundry other fittings.

In the hot-working of nickel brasses, forging is the exception rather than the rule. The more usual procedure is extrusion to section, tube, or rod. The rod serves as the basis material for hot-stamping or pressing in closed dies. It is generally recognized that forging is no criterion of the extrudability of an alloy. Some alloys crack under forging but extrude well; others will stand gradual reductions in area by forging, but fail under such reductions of area in one stroke (about 95 per cent.), as mentioned by the author, in his extrusion. For this reason, the author has restricted his choice of alloys for extrusion. The microstructures of the extruded bars (Figs. 9–14) suggest that the extruding temperature range is very limited, or that there was a marked decrease in temperature between the beginning and end of extrusion, possibly due to the ratio of billet length to rod diameter being too high, or to too slow extrusion. In Fig. 9, the presence of the β constituent suggests that a longer heating time should have been allowed, when diffusion due to coring and a nearer approach to the equilibrium structure would have obtained before extrusion.

Referring now to the alloys containing lead and the machinability tests, it was shown by Desch in 1920, and amply confirmed since that date in practice, that the microstructure of $\alpha + \beta$ brasses is also of importance, and a "banded" structure gives improved machining quality. The microsection shown in Fig. 16 is not of this type. One peculiarity observed in practice, and recorded by the author without comment, is the increase in mechanical strength and hardness with small additions of lead. The alloy E11 (Table II) containing 0·56 per cent. lead shows for the test on the front end an increase of 1·4 tons/in.^{2} in the tensile strength, an increase of 22 on the diamond pyramid hardness, and a decrease of machinability number. With a 15 per cent. nickel alloy, 2 per cent. lead produces an even more marked increase in hardness. It is claimed that nickel increases the solubility of lead in copper, but whether it exerts a similar action in copper–zinc alloys is not known and the author's observations on this point would be of interest.

With less than 10 per cent. of nickel, the addition of lead tends to give the

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* Chief Metallurgist, Manganese Bronze and Brass Company, Ltd., London.

alloys a yellow tinge, while small amounts of iron or manganese whiten them, but harden them. Additions of manganese up to 2–3 per cent. improve the extruding properties of the 15 per cent. nickel brasses. The author's statement that extruded brasses may be prone to season-cracking is misleading. In material extruded under normal conditions the liability is very small, but is greatly increased by drawing. Reeling by applying stresses of opposite sign will reduce the tendency in drawn bars, but severe reeling of undrawn bars can render some alloys susceptible to season-cracking. Will the author state from what part of the extruded bar the samples were chosen for the season-cracking test? It would be of some interest to know what was the microstructure of alloy E10 containing 0·26 per cent. silicon; and whether the compound nickel silicide appeared.

Finally, I should like to direct the author's attention to an article by W. R. Barclay,* in which reference is made to an alloy containing (approximately) nickel 20, copper 60, and zinc 20 per cent. and an illustration given of a section, by no means uniform in thickness, extruded in this alloy. He will also find confirmation of my remarks relating to extruding temperature and speed. Much more work remains to be done on this range of alloys, and it is hoped that the author will be able to extend his investigations to include more of the high-nickel alloys, and perhaps to make some reference to their properties at temperatures above normal.

Mr. W. R. BARCLAY,† O.B.E. (Past-President): The author speaks of the addition of manganese as a deoxidizing agent, which it probably is within limits; in connection with the casting of all nickel silver alloys for hot-working purposes, however, it must be admitted that the value of manganese is very largely as a desulphurizing rather than as a deoxidizing agent. If in the scrap used there is likely to be any appreciable amount of sulphur, rather more manganese can be used with advantage. In my experience, it is possible to add quite an appreciable percentage of manganese without any detriment to either the hot-working or the cold-working properties of these alloys.

Although I know that the author would not wish to give this impression, there seems to run through the paper an idea that the commoner commercial nickel silvers of the order of nickel 20, copper 60, and zinc 20 per cent., are not hot-workable. It is wise for all industrial workers in this field to realize that all the commercial nickel silvers can be easily hot-worked, and it is rather a reflection on English and American practice in the production of these alloys that advantage has not been taken of their hot-working properties. I use the term "hot-working" in a broad sense, and as applied not only to extrusion, but to hot-rolling. The factors which it is necessary to control are the heating temperature, *i.e.* in the preliminary heating before hot-working, the pressures or pinches required, and the speed of rolling. The hot-working range in, say, a 20 : 60 : 20 alloy of the typical α type is comparatively narrow, but not too narrow to be industrially practicable, and when I see, as I do, some of the large Continental works casting nickel silver in 500-kg. slabs, hot-working down very rapidly to, say, 6 or 4 mm., and subsequently cold-rolling, I appreciate the great technical and economic advantages which ensue from that procedure, and I would emphasize the desirability of its application to English practice.

Dr. COOK (*in reply*): Concerning the remarks of Professor Jones, the casting temperatures were varied according to the composition of the alloy

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* W. R. Barclay, *Met. Ind.* (*Lond.*), 1935, 47, 494.

† Consulting Metallurgist, The Mond Nickel Company, Ltd., London.

being cast, but for the 45 : 45 : 10 alloy, for example, and for most of those produced as billets and subsequently extruded, the temperature was of the order of 1150° or 1175° C. From my observations on the structure of these alloys I would suggest that Figs. 5 and 6 (Plate XIII) show the β and γ phases. The particular sized rectangular bar was not chosen for any special reason, but it is perhaps an even better and more searching test of the forgeability of a material to reduce it from a rectangular section to a round than merely from a larger to a smaller round. The more pronounced change in the Izod figures in Table II, referred to by Professor Jones, is, I think, due to a change in the major composition of the alloy rather than to the presence of 0·2 per cent. manganese, although the addition of deoxidants is not without some effect. The amount of lead shown in Fig. 15 is very much less than that which would be seen in a straight brass with a similar lead content. The solubility of lead in brass is increased by the presence of nickel and, as Professor Jones has remarked, this explains why the machinability value of alloy E13 is not so good as that of the standard alloy. Since the specimens for the season-cracking test were in contact with mercury for no less a period than a week, as mentioned in the paper, I think that anyone familiar with season-cracking tests, and the significance and interpretation of the results obtainable from them, would agree that the test as described was sufficiently searching. There are various modifications of the season-cracking test which is, perhaps, applied to the brasses more than to any other group of alloys. In commercial laboratories the test is commonly carried out by first cleaning the article or specimen by a nitric acid dip and immersing it in a solution of 1 per cent. mercurous nitrate and 1 per cent. nitric acid for 15 minutes. It is then usually allowed to stand with mercury on it, but outside the solution, for 1 hr. If no cracking has developed after this time, it is assumed not necessarily that the material is absolutely free from season-cracking tendencies, but that under normal conditions of service and storage it is most unlikely that season-cracking will ensue. There are other and more searching variations of the test. For example, using the same solution, the article is allowed to stand in contact with mercury for 24 hrs. and to pass the test it must be free from cracking at the end of this time. I do not know of, and have never heard of, a case where articles which have stood up to a 24-hr. season-cracking test failed subsequently, however onerous the conditions. It will, of course, be appreciated that an article or component may be stressed in service sufficiently to cause it to fail subsequently by season-cracking, even though it was initially in a stress-free condition. In reply to the question raised by Mr. Newson, specimens for season-cracking tests were taken from both the front and back ends of the rods.

Both Dr. Pfeil and Mr. Barclay have emphasized the fact that alloys of higher nickel content, particularly those in the α region, can be extruded. This, of course, is perfectly true, and there is no suggestion in the paper to the contrary. On the other hand, those alloys of the copper–zinc–nickel series which are of the α–β type are more easily and readily hot-workable than those of the α type, but it is only with the former that the paper is concerned—as its title indicates. The alloys have been considered, therefore, as special brasses with nickel additions, which they are, rather than as nickel alloys. It should be borne in mind that these alloys are extruded in various forms, *e.g.* round rod, or sections for architectural and decorative work, and as round rod they are produced and used for the production of hot-stampings. It must be remembered that material for hot-stamping purposes has to hot-stamp relatively easily, and alloys of this kind should hot-stamp satisfactorily over as wide a temperature range as possible. I can imagine that many of the high-nickel alloys, which can be extruded by using higher pressures and temperatures than those used in making the alloys described in the paper, would probably give rise to some difficulty in the actual production of hot-stampings.

In examining microstructures of these several alloys, no additional constituent was noticed in the alloy which contained 0·5 per cent. silicon.

I agree with Mr. Barclay that although manganese may act as a deoxidant to some extent, its effect in other directions, particularly in removing sulphur, is most important in the production of these alloys.

CORRESPONDENCE.

The Author (*in further reply*): Although several types of machinability tests have been devised, there are so many different ways of machining metal that no one test can be expected to indicate machinability under widely varying conditions. When, however, it is a question of comparing the relative machinability of different materials under identical conditions of machining, then the penetration method which I used, and which has been previously used, is, perhaps, as good as any other.

In spite of the explanatory matter contained in the text, Mr. Newson does not appear to have appreciated the purport of the paper. The interest in these alloys, of course, lies in the combination of colour, mechanical and physical properties, and hot-workability, and the scope of the work is clearly indicated by the contents of the paper itself. Nickel is not added to brass primarily to increase its strength, and anyone with an elementary knowledge of the metallurgy of brass is aware of what Mr. Newson takes the trouble to point out, namely that brasses of greater tensile strength can be obtained by additions of iron, aluminium, and manganese. The results of forging tests were taken, not as an indication of extrudability, but as a guide to the ease with which the alloys could be hot-worked generally, and particularly by such a process as hot-stamping. The choice of alloys for extrusion was determined, not as Mr. Newson incorrectly suggests, by the results of forging tests, but, as clearly stated in the paper, from a consideration also of the mechanical and physical properties of cast and forged alloys and of their microstructures. With regard to Mr. Newson's observation that Fig. 16 does not show a "banded" type of structure, it will be appreciated that the machinability tests were not carried out with the object of determining the effect of any particular type of structure, but to obtain comparative results between the different alloys examined. It is true that the usual types of brasses as extruded are not very prone to season-cracking, but it is equally true that in certain circumstances, and after some treatments, they may season-crack. Although Mr. Newson states that the observation in the paper, in the section relating to season-cracking, that "extruded brasses may be prone to season-cracking" is misleading, he proceeds to confirm my statement by itemizing several conditions under which such cracking can occur. The alloys dealt with in the paper are members of an interesting group, concerning which very little information has hitherto been published, and on which much further work could be usefully carried out.

THE NICKEL–COPPER–MAGNESIUM ALLOYS.* 7

By Professor W. R. D. JONES,† D.Sc., Member, and K. J. B. WOLFE,‡ M.Sc.

Synopsis.

Experiments have been carried out on the effect of adding copper and nickel to magnesium. The improved mechanical properties given to magnesium, when in the cast condition, by small additions up to about 2 per cent. copper are enhanced by the addition of nickel, if the combined alloy content be 2¼–2½ per cent. A nickel content of ½–1 per cent. (in the combined alloy content) has a greater effect than a corresponding copper content. These alloys are forged or rolled readily and, provided that care is taken to prevent cold-work, reasonably good ductility values are obtained. In the case of forged or rolled alloys, the beneficial effect of the addition of nickel as well as copper is not so pronounced; the effect of nickel depends to some extent on the proportion of copper present in the alloy. Billets which have been rolled after a preliminary drawing give better mechanical properties than those which have been drawn down to the same size.

This paper deals with the effect of nickel on the magnesium-rich copper–magnesium alloys, which have been described in this *Journal*.[1]

Materials.

The materials used had the compositions:

Electrolytic Copper:

	Per Cent.
Iron	0·002
Tin	0·005
Bismuth	0·0002
Nickel	trace
Sulphur	trace
Lead	nil
Manganese	0·008

Extruded magnesium rod (free from flux):

Silicon	0·018
Iron	0·013
Manganese	trace
Zinc	trace
Copper	nil
Lead	nil

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* Manuscript received July 21, 1937. Presented at the Annual General Meeting, London, March 9, 1938.

† Department of Metallurgy and Fuel Technology, University College, Cardiff.

‡ Research Student, University of Wales.

Nickel shot:

	Per Cent.
Iron	0·178
Carbon	0·043
Cobalt	0·025
Copper	0·019
Silicon	0·010
Sulphur	trace
Tin	nil
Lead	nil
Manganese	nil
Magnesium	nil
Zinc	nil

CASTING OF THE ALLOYS.

The method adopted was, in general, that described previously.[1] The alloys were melted in a bottom-pouring steel crucible, which had a tightly fitting lid carrying a stirrer and an iron thermocouple sheath, all of which had been thoroughly "broken-in" to avoid any iron pick-up by the alloys. An excellent flux was "Elrasal," a proprietary flux, kindly supplied by Messrs. J. Stone & Co., Ltd., Deptford. Immediately before use, the flux was melted in an iron ladle and poured on to a cold iron slab. An amount equal to 2 per cent. by weight of metal melted was placed in the centre of the charge. The nickel in the alloy was added in the form of turnings from a 50 : 50 nickel–copper hardener, any additional copper required being added as thin strip. During the melting period the bath was under pyrometric control, and at no period was the temperature allowed to exceed 700°–710° C. The crucible and its contents were placed in a circular gas-fired furnace, which had been preheated to such a high temperature that the charge was melted in about 10 minutes. The melt was thoroughly stirred for 10 minutes, and the crucible withdrawn from the furnace. When the temperature of the bath had decreased to about 450° C., to ensure complete solidification, the crucible was replaced in the hot furnace and the metal remelted rapidly and allowed to remain undisturbed for 10 minutes at 700° C., so that any incorporated flux might come to the top. This procedure is essential in the case of alloys which contain more than 4 per cent. copper and/or nickel, because the flux tends to become viscid and heavy from the absorption of the oxides of nickel and copper, so that complete separation of metal and slag is comparatively sluggish, owing to the small difference in the densities of the molten metal and slag. The crucible was then placed gently in a rigid casting device, the mould * (which was movable) placed in position

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* In casting the ingots used to determine the properties of chill-cast bars, the mould used was a bolted split slab of forged steel 2 in. thick, 10 in. long, and 8 in.

underneath, and the metal quietly teemed by raising the stopper. Group casting of the 1-in. diameter bars was tried, but was not so successful as casting each ingot separately. The optimum casting temperature for all the alloys prepared was 700° C., *i.e.* about 70° C. above the freezing point. The moulds were preheated to 350°–450° C., and dressed with a thin layer of a mixture of graphite and linseed oil, a dressing which tends to keep cold-shutting to a minimum. Care was required in the teeming to maintain an even and steady stream of metal falling direct to the bottom of the mould, which should be vertical, otherwise surface folding will result even with a mould preheated to a high temperature. The rate of teeming was decreased appreciably at the end of the pouring to allow " feeding " of the ingot so that piping was minimized. Mould temperature is of importance, since it was impossible to produce an ingot free from cold-shut if the mould were only slightly warmed. When using this flux, the total melting loss was fairly constant, being about ½–¾ per cent. of the total charge. Other fluxes were tried, but the melting losses were much higher, in some cases being between 10 and 15 per cent.

Trouble was experienced with those ingots which contained a comparatively high alloy content, and particularly with those which contained more than 4 per cent. nickel. Although these ingots had good surfaces, they were unsound, and on machining generally fell to pieces after the surface layer had been removed. Visual examination then showed a series of small hair-line cracks along the ingots at intervals of about 1 in. (Figs. 1 and 2, Plate XVI). Fig. 3 (Plate XVI) shows an alloy which contains copper 6 and nickel 5 per cent. It will be seen that the path of the fracture lies between the crystals of magnesium and the compound, the compound not being sufficiently ductile to withstand the tensional stresses on cooling. Examination of the mechanical properties (see Figs. 5–7) shows that the maximum stress, ductility, and hardness values generally increase with increase in alloy content up to about 1 per cent. nickel and 2–3 per cent. copper, after which the strength and ductility decrease, whilst the hardness still increases. Up to this alloy content, the amount of compound is not sufficient to decrease the ductility as the tensile strength increases; above this content the amount of compound increases, and it is so hard and brittle that the strength and ductility decrease. It can be reasonably inferred that the cracks shown in Fig. 3 (Plate XVI) are indicative of micro-shrinkage. Many experiments were carried out, with an alloy containing 6 per cent.

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high, with five circular polished holes of 1 in. diameter equally spaced so that each bar was surrounded by the same mould wall, and the chilling effect was the same so far as possible for all the bars. The approximate weight of each melt was 1000 grm.

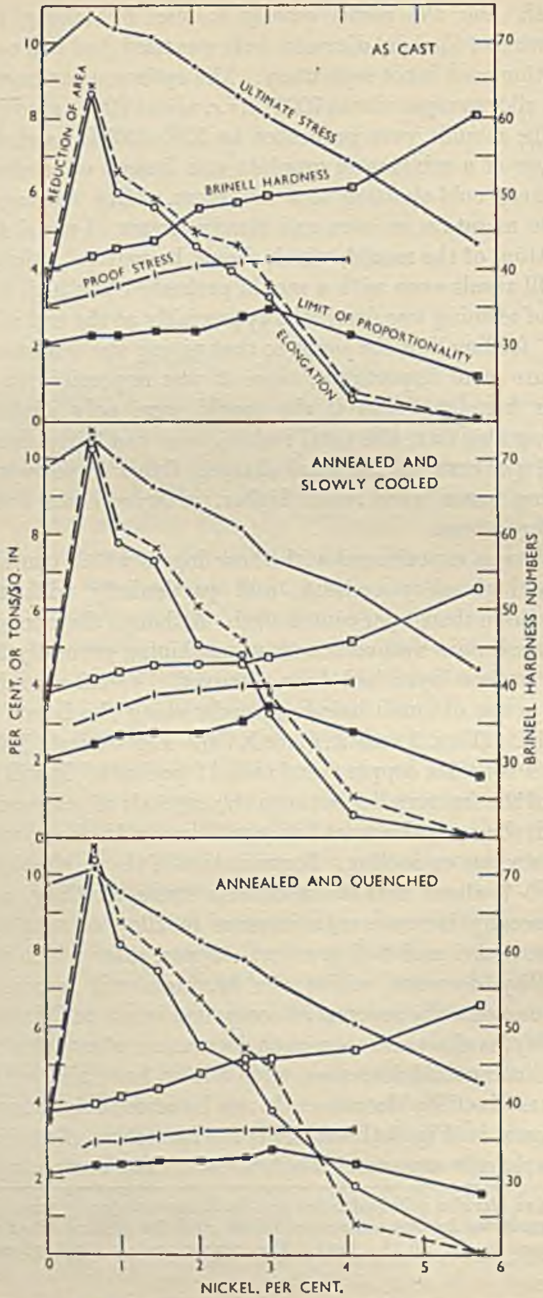

FIG. 4.—The Mechanical Properties of Cast and Heat-Treated Alloys Containing 2 Per Cent. Copper and Varying Nickel Content.

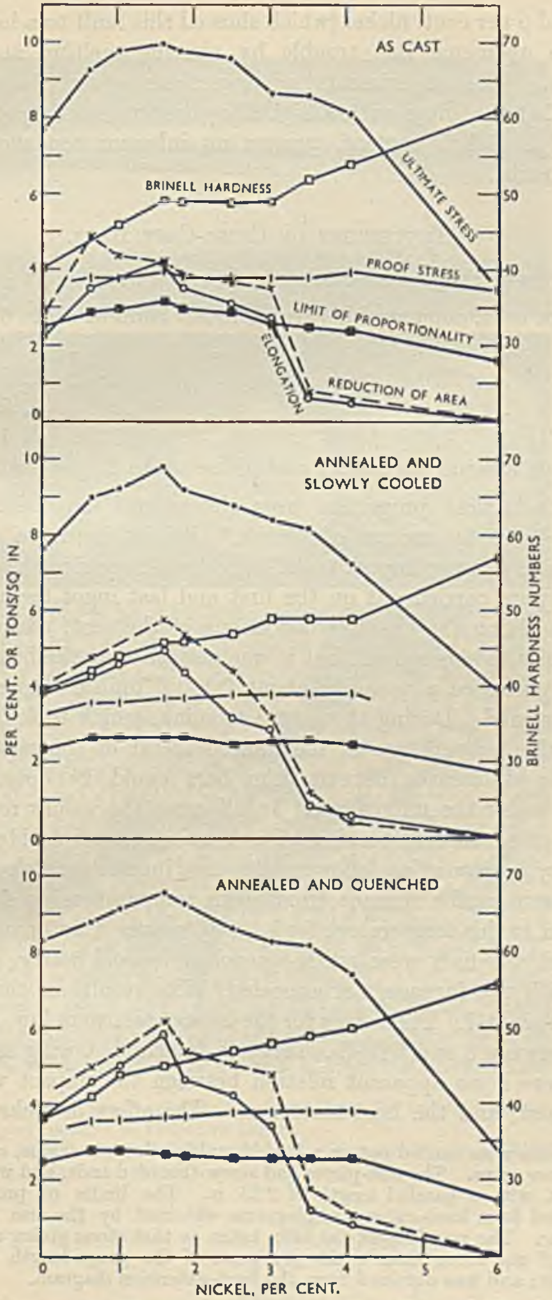

FIG. 5.—The Mechanical Properties of Cast and Heat-Treated Alloys Containing 3 Per Cent. Copper and Varying Nickel Content.

copper and 5 per cent. nickel (which showed this fault to a high degree), to try to overcome this trouble by altering melting and teeming conditions. The experiments were not successful, however, and it seems that the alloys with a high alloy content, and especially those with a high nickel content, possess an inherent tendency to form hair-line cracks.

Properties of Chill-Cast Bars.

Six series of alloys were made consisting of:

1. 2 per cent. copper with varying nickel content up to 6 per cent.
2. 3 ,, ,, ,, ,, ,, ,, ,, ,, ,, 6 ,, ,,
3. 4 ,, ,, ,, ,, ,, ,, ,, ,, ,, 5 ,, ,,
4. 6 ,, ,, ,, ,, ,, ,, ,, ,, ,, 5 ,, ,,
5. 8 ,, ,, ,, ,, ,, ,, ,, ,, ,, 1 ,, ,,
6. Equal amounts of copper and nickel up to 10 per cent.

The mechanical properties were determined on 1-in. diameter chill-cast bars, by means of tensile,* Brinell hardness (10/500/30 seconds), and Charpy impact tests. The tensile tests in the "as cast" condition were carried out on the first and last ingot teemed in each cast, thus giving the extreme conditions of the cast. The results of the tests on the bars agreed, but it was noticed that the last ingot cast generally possessed a tenacity about 0·1–0·2 ton/in.^{2} more than the first bar teemed. During the actual teeming, which took about 1–1½ minutes, the temperature of the molten metal in the pot decreased 20° C. No differences between the bars could be detected when examined under the microscope. In all cases the values recorded are the mean of concordant results. The heat-treatment decided on after preliminary tests was as follows: the cast ingots were slowly heated in an electric muffle furnace from room temperature to 450° C. and maintained at this temperature for 1 hr. by means of automatic control, after which the bars were either quenched in cold water, or allowed to cool with the furnace, *i.e.* annealed. The results of the tests are shown in Figs. 4–7. The values for the impact test were low, all of them ranging between 3 and 5 ft.-lb. energy to fracture. Owing to these low values, there is no apparent relation between the impact values, the alloy content, and the heat-treatment. The effect of nickel on alloys

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* The tests were carried out on a Riehlé multiple-lever machine, carrying self-centring screw grips. The test-pieces had screw-threaded ends, and were 0·564 in. in diameter, with a parallel length of 2·25 in. The limits of proportionality were obtained from load–extension diagrams obtained by the use of a Ewing extensometer. The proof stress has been taken as that stress giving a permanent extension of not more than 0·025 per cent. of the gauge-length of 2·00 in., *i.e.* 0·0005 in., and was obtained from the load–extension diagram.

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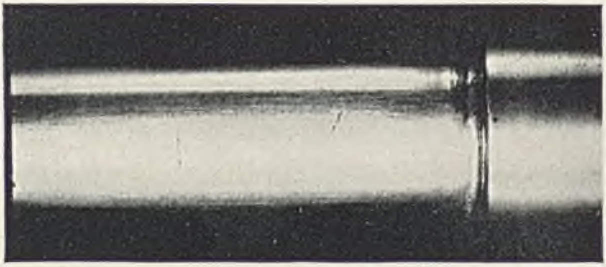

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Fig. 1.—Hair-Line Cracks in Cast Alloy Revealed by Machining.
Fig. 2.—Fractures of Defective Ingots.
Fig. 3.—Cracks in Cast Alloy Containing Copper 6% and Nickel 5%. Etched. × 50.

PLATE XVII.

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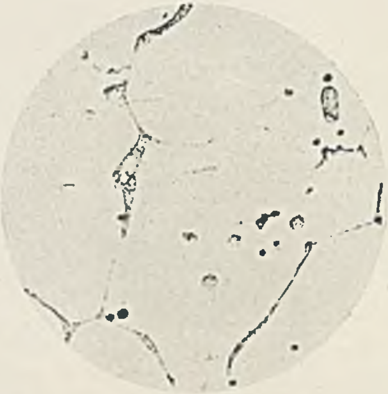

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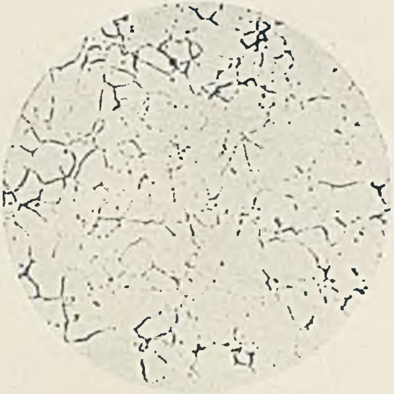

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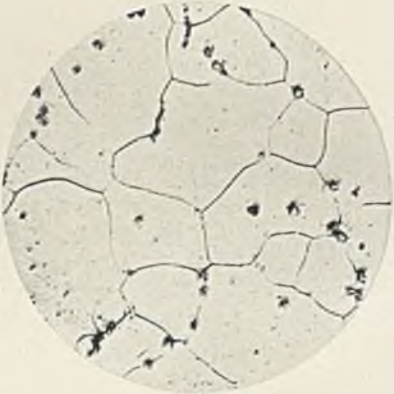

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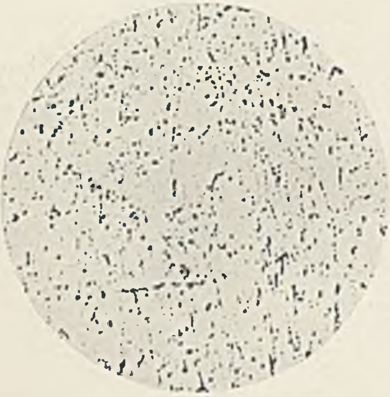

FIGS. 8–13.—Alloy No. 73 (Copper 2·14, Nickel 0·56%). Etched in 0·1% Solution of HNO_3 in Alcohol.

Fig. 8.—As Cast. × 350. Fig. 9.—As Cast. × 50. Fig. 10.—Cast Alloy Heated to 450° C. and Quenched in Water. × 350. FIG. 11.—As Forged. Transverse Section. × 350. Fig. 12.—As Forged. Longitudinal Section. × 50. Fig. 13.—As Rolled. Longitudinal Section. × 50.

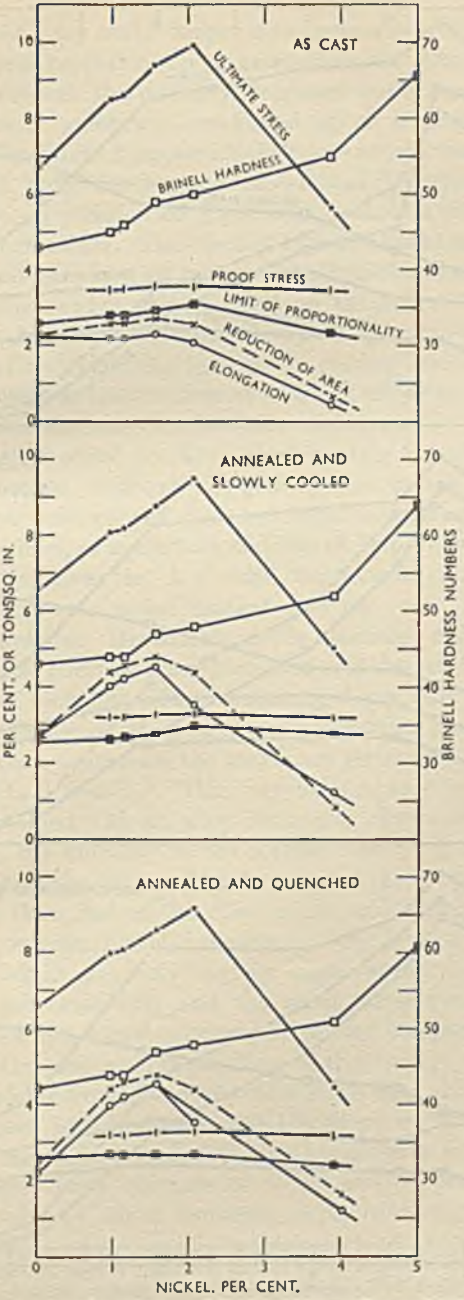

FIG. 6.—The Mechanical Properties of Cast and Heat-Treated Alloys Containing 4 Per Cent. Copper and Varying Nickel Content.

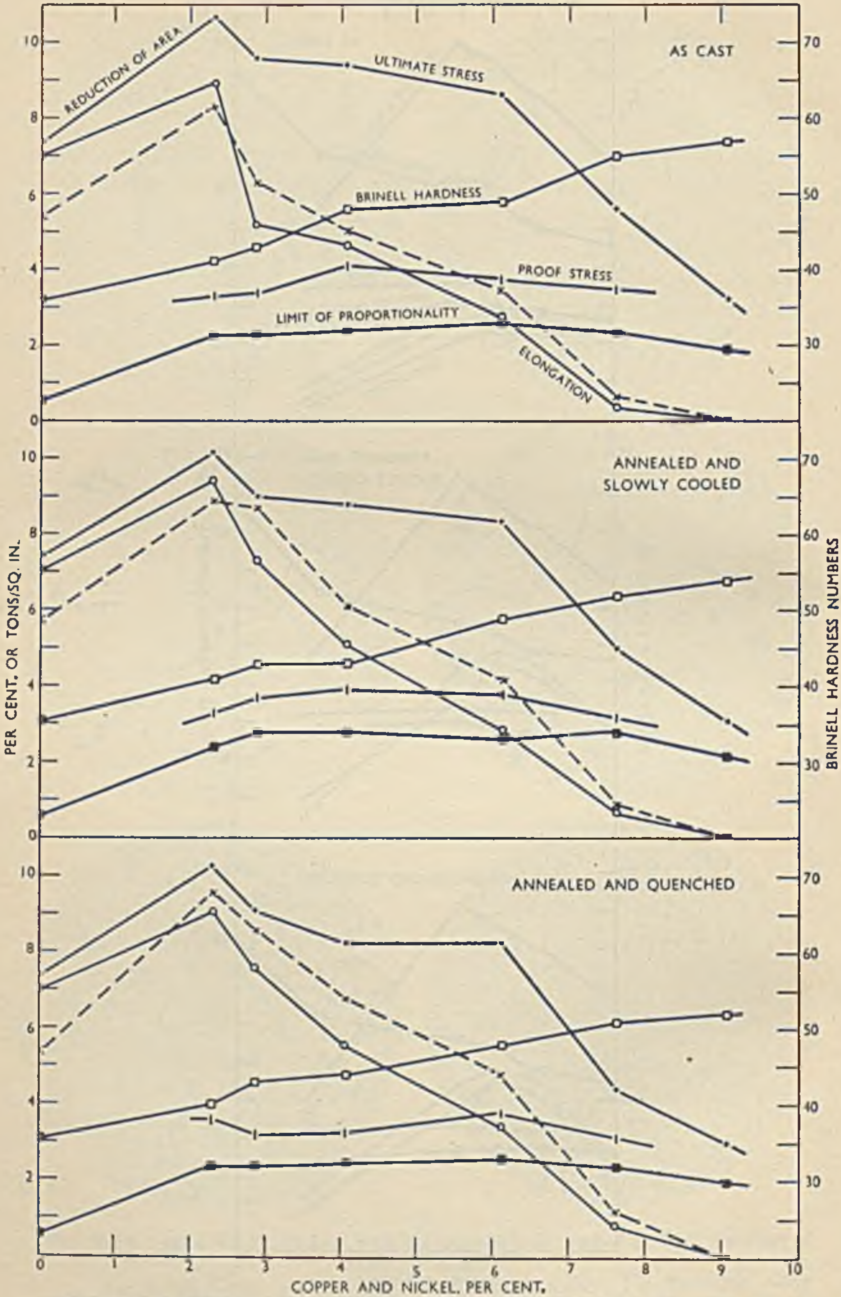

FIG. 7.—The Mechanical Properties of Cast and Heat-Treated Alloys Containing Equal Amounts of Copper and Nickel.

containing about 2 per cent.* copper is to cause a general improvement in the mechanical properties up to an addition of about ¾ per cent., above which amount the ductility decreases more rapidly than the tenacity, which is practically unaffected up to a nickel content of 1½ per cent. The limit of proportionality does not decrease until more than 3 per cent. nickel has been added, whereas the proof stress, which increases up to an addition of 2 per cent. nickel, is not affected by further increase of nickel. The effect of heat-treatment on the tenacity is negligible, but it causes an increase in elongation and reduction of area, having a somewhat greater effect on the latter. The hardness of the alloys in this series increases slowly until 4 per cent. nickel has been added, after which the increase is sudden and comparatively severe. The effect of heat-treatment followed either by quenching or slow cooling is to decrease the hardness slightly.

When nickel is added to alloys which contain 3 per cent.† copper, the maximum stress, although not greater than in the case of alloys containing 2 per cent. copper, does not begin to decrease until 2½ per cent. nickel is added, as against an addition of 1½ per cent. in the latter series. There is, however, a decided decrease in ductility, which becomes very low at a nickel content of 3 per cent. There is little difference in hardness. Heat-treatment is beneficial, and in this series again has a greater effect on the reduction of area than on the elongation.

The effect of nickel on alloys containing 4 per cent. copper ‡ (the mechanical properties of which in the cast condition are poor) is of no benefit, other than to increase the maximum stress at a nickel content of 2 per cent. to 9 tons/in.^{2}. This may be compared with a value of 11 tons/in.^{2} obtained with an alloy containing copper 2·08 and nickel 0·65 per cent., the ductility in the former case being only one-third as good as that in the latter. The ductility of the alloys in this series is much lower than that of the other series, and with an addition of more than 3 per cent. nickel decreases to very low values (less than 1 per cent.), which are only slightly improved by heat-treatment. The limit of proportionality and the proof stress remain constant, independently of the nickel content, at values comparable with the alloys of the other series. The hardness of these alloys does not begin to differ appreciably from that of the other series until almost 4 per cent. of nickel has been added, above which the alloys are definitely harder.

Owing to the difficulty of obtaining sound bars when the alloys contain relatively large amounts of nickel and copper, it was only possible in a series of alloys containing 6 per cent. copper to employ

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* The maximum copper variation in this series is 1·95–2·13 per cent.

† The maximum copper variation in this series is 2·96–3·12 per cent.

‡ The maximum copper variation in this series is 3·92–4·17 per cent.

a maximum nickel addition of 1½ per cent. The results of the mechanical tests on this series are given in Table I, from which it will be seen that the tenacity and ductility are much lower and the hardness is much greater than for any other series, so that these alloys are definitely inferior.

TABLE I.—*The Mechanical Properties of Chill-Cast Bars Containing 6 Per Cent. Copper with Varying Nickel Content.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Condition.	Limit of Proportionality, Tons/in.^{2}.	Proof Stress, Tons/in.^{2}.	Ultimate Stress, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	Brinell Hardness No.
24	5·95	0·46	As cast.	3·6	4·1	8·9	2·0	2·9	51
24A	„	„	Slowly cooled from 450° C.	3·7	3·8	8·6	4·0	3·0	45
24Q	„	„	Quenched from 450° C.	3·6	3·9	8·4	3·4	4·4	45
25	6·14	1·07	As cast.	3·7	4·0	8·8	1·8	2·4	52
25A	„	„	Slowly cooled from 450° C.	3·6	3·9	8·2	3·4	2·2	47
25Q	„	„	Quenched from 450° C.	3·5	3·9	8·3	3·0	4·2	46
26	6·19	1·42	As cast.	3·3	4·0	7·0	0·4	0·6	53
26A	„	„	Slowly cooled from 450° C.	3·6	3·7	6·2	0·8	1·0	49
26Q	„	„	Quenched from 450° C.	3·7	3·9	6·0	0·6	1·0	48

Table II gives the Brinell hardness values of the alloys containing 8 per cent. copper. These alloys could not be machined to give tensile test-pieces, owing to the presence of hair-line cracks.

TABLE II.—*The Brinell Hardness of Chill-Cast Bars Containing* 8 *Per Cent. Copper with Varying Nickel Content.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Condition.	Brinell Hardness No.
33	8·15	0·56	As cast.	53
33A	„	„	Slowly cooled from 450° C.	51
33Q	„	„	Quenched from 450° C.	50
34	8·14	1·16	As cast.	56
34A	„	„	Slowly cooled from 450° C.	55
34Q	„	„	Quenched from 450° C.	52

Fig. 7 gives the results of tests on chill-cast alloys containing equal amounts of copper and nickel. It will be seen that the tenacity increases to a maximum of about 11 tons/in.^{2} with 2¼ per cent. copper and nickel, after which it decreases gradually until a total alloy content of 6½ per cent. is present, beyond which the tenacity decreases rapidly. The limit of proportionality and proof stress are increased by an alloy addition up to 2 per cent., and are then practically constant. The ductility figures are parallel with those giving the values for the maximum stress up to a combined alloy content of over 2 per cent., above which the values decrease at a greater rate than those of the maximum stress. The reduction of area is less than the corresponding elongation up to an alloy content of about 2½ per cent. for the alloys both in the " as cast " as well as in the heat-treated conditions, but in the case of alloys containing more than this amount of copper and nickel, the reduction of area is the higher value. The optimum properties are given by an alloy content of 2¼ per cent., in which there are equal proportions of copper and nickel, alloy No. 30 in Table III. The only alloy whose mechanical properties equal these values is No. 1, containing copper 2·08 and nickel 0·65 per cent. Alloy No. 31, which contains a total alloy content of 2·82 per cent. (copper 1·34, nickel 1·48 per cent.) does not possess such good mechanical properties as either No. 1 or No. 30. The results of tests on chill-cast copper–magnesium alloys containing no nickel are also given in Table III.

Table III.—*The Mechanical Properties of Chill-Cast Bars Containing Nickel and/or Copper.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Condition.	Limit of Proportionality, Tons/in.^{2}.	Proof Stress, Tons/in.^{2}.	Ultimate Stress, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	Brinell Hardness No.	Density.
30	1·14	1·12	As cast.	2·3	3·3	10·7	8·9	8·3	41	1·77
30A	,,	,,	Slowly cooled from 450° C.	2·4	3·3	10·2	9·4	8·9	41	...
30Q	,,	,,	Quenched from 450° C.	2·4	3·6	10·3	9·1	9·6	40	...
(1)	1·15	nil	As cast.	1·6	...	8·2	6·2	3·9	38	1·75(9)
1	2·08	0·65	As cast.	2·3	3·4	10·8	8·7	8·9	42	1·78
1A	,,	,,	Slowly cooled from 450° C.	2·5	3·2	10·6	10·8	10·8	41	...
1Q	,,	,,	Quenched from 450° C.	2·4	3·0	10·2	10·4	10·8	40	...
(2)	1·88	nil	As cast.	2·0	...	9·7	3·3	3·5	39	1·77(0)
(3)	2·83	nil	As cast.	2·5	...	7·7	2·3	2·8	40	1·78(3)
31	1·34	1·48	As cast.	2·3	3·4	9·6	5·2	6·3	43	1·78+
31A	,,	,,	Slowly cooled from 450° C.	2·8	3·7	9·0	7·3	8·7	43	...
31Q	,,	,,	Quenched from 450° C.	2·4	3·2	9·1	7·6	8·6	43	...
(0)	nil	nil	As cast.	0·6	...	7·4	7·0	5·4	30	1·746

These nickel-free alloys are comparatively weak, possess little ductility, and have a low limit of proportionality; the best mechanical properties are obtained by the addition of about 2 per cent. copper to magnesium—alloy No. (2). On comparing the values, it is seen that the addition of nickel definitely improves the mechanical properties of the copper–magnesium alloys. In conclusion, it can be stated that the improved mechanical properties given to magnesium by small additions—up to about 2 per cent. copper—are enhanced by nickel if the combined nickel and copper content be 2¼–2½ per cent., and that a nickel content of ½–1 per cent. (in the combined alloy content) has a greater effect than a corresponding copper content. One useful effect of the addition of nickel is observed by the fact that the values for reduction of area are generally higher than the corresponding values for elongation. The reduction of area at fracture is a better criterion of the ductility than the elongation, and it is a useful indication of the ability of the material to withstand shock. A further advantage of nickel is an increased limit of proportionality and proof stress up to a nickel content of about 1 per cent.; after which the values are practically constant, being unaffected by an increase in copper content, or nickel content, or by heat-treatment.

THE FORGING OF THE ALLOYS.

Preliminary experiments showed that these alloys are not capable of being cold-worked, and, even if the alloys had been hot-forged, the amount of cold-work they withstand subsequently by forging or rolling is still very low.

In these experiments the preliminary work on hot-forging, which was carried out on chill-cast 1-in. diameter bars, showed that up to a total alloy content of 4 per cent., forging can be carried out without difficulty, and that if the alloys contain more than 8 per cent. total alloy content, and especially if the alloys contain more than 4 per cent. nickel, the forging properties are practically negligible, fracture taking place after very little work has been done on the ingots.

Three series of alloys were cast, to investigate the properties of the forged and rolled bars:

1. ½ per cent. copper with ½, 1, and 2 per cent. nickel.
2. 1 ,, ,, ,, ,, ,,
3. 2 ,, ,, ,, ,, ,,

Ingots which were 2½ in. in diameter were cast * as described

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* In casting the ingots, about 5 lb. of metal was melted and teemed into a split circular cast iron mould of ⅞-in. wall-thickness, 18 in. long, having an internal diameter of 2½ in. The mould tapered slightly, and the interior surface was polish-finished.

previously, and then machined to remove any possible surface defects. The ends of the ingots were machined hemispherical, as this tended to prevent any cracking during forging. The ingots were heated from the cold to 450° C. and maintained (under pyrometric control) at that temperature for 1 hr. Forging was carried out by an electrically-driven 60 lb. hammer, giving 250 strokes per minute. All the tools, including the hammer and anvil blocks, were kept at a good black heat (about 400°–450° C.). The bars were swaged down as rapidly as possible, keeping the cross-section of the bar circular and not hammering into a square section and then swaging round.

After a few light preliminary blows, the bars "toughened up" considerably, and would then withstand heavy and rapid blows. The most satisfactory forging temperature range for these alloys is 350°–450° C. The lower limit of temperature is most important, because, even if the temperature be high enough to permit of the bar being forged down, forging at a lower temperature forces the drawing down, and an undue amount of cold-work takes place, which affects the mechanical properties. Alloys forged at a low temperature have poor ductility, although the tenacity may be unaffected. After the ingot had been drawn down from a diameter of 2½ in. to 1½ in., the billet was cut in half, one half being reserved for rolling whilst the other half was reheated to 450° C. and drawn down further to a diameter of ⅞ in. The forged bars give a sonorous ring when struck if the forging has been carried out properly, but the presence of flaws, cracks, and severe cold-work causes the bar to give a much "duller" note.

The mechanical properties * of the drawn bars were determined in the "as forged" condition and after a heat-treatment which consisted

TABLE IV.—*The Mechanical Properties of the Forged Bars.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Limit of Proportionality, Tons/in.^{2}.	Proof Stress, Tons/in.^{2}.	Ultimate Stress, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	Brinell Hardness No.
F67	0·46	0·52	4·8	6·5	13·7	5·6	7·0	40
F68	0·53	1·08	4·9	6·6	14·3	4·8	6·4	42
F69	0·52	2·03	4·9	6·6	14·3	4·5	6·0	45
F70	1·05	0·51	4·8	6·4	14·1	5·1	7·8	45
F71	1·04	1·08	5·1	6·9	15·0	4·3	5·3	49
F72	1·10	2·12	5·2	7·2	15·2	3·4	4·4	51
F73	2·14	0·56	5·4	7·4	15·7	4·4	5·7	47
F74	2·08	1·12	5·2	7·1	15·4	4·0	5·1	51
F75	2·14	2·18	5·3	7·3	15·8	2·4	4·1	52

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* The results of notched-bar tests carried out on a Charpy machine gave values from 3 to 6 ft.-lb. energy to fracture and are too low to have any real value.

as before, in heating the bars at 450° C. for 1 hr., and either quenching in water or allowing the bars to cool down with the furnace.

The results of these tests are given in Tables IV, V, and VI, from which it will be seen that the addition of nickel causes some improvement in the mechanical properties. There is little difference in the limit of proportionality or in the proof stress, while the ultimate stress is increased by a small increase in the nickel and/or copper content. The ductility of the alloys is improved by the addition of ½ per cent. nickel and 1 per cent. copper, but is decreased if the nickel is increased, or if the copper is increased beyond this amount, the greater effect being caused by the nickel content. The addition of nickel increases the hardness by about 2 Brinell numbers per 1 per cent. nickel, a greater increase than that due to copper. The beneficial effect of the addition of nickel depends on the proportion of copper, the best results being

Table V.—*The Mechanical Properties of Forged Bars After Quenching from* 450° *C.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Limit of Proportionality, Tons/in.^{2}.	Proof Stress, Tons/in.^{2}.	Ultimate Stress, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	Brinell Hardness No.
F67Q	0·46	0·52	4·6	6·3	13·5	6·8	7·6	39
F68Q	0·53	1·08	4·8	6·2	14·0	4·9	7·4	42
F69Q	0·52	2·03	4·7	6·4	14·2	4·9	6·7	43
F70Q	1·05	0·51	4·3	6·1	13·9	5·8	7·8	44
F71Q	1·04	1·08	4·8	6·8	14·0	5·6	5·8	45
F72Q	1·10	2·12	5·0	6·8	14·7	4·9	5·6	49
F73Q	2·14	0·56	5·2	7·1	14·8	6·1	6·7	43
F74Q	2·08	1·12	4·9	6·8	14·7	5·5	6·3	49
F75Q	2·14	2·18	4·8	6·9	15·1	4·1	4·6	51

Table VI.—*The Mechanical Properties of Forged Bars after Slow Cooling from* 450° *C.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Limit of Proportionality, Tons/in.^{2}.	Proof Stress, Tons/in.^{2}.	Ultimate Stress, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	Brinell Hard ness No.
F67A	0·46	0·52	4·6	6·2	13·3	7·1	7·9	38
F68A	0·53	1·08	4·8	6·5	14·1	4·9	7·2	41
F69A	0·52	2·03	4·9	6·3	14·3	4·6	6·9	41
F70A	1·05	0·51	4·8	6·4	14·1	5·1	7·8	45
F71A	1·04	1·08	4·8	6·7	13·8	5·9	6·1	43
F72A	1·10	2·12	5·1	7·0	14·4	5·1	5·7	47
F73A	2·14	0·56	5·0	7·0	14·5	6·2	7·1	42
F74A	2·08	1·12	4·8	6·8	14·4	5·4	6·2	49
F75A	2·14	2·18	4·8	6·9	15·1	4·1	4·6	51

obtained with an addition of ½ per cent. nickel to an alloy containing about 1 per cent. copper. Heat-treatment does not have much effect on these alloys, probably because of the care taken to control the finishing temperature of forging, there being only a slight decrease of about ½ ton/in.^{2} in the ultimate stress, and a corresponding increase in ductility. It is interesting to note that heat-treatment causes no change in the properties of alloy No. 70, which contains 1·05 per cent. copper and 0·51 per cent. nickel, and which possesses the optimum mechanical properties. In the case of the forged alloys, as well as with the chill-cast alloys, the values for the reduction of area are again consistently better than those for the corresponding elongation.

The Rolling of the Alloys.

The experiments on the rolling of these alloys were carried out on a Robertson 3-high, 24 in. non-reversing mill, using a rolling speed of 60 ft./minute. Preliminary trials were carried out on alloys in the cast and forged conditions. It was not possible to cold-roll any alloy in the cast state, and alloys which had been previously drawn down hot would withstand very little cold-rolling. Ingots and forged billets were hot-rolled after being heated and maintained at 450° C. for 1 hr. Ingots with a total copper and nickel content of 4 per cent. which had received a preliminary forging from 2½ in. to 1½ in. diameter rolled well; the rolling properties of alloys containing 4–8 per cent. total copper and nickel were indifferent, and particular care was necessary if the nickel content was more than 4 per cent. Alloys with a higher content of nickel and copper could not be rolled successfully. Alloys roll better after a preliminary forging, owing to the fact that the cast structure has been already broken down, and the eutectic divorced and the compound dispersed evenly through the metal. The grains of magnesium have been oriented in the direction of forging, and deformation can take place with the greatest possible ease as shown by the considerable toughening after the first few hammer blows.

The three series of alloys cast and drawn from 2½ to 1½ in. in diameter were used. The half-billets which were not drawn down to ⅞ in. under the hammer were reheated to 450° C. for 1 hr., and were rolled down to ⅞ in. diameter in four passes, without intermediate reheating. The four passes were (i) 1½–1⅜ in.; (ii) 1⅜–1¼ in.; (iii) 1¼–1 in.; and (iv) 1 in.–⅞ in. Between each pass the bars were turned through 90°. If the temperature of the bar was above the lower limit of forging of 350° C., the bars emerged from the mill quite straight, but when any amount of cold-work took place, or excessive reduction, the bars curled on passing out of the mill. The rolled bars had a silvery lustre and good skin, owing to a fine dressing of magnesium left on the mill grooves after one pass of a billet. The mechanical properties were determined on these bars in the "as rolled" condition, and after a heat-treatment similar to that given to the forged bars, *i.e.* quenching in water or slow cooling after having been maintained at 450° C. for 1 hr. The results of the tests are given in Tables VII, VIII, and IX.*

TABLE VII.—*The Mechanical Properties of the Rolled Bars.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Limit of Proportionality, Tons/in.^{2}.	Proof Stress, Tons/in.^{2}.	Ultimate Stress, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	Brinell Hardness No.
R67	0·46	0·52	5·3	8·1	16·5	7·4	8·8	42
R68	0·53	1·08	5·5	8·1	16·7	6·2	7·9	45
R69	0·52	2·03	5·5	8·3	16·7	6·1	7·0	47
R70	1·05	0·51	5·6	8·4	17·3	6·6	6·9	49
R71	1·04	1·08	5·7	8·4	17·2	6·0	6·9	50
R72	1·10	2·12	5·6	8·3	17·6	5·1	5·5	52
R73	2·14	0·56	5·8	8·6	17·9	6·2	7·3	49
R74	2·08	1·12	5·7	8·7	17·0	5·2	5·8	51
R75	2·14	2·18	5·8	8·6	17·7	4·0	4·2	52

TABLE VIII.—*The Mechanical Properties of Rolled Bars after Quenching from* 450° *C.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Limit of Proportionality, Tons/in.^{2},	Proof Stress, Tons/in.^{2}.	Ultimate Stress, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	Brinell Hardness No.
R67Q	0·46	0·52	5·0	7·8	15·6	8·1	10·5	40
R68Q	0·53	1·08	5·3	7·7	15·3	7·9	9·2	42
R69Q	0·52	2·03	5·4	8·0	15·6	7·2	7·2	44
R70Q	1·05	0·51	5·4	8·1	16·6	8·4	5·4	45
R71Q	1·04	1·08	5·4	7·9	16·3	8·0	7·1	46
R72Q	1·10	2·12	5·4	8·0	16·6	7·7	6·4	48
R73Q	2·14	0·56	5·5	8·4	16·7	7·6	9·0	47
R74Q	2·08	1·12	5·4	8·4	16·8	6·4	6·8	48
R75Q	2·14	2·18	5·7	8·3	16·9	4·7	4·9	51

The conclusions obtained from the tests carried out on the forged bars are substantiated generally in this case. The best results are given by a nickel addition of 0·5 per cent. with a copper addition up to 2 per cent., *i.e.* a higher copper addition than in the case of ingots which were forged only. In the total copper and nickel added the nickel content has a more beneficial effect than the copper. Heat-treatment has little effect, merely decreasing the ultimate stress by 1 ton/in.^{2} and increasing the ductility by about 2 per cent. on corresponding alloys.

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* The results of notched-bar tests carried out on a Charpy machine gave values from 3–6 ft.-lb. energy to fracture and are too low to have any real value.

TABLE IX.—*The Mechanical Properties of Rolled Bars after Slow Cooling from* 450° *C.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Limit of Proportionality, Tons/in.².	Proof Stress, Tons/in.².	Ultimate Stress, Tons/in.².	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	Brinell Hardness No.
R67A	0·46	0·52	5·1	7·7	14·9	9·4	10·8	40
R68A	0·53	1·08	5·2	7·9	15·2	9·2	9·6	42
R69A	0·52	2·03	5·4	8·1	15·4	7·2	7·9	44
R70A	1·05	0·51	5·3	8·3	16·4	8·8	5·6	45
R71A	1·04	1·08	5·2	8·0	15·9	8·2	7·5	45
R72A	1·10	2·12	5·3	8·1	16·4	7·6	6·2	49
R73A	2·14	0·56	5·5	8·4	16·7	7·8	9·4	47
R74A	2·08	1·12	5·3	8·6	16·6	5·9	6·4	49
R75A	2·14	2·18	5·6	8·2	15·9	5·1	5·6	50

On comparing the test results for the alloys which were forged from 2½ to ⅞ in. in diameter with those which were rolled from 1½ to ⅞ in. after having been forged from 2½ to 1½ in. in diameter, given in the corresponding Tables (Tables IV and VII; V and VIII; VI and IX) it will be seen that better results are obtained by rolling billets than by forging only. The limit of proportionality, the proof stress, the ultimate stress, and the elongation, are improved by 0·5, 2, and 2 tons/in.^{2} and 2 per cent. respectively, while the reduction of area is definitely improved in alloys containing up to 1 per cent. nickel and 1 per cent. copper, beyond which proportions rolling does not appear to have had much effect. The effect of heat-treatment on the forged and on the rolled bars is small, probably because of the careful control of forging temperature to prevent cold-work, which seriously decreases the ductility.

A general discussion as to the mechanical properties is helped by a consideration of Table X.

Alloy No. F7, containing 2 per cent. copper, has better mechanical properties than alloy No. 73, which contains 2 per cent. copper and ½ per cent. nickel, whether the latter alloy is in the forged or rolled condition. After annealing, however, the alloy containing nickel is superior, and particularly so after rolling. This may possibly be due to the fact that alloy No. F7 had been cold-worked somewhat in the drawing operation. The same remarks apply to a comparison of alloy No. 7 with No. 71 which contains 1 per cent. copper and 1 per cent. nickel. By comparing alloy No. F4, containing 1 per cent. copper, with alloy No. 70, which contains ½ per cent. nickel in addition, it is seen that the nickel addition causes no improvement unless the forged bar has been annealed; a further addition of ½ per cent. nickel, in alloy No. 71, is of no advantage. A comparison of alloy F4 with

TABLE X.—*The Mechanical Properties of Forged, Rolled, and Heat-Treated Alloys.*

No.	Copper, Per Cent.	Nickel, Per Cent.	Condition.	Limit of Proportionality, Tons/in.^{2}.	Proof Stress, Tons/in.^{2}.	Ultimate Stress, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction of Area, Per Cent.	Brinell Hardness No.	Density.
F0 *	nil	nil	As forged.	4·2	7·3	15·9	11·2	15·9	37	1·742
F0H	,,	,,	Quenched from 470° C.	3·9	6·3	15·4	10·1	11·0	37	...
F0A	,,	,,	Slowly cooled from 470° C.	4·5	6·3	15·1	6·8	7·0	36	...
F4 *	1·02	nil	As forged.	5·8	8·6	17·8	8·9	13·3	39	1·758
F4H	,,	,,	Quenched from 460° C.	5·7	7·4	15·3	8·7	8·4	41	...
F4A	,,	,,	Slowly cooled from 460° C.	5·6	7·3	15·3	4·6	6·0	38	...
F67	0·46	0·52	As forged.	4·8	6·5	13·7	5·6	7·0	40	1·76
F67Q	,,	,,	Quenched from 450° C.	4·6	6·3	13·5	6·8	7·6	39	...
F67A	,,	,,	Slowly cooled from 450° C.	4·6	6·2	13·3	7·1	7·9	38	...
R67	0·46	0·52	As rolled.	5·3	8·1	16·5	7·4	8·8	42	1·76
R67Q	,,	,,	Quenched from 450° C.	5·0	7·8	15·6	8·1	10·5	40	...
R67A	,,	,,	Slowly cooled from 450° C.	5·1	7·7	14·9	9·4	10·8	40	...
F70	1·05	0·51	As forged.	4·8	6·4	14·1	5·1	7·8	45	1·77
F70Q	,,	,,	Quenched from 450° C.	4·3	6·1	13·9	5·8	7·8	44	...
F70A	,,	,,	Slowly cooled from 450° C.	4·8	6·0	13·8	5·6	7·9	42	...
R70	1·05	0·51	As rolled.	5·6	8·4	17·3	6·6	6·9	49	1·77
R70Q	,,	,,	Quenched from 450° C.	5·4	8·1	16·6	8·4	6·4	45	...
R70A	,,	,,	Slowly cooled from 450° C.	5·3	8·3	16·4	8·8	6·6	45	...
F7 *	1·95	nil	As forged.	6·4	8·8	18·7	8·1	12·0	42	1·77
F7H	,,	,,	Quenched from 455° C.	6·6	7·8	15·4	8·0	8·0	44	...
F7A	,,	,,	Slowly cooled from 455° C.	5·8	7·5	15·5	4·0	5·4	39	...
F71	1·04	1·08	As forged.	5·1	6·9	15·0	4·3	5·3	49	1·77
F71Q	,,	,,	Quenched from 450° C.	4·8	6·8	14·0	5·6	5·8	45	...
F71A	,,	,,	Slowly cooled from 450° C.	4·8	6·7	13·8	5·9	6·1	43	...
R71	1·04	1·08	As rolled.	5·7	8·4	17·2	6·0	6·9	50	1·77
R71Q	,,	,,	Quenched from 450° C.	5·4	7·9	16·3	8·0	7·1	46	...
R71A	,,	,,	Slowly cooled from 450° C.	5·2	8·0	15·9	8·2	7·5	45	...
F73	2·14	0·56	As forged.	5·4	7·4	15·7	4·4	5·7	47	1·78
F73Q	,,	,,	Quenched from 450° C.	5·2	7·1	14·8	6·1	6·7	43	...
F73A	,,	,,	Slowly cooled from 450° C.	5·0	7·0	14·5	6·2	7·1	42	...
R73	2·14	0·56	As rolled.	5·8	8·6	17·9	6·2	7·3	49	1·78
R73Q	,,	,,	Quenched from 450° C.	5·5	8·4	16·7	7·6	9·0	47	...
R73A	,,	,,	Slowly cooled from 450° C.	5·5	8·4	16·7	7·8	9·4	47	...

No. 67, which contains ½ per cent. copper and ½ per cent. nickel is interesting, since it shows that the alloy containing nickel possesses improved mechanical properties. It has been shown that an addition of 1½–2 per cent. copper to magnesium is beneficial by causing a relatively considerable increase in tenacity without seriously decreasing the ductility; the addition of nickel results in improved mechanical properties, and it is probable that the alloys are more resistant to shock.

MICROSTRUCTURE.

Copper and nickel are practically insoluble in magnesium, since an alloy containing 0·025 per cent. copper and 0·025 per cent. nickel was made which, after forging followed by prolonged annealing for 200 hrs. at 450° C., showed the presence of a second constituent when examined under the microscope. This alloy was not capable of age-hardening, as shown by Brinell hardness determinations after a preliminary treatment at 450° C. This new constituent appears as soon as copper or nickel is added to magnesium. The structure of the compound Mg_2Cu has been determined,[2] but at the present time there is no definite information regarding the structure of the compound Mg_2Ni. The inter-atomic distances of copper and nickel are, respectively, 2·55 and 2·49 A, values which lie well within the limits of isomorphous tolerance. In view of the isomorphism which is known to exist between copper and nickel (ionic radii or inter-atomic distances are of the same order), and the further analogy which obtains between the structure of the compounds of magnesium with the metals of Group IV (Pb, Sn, Ge (and Si)), it appears probable that the constituent which separates in the present system is a solid solution of the compounds Mg_2Cu and Mg_2Ni. In the cast state, the constituent forms a globular type of eutectic with magnesium which is easily divorced on annealing. Forging and rolling cause a complete breakdown of the cast structure, and the compound is distributed throughout the metal instead of being situated at the grain boundaries. The size of the particles of compound in the rolled bars is smaller than that in the forged bars. After deformation, the microstructure consists of almost pure magnesium, with the compound distributed more or less regularly throughout the metal in the direction of forging, and independent of the grain-size of the groundmass, which depends on the deformation and heat-treatment to which the alloy has been subjected. Typical structures are shown in Figs. 8–13 (Plate XVII), which are photomicrographs of alloy No. 73 containing 2·14 per cent. copper and 0·56 per cent. nickel.

SUMMARY.

Experiments have been carried out on the effect of adding nickel and copper to magnesium. The improved mechanical properties given to magnesium when in the "as cast" condition by small additions up to about 2 per cent. copper are enhanced by the addition of nickel if the combined alloy content be $2\frac{1}{4}$–$2\frac{1}{2}$ per cent. A nickel content of $\frac{1}{2}$–1 per cent. (in the combined alloy content) has a greater effect than a corresponding copper content. A useful result due to the addition of nickel is that the values for reduction of area are generally higher than the corresponding values for the elongation. These alloys are readily forged or rolled, and, provided that care is taken to prevent cold-work, reasonably good ductility values are obtained. In the case of forged and/or rolled alloys, the beneficial effect of the addition of nickel as well as copper to magnesium is not so pronounced; the effect of nickel depends to some extent on the proportion of copper. In the case of forged bars, the best results are given by an addition of $\frac{1}{2}$ per cent. nickel to 1 per cent. copper, but if the billet is rolled after a preliminary drawing down under the hammer the copper should be increased to 2 per cent. to give the best values for the mechanical properties. Billets which have been rolled after a preliminary drawing down, give better mechanical properties than those which have been drawn down to the same size.

REFERENCES.

[1] W. T. Cook and W. R. D. Jones, *J. Inst. Metals*, 1926, **36**, 157.
W. T. Cook and W. R. D. Jones, *J. Inst. Metals*, 1927, **38**, 103.
W. R. D. Jones, *J. Inst. Metals*, 1928, **40**, 85.
W. R. D. Jones, *J. Inst. Metals*, 1931, **46**, 395.
[2] P. P. Ewald and C. Herman, *Z. Krist.*: "*Strukturbericht*," 1930.

ALLOYS OF MAGNESIUM. PART VII.—THE MECHANICAL PROPERTIES OF SOME WROUGHT ALUMINIUM–MAGNESIUM AND SILVER–ALUMINIUM–MAGNESIUM ALLOYS.*

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SYNOPSIS.

The mechanical properties of pressed magnesium alloys containing up to 10 per cent. of aluminium, with and without the addition of silver, were studied.

The effect of various amounts of reduction during forging was investigated, as well as the effect of the temperature at which the forging took place. It is shown that forging at 200° C., after a preliminary breaking down at 380° C., causes a marked increase in tensile strength, without appreciable loss of ductility, particularly in the case of alloys containing a small quantity of silver. The highest tensile strength was obtained with an alloy containing 8·5 per cent. aluminium and 4·2 per cent. silver, and the best elongation with an alloy containing 4 per cent. aluminium and 1·5 per cent. silver, the ultimate stresses being 30 and 24 tons/in.^{2}, and the elongations 5 and 13·4 per cent., respectively.

Special attention may be directed to the alloy containing 6·5 per cent. of aluminium and 1·5 per cent. of silver, which has an ultimate stress of 27·3 tons/in.^{2}, a 0·1 per cent. proof stress of 21·3 tons/in.^{2}, and an elongation of 11·5 per cent.

INTRODUCTION.

THIS paper is Part VII 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.[1–6]

Part II of the research dealt with the mechanical properties of six different series of alloys in the wrought state. Many other alloys were investigated later, and the results were published in a monograph entitled "Magnesium and its Alloys." [7] The more important of them may be briefly summarized here for the sake of completeness.

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The addition of 2–3 per cent. of silver to an alloy containing about 8 per cent. aluminium gives alloys which, in the heat-treated condition, have an ultimate stress of 25 tons/in.^{2}, a proof stress of 17 tons/in.^{2}, and an elongation of 4 per cent.

The addition of calcium improves the ultimate stress of magnesium at moderate temperatures (about 200° C.).

Cerium has a marked effect in increasing the strength of magnesium at high temperatures (300° C.), while the addition of cobalt leads to a still further increase. Thus, an alloy containing cerium 10, cobalt 1·5, and manganese 1·5 per cent. has an ultimate stress of 7·4 tons/in.^{2} at 300 ° C., as compared with one of less than 5 tons/in.^{2} for a 9 per cent. aluminium–magnesium alloy at that temperature.

In Part II of the research, the mechanical properties of some aluminium–magnesium alloys were studied, and preliminary work was also carried out on the effect of mechanical treatment. Later, the effect of adding silver to aluminium–magnesium alloys was studied, but all these investigations were rather in the nature of preliminary surveys, and the present paper deals with a more complete investigation of both series of alloys. It is divided into three sections, dealing respectively with :

1. Aluminium–magnesium alloys,
2. Silver–aluminium–magnesium alloys,
3. The effect of different amounts of work on the hardness of both the binary and the ternary alloys, and the effect of the temperature at which deformation is carried out on the mechanical properties of these alloys.

1. ALUMINIUM–MAGNESIUM ALLOYS.

TABLE I.—*Compositions of the Alloys Investigated.*

Alloy No.	Nominal, Per Cent.		By Analysis, Per Cent.		
	Aluminium.	Manganese.	Aluminium.	Manganese.	Zinc.
1	8·5	0·5	8·56	...	...
2	9·0	,,	9·14	...	0·27
3	9·5	,,	9·57	...	...
4	10·0	,,	10·21	0·58	...
5	11·0	,,	10·72	...	...
6	12·0	,,	12·25	...	...
7	13·0	,,	12·60	...	...
8	14·0	,,	13·78	...	...
9	15·0	,,	14·73	...	...

The mechanical properties of forged aluminium–magnesium alloys have been studied by various authors.[8, 9] Perhaps the most complete work is that of Dumas and Rockaert,[9] who investigated the Brinell hardness of the alloys containing from about 2 to 18 per cent. aluminium. Their curves are somewhat irregular, but there is a marked increase in hardness between 8 and 9 per cent., after which there is a decrease to 9·5 per cent. In view of this, it was decided to study the mechanical properties of a series of wrought alloys with compositions covering the range 8·5 to 15 per cent. aluminium, and the alloys shown in Table I were made up. Alloy No. 2 had been made previously, and contained 0·27 per cent. zinc; it was in the form of a 1½ in. diam. bar, which had been forged from a 3 in. billet. Apart from this it received the same treatment as all the other bars.

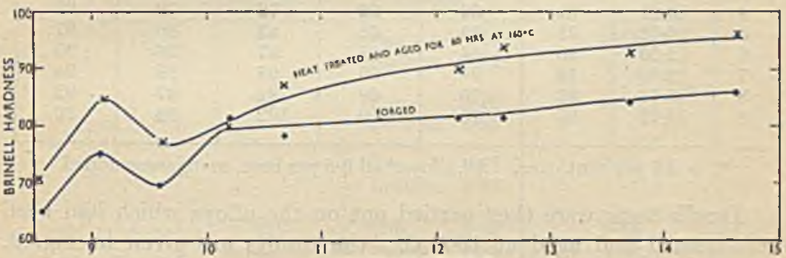

Fig. 1.—Brinell Hardness of Aluminium–Magnesium Alloys in the Forged and Aged Conditions.

The alloys were cast into ingots, 2 in. square, heated for about 8 hrs. at 360°–380° C., and forged to 1 in. diam. bars in one stage, at 350°–380° C., the dies being maintained at 385° C. ± 5°. The press and dies used have been described previously.[7] All the alloys forged well in the press.

Sections cut from each bar were treated as follows:

1. No treatment.
2. Annealed at 350° C. for 1 hr. and air-cooled.
3. Heat-treated at 390°–405° C. for 1½ hrs. and quenched in water.
4. Treated as (3) and age-hardened at 160° C. for (*a*) 20 hrs., (*b*) 36 hrs., (*c*) 60 hrs.

Brinell hardness measurements were made on all the specimens, and the results are given in Table II, while the results on the forged specimens and on those aged for 60 hrs. are reproduced in Fig. 1.

It will be observed that the hardness of both the forged and the age-hardened material reaches a maximum in the neighbourhood of 9 per cent. aluminium,* and this is also faintly noticeable in the annealed material.

Table II.—*Brinell Hardness of the Aluminium–Magnesium Alloys, in the Forged, Annealed, Quenched, and Aged Conditions.*

No.	Aluminium, Per Cent.	Brinell Hardness (5/125/30).					
		As Forged.	Annealed at 350° C. for 1 hr.	Quenched from 390°–405° C.	Aged at:		
					160° C. for 20 Hrs.	160° C. for 36 Hrs.	160° C. for 60 Hrs.
1	8·56	66	57	58	65	67	71
2	9·14*	74	61	59	75	79	83
3	9·57	68	60	60	68	75	77
4	10·21	81	59	62	78	79	83
5	10·72	78	59	62	83	86	87
6	12·25	80	64	65	87	84	90
7	12·60	79	64	66	95	90	94
8	13·78	83	70	69	91	87	92
9	14·73	85	75	69	102	98	96

* + 0·3 per cent. zinc. All alloys had 0·5 per cent. manganese added.

Tensile tests were then carried out on the alloys which had been heat-treated and aged at 160° C.; the results are given in Fig. 2.

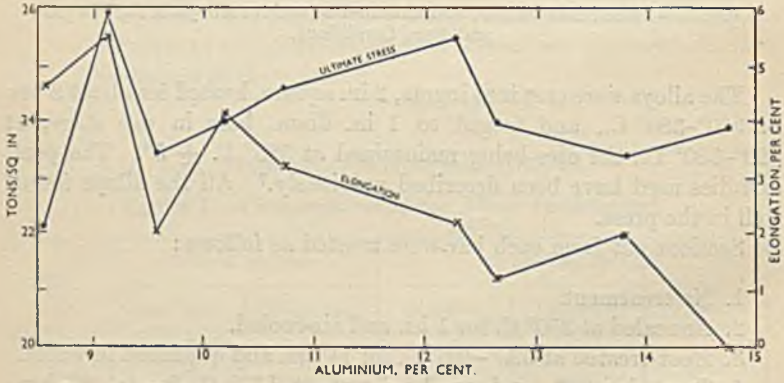

Fig. 2.—Mechanical Properties of Heat-Treated and Aged Aluminium–Magnesium Alloy Forgings.

While the curves are very erratic, a marked maximum will be observed at about 9 per cent. aluminium, both in ultimate stress and elongation.

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* But see p. 182, where it is shown that this maximum is almost certainly spurious, being due, probably, to segregation in the ingots. This may also be the cause of the maximum found by Dumas and Rockaert.

It was then decided to investigate more closely the properties of the alloys whose compositions were in the neighbourhood of 9 per cent. aluminium, and for this purpose six alloys containing from 8·5 to 10 per cent. aluminium were cast in the form of $3\frac{1}{2}$ in. diam. ingots. At this stage it was suspected that the composition of the material was not constant throughout the length of the ingot. Thin cross-sections were therefore cut from the top and bottom of each ingot, and analyzed. The nominal compositions of the ingots, and the results of these analyses are given in Table III.

TABLE III.

No.	Aluminium, Per Cent.		Difference Between Top and Bottom.
	Nominal.	Analysis.	
1	8	Top 7·74 Bottom 8·51	0·77
2	8·5	Top 8·18 Bottom 8·92	0·74
3	9·0	Top 8·67 Bottom 8·87	0·20
4	9·0	Top 9·02 Bottom 9·36	0·34
5	9·5	Top 9·33 Bottom 10·03	0·70
6	10·0	Top 9·10 Bottom 10·64	1·54

0·5 per cent. manganese was added to each melt.

The cause of this lack of uniformity was studied, and methods for its prevention were devised, which are discussed in the Appendix. In the meantime it was decided to make use of the lack of uniformity in the bars already cast to obtain a greater number of compositions. The $3\frac{1}{2}$-in. bars were press-forged at 380° C. to a diameter of $1\frac{9}{16}$ in., the resulting bar being cut into three pieces: *AC*, *CX*, *XZ* (Fig. 3). Pieces *AC* and *XZ* were each 11 in. long, and *CX* was the remainder of the bar—usually about 18 in. long. It was assumed that the composition of *AC*, which was from the top of the billet, was sufficiently accurately represented by the analysis already made on the top of the billet and that of the piece *XZ*, by the analysis of the bottom, while the composition of the centre piece *CX* was assumed to be the mean of those of *AC* and *XZ*. That this was justified was confirmed analytically in some

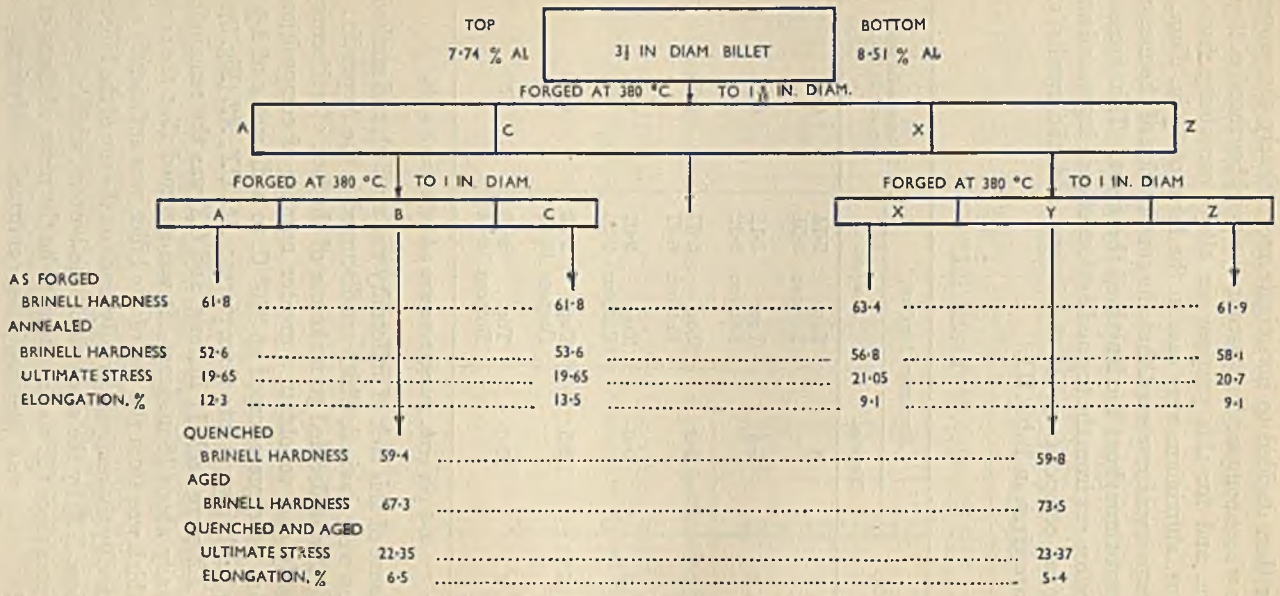

FIG. 3.—Forging of a Billet for Testing Mechanical Properties.

of the bars, while the comparative uniformity of composition of the end-pieces was confirmed by the mechanical tests about to be described.

The bar *CX* was left aside for special treatment (described on p. 189), while the bars *AC* and *XZ* were press-forged at 380° C. to 1 in. diam., and each cut up into three bars: *A*, *B*, and *C*; and *X*, *Y*, and *Z*, respectively. The Brinell hardness was determined on each of the specimens *A*, *C*, *X*, and *Z* in the forged condition, and then the specimens were annealed at 350° C. and tested in tension. The results obtained on one of the alloys are given in Fig. 3, from which it will be seen that *A* and *C* agree very well with each other, as do *X* and *Z*, but that the difference between the pairs is very great, particularly in the annealed state. This tends to justify the assumption that the composition of *A*, *B*, and *C* can be taken as that of the top of the original billet, and that of *X*, *Y*, and *Z* as that of the bottom of the billet.

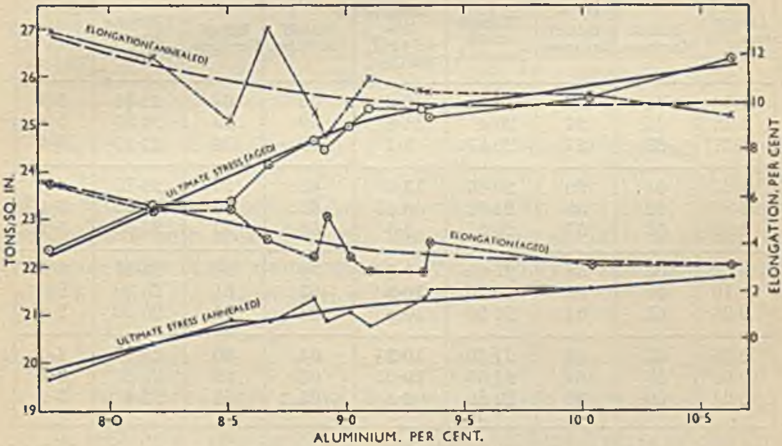

Fig. 4.—Mechanical Properties of Aluminium–Magnesium Alloy Forgings.

The bars *B* and *Y* were then heat-treated at 400° ± 5° C. for $1\frac{1}{2}$ hrs., quenched in oil, and the Brinell hardness determined. They were next aged at 160° C. until the maximum hardness was attained, and the Brinell hardness, ultimate stress, and elongation determined. The results obtained on one of the alloys are shown in Fig. 3.

The six ingots mentioned in Table III were treated in this way, and alloys having twelve different compositions were obtained. The results of the mechanical tests are given in Table IV, while the ultimate stresses and elongations are plotted in Fig. 4. The maxima in the ultimate stress and elongation curves shown in Fig. 2 no longer occur. The points are somewhat erratic, but the heavy lines in Fig. 4

are probably fair curves drawn through the points, and the most that can be said is that near to 9 per cent. aluminium the properties begin to change less rapidly with change in composition. It is suggested that the changes shown in the earlier curves, and in those of Dumas and Rockaert, are due to segregation, which made the composition of the specimens used in the tests uncertain.

TABLE IV.—*Mechanical Properties of Aluminium–Magnesium Bars in Various Conditions.*

State.	Forged.	Annealed at 350° C.			Quenched from 400° C.	Quenched from 400° C. and Aged at 160° C.		
Aluminium, Per Cent.	Brinell Hardness.	Brinell Hardness.	Ultimate Stress, Tons/in.^{2}.	Elongation on $4\sqrt{A}$, Per Cent.	Brinell Hardness.	Brinell Hardness.	Ultimate Stress, Tons/in.^{2}.	Elongation on $4\sqrt{A}$, Per Cent.
7·74	62	53	19·65	12·9	59	67	22·35	6·5
8·18	64	57	20·4	11·8	59	73	23·30	5·4
8·51	63	57	20·87	9·1	60	74	23·37	5·4
8·67	61	60	20·85	13·0	62	75	24·15	4·2
8·87	62	59	21·32	9·55	62	76	24·65	3·4
8·92	63	57	20·87	8·5	58	75	24·45	5·1
9·02	63	58	21·05	9·78	58	80	24·95	3·4
9·10	67	60	20·75	10·9	63	81	25·30	2·8
9·33	61	61	21·30	10·4	63	84	25·30	2·8
9·36	63	58	21·50	10·35	64	80	25·15	4·0
10·03	63	62	21·55	10·05	63	89	25·55	3·1
10·64	66	60	21·80	9·4	65	84	26·4	3·1

2. SILVER–ALUMINIUM–MAGNESIUM ALLOYS.

Earlier work had indicated that better mechanical properties could be obtained by adding 2 or 3 per cent. of silver to aluminium magnesium alloys. In view of the erratic results obtained on the binary aluminium–magnesium alloys, owing to the uncertainty of composition introduced by segregation, it was feared that the apparent improvement previously observed might be spurious. To test this, an alloy was made up containing about 8.3 per cent. aluminium and 2·75 per cent. silver, with the usual 0·5 per cent. manganese. Analyses of the top and bottom of this billet gave:

End of Billet.	Aluminium, Per Cent.	Silver, Per Cent.
Top	8·01	2·67
Bottom	8·64	2·97

The billet was treated with the binary alloys discussed above, so as to give a number of test-pieces from each end as well as a middle section. The results of mechanical tests, together with results for binary alloys containing 8·0 and 8·64 per cent. aluminium, obtained by interpolation on the curves of Fig. 4, are given in Table V.

Table V.—*Effect of Silver on the Mechanical Properties of Some Aluminium–Magnesium Alloys.*

Composition.		Annealed.		Heat-Treated and Aged.	
Aluminium, Per Cent.	Silver, Per Cent.	Ultimate Stress, Tons/in.^{2}.	Elongation on $4\sqrt{A}$, Per Cent.	Ultimate Stress, Tons/in.^{2}.	Elongation on $4\sqrt{A}$, Per Cent.
8·0	...	20·3	12·0	22·8	6·0
8·01	2·67	20·9	10·7	26·9	2·8
8·64	...	20·9	10·5	24·2	4·2
8·64	2·97	21·8	9·7	27·1	4·8
10·67	...	21·5	10·0	26·3	3·0

Figures are also taken from Fig. 4 for an alloy containing 10·7 per cent. aluminium, *i.e.* one with the same amount of added metal as the alloy with 2·67 per cent. silver. These results show that, for alloys which have been treated in the manner outlined, little is gained by replacing some of the aluminium by silver. This matter is further dealt with, however, in a later section (p. 189).

3. THE EFFECT OF THE AMOUNT AND TEMPERATURE OF FORGING ON THE PROPERTIES OF AN ALUMINIUM–MAGNESIUM ALLOY.

In making a large forging from a billet, different parts of the final product will receive different amounts of reduction. It was important, therefore, to study the effect on the mechanical properties of varying amounts of reduction, and results obtained in this study suggested that improved properties might be obtained by giving a supplementary reduction at a lower temperature. The effect of forging temperature was also investigated.

In order to study the effect of various amounts of work, an alloy containing 8·6 per cent. aluminium and 0·5 per cent. manganese was cast into the form of a 3½-in. billet, which was preheated at about 370° C. for 12 hrs. A length of about 2 in. of the billet was then reduced by hot-pressing to 2·75 in. diam. and a further 2-in. length to 3 in. diam. (Table VI, *B* and *A*). The remainder of the bar was then forged to 2·75 in. diam., a disc from the centre of each 2-in. portion was cut off, the dies changed, the bar reheated, and further reductions made as shown in Table VI (Nos. *C*, *D*, *E*, and *F*). A

TABLE VI.—*Brinell Hardness of an* 8·6 *Per Cent. Aluminium–Magnesium Alloy After Different Amounts of Reduction. Brinell Hardness* (5/125/30).

No.	Reduction, Per Cent.	As Forged.			Annealed at 350° C., 1 Hr.			Heat-Treated for 1¼ Hrs. at 400° C., Quenched and Aged at 160° C.																	
								Quenched.			Aged 5 Hrs.			Aged 22 Hrs.			Aged 45 Hrs.			Aged 72 Hrs.			Aged 90 Hrs.		
		Position.			Position.			Position.			Position.			Position.			Position.			Position.			Position.		
		1.	2.	3.	1.	2.	3.	1.	2.	3.	1.	2.	3.	1.	2.	3.	1.	2.	3.	1.	2.	3.	1.	2.	3.
A	25	65*	62	59	60	60	56	58	59	55	61	60	56	69	66	62	72	69	66	74	72	68	75	71	66
B	40	65*	66*	64*	61	59	58	58	57	56	60	58	60	71	67	67	75	69	69	76	75	75	75	71	70
C	50	62*	...	61*	61	...	59	57	...	57	60	...	59	69	...	69	74	...	73	...	...	...	75	...	75
D	60	62*	...	64*	57*	...	58	58	...	58	63	...	61	66	...	66	73	...	73	...	...	...	75	...	75
E	70	65*	...	65*	57	...	57	61	...	63	63	...	64	66	...	65	73	...	73	...	...	...	76	...	76
F	80	62*	...	64*	61	...	59	59	...	58	63	...	62	69	...	71	73	...	73	75	...	75	77	...	77
G	85	64*	...	64*	58	...	60	58	...	58	62	...	62	71	...	71	73	...	72	...	...	...	78	...	78
H	87	63*	...	63	60	...	60	57	...	57	58	...	61	71	...	70	72	...	72	...	...	...	76	...	77
J$_1$	92	68*	...	74	60	...	60	53	...	55	59	...	61	71	...	71	74	...	74	75	...	77	79	...	79
J$_2$		68*	...	68	59	...	60	53	...	53	64	...	61	71	...	71	74	...	74	77	...	77	79	...	79

* Mean of two tests.

portion of the bar was then cut off and reheated, the dies changed, and samples *G*, *H*, and *J* of Table VI obtained.

The forging temperature was 360°–380° C., and the dies were maintained at this temperature throughout the operation. When it was necessary to change the dies, the bar was reheated to the forging temperature as quickly as possible.

In this way nine discs were obtained from bars which had been given the reductions shown in Table VI.

Brinell measurements were first made on the bars in the press-forged conditions. The discs were then annealed at 350° C. for 1 hr., air-cooled, and again tested for hardness. This was followed by annealing for 1½ hrs. at 390°–405° C. and quenching. After their hardnesses had been measured in this condition, the alloys were age-hardened at 160° C. for the times indicated in Table VI, and the hardnesses redetermined. Thus eight series of Brinell hardness values were obtained on each section.

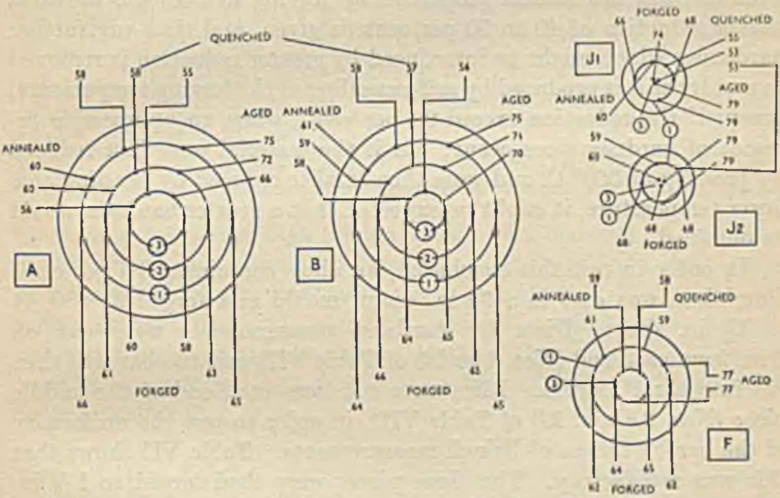

FIG. 5.—Hardness Penetration in 8·6 Per Cent. Aluminium Alloy Bar with Varying Degrees of Reduction.

On the two larger discs, tests were made at three different distances from the centre, and on the rest, at two distances. Fig. 5, which is a diagrammatic illustration of discs *A*, *B*, *F*, and *J*, shows the approximate positions of the tests more clearly than a description would. The results obtained, except for those at intermediate stages of ageing, are also shown in this figure. Some of the tests on the smaller discs were made on opposite faces.

Conclusions that can be reached from these tests are:

1. After 40–50 per cent. reduction has been given, the work appears to have penetrated to the centre of the material, and further forging does not lead to any increase in hardness until the reduction has reached about 90 per cent., when the forged material hardens appreciably.
2. Annealing produces a slight general softening of all the discs.
3. Material which has received the greatest degree of deformation (up to about 50 per cent.) age-hardens most rapidly and to the greatest extent. More than 50 per cent. deformation has no further effect.

It would appear, therefore, that it is possible to obtain material with uniform mechanical properties by forging at 380° C., provided that a reduction of 40 to 50 per cent. is given, and that any further hardening which might be introduced by greater reduction is removed as rapidly as it is produced by self-annealing at the forging temperature, except if the reduction exceed 90 per cent., when an appreciable increase of hardness does occur; but if the material were first reduced by pressing at 380° C. and were then further reduced by pressing at a lower temperature, it might be expected that a greater hardness would be obtained.

In order to test this conclusion, an alloy containing 8·5 per cent. aluminium was cast in a 3½ in. diam. mould and forged at 380° C. to 1¾ in. diam. Discs for hardness measurements were cut off 2 in. from each end (Nos. 1 and 3 of Table VII) and the bar was then cut into three lengths. Discs were cut from each end of the middle piece (Nos. 2*A* and 2*B* of Table VII), in order to test the uniformity of the bar by means of Brinell measurements. Table VII shows that this was satisfactory. The three pieces were then forged to 1 7/16 in. diam. at 300°, 250°, and 200° C., respectively. Discs for hardness measurements were cut from each piece, the dies changed, and the pieces reduced, at the above temperatures, to 1⅛ in. diam. over half their length and to 1 in. over the remainder. Discs for hardness measurements were then cut from each end of each bar. In this way discs were obtained representing 75 per cent. reduction at 380° C., and further reductions of about 33, 60, and 70 per cent. each at 300°, 250°, and 200° C. All the pieces forged quite well, without any apparent cracking: the piece forged at 200° C. appeared to be extremely hard, and some difficulty was experienced in obtaining the first reduction of about 33 per cent. The second and third reductions were obtained much more easily.

It must be emphasized that these remarks, as well as the data to be given below, refer only to material which has had the preliminary

TABLE VII.—*Effect of Amount and Temperature of Reduction on the Brinell Hardness of a Magnesium Alloy Containing* 8·5 *Per Cent. Aluminium.* (*Brinell Hardness* (5/125/30).)

No.	Forging Temperature, ° C.	Reduction. Per Cent.	As Forged. Position.		Annealed at 350° C., 1 Hr. Position.		Quenched after 1 hr. at 400° C. Position.		Aged at 160° C. for 24 Hrs. Position.		Aged at 160° C. for 48 Hrs. Position.		Aged at 160° C. for 3½ Days. Position.	
			1.	2.	1.	2.	1.	2.	1.	2.	1.	2.	1.	2.
1	380	75	62	63	61	61	57	57	77	78	80	81	78	78
2*A*			64	64	60	61	55	55	76	75	78	78	75	75
2*B*			60	63	...	...	...	...	...	...	...	...	...	...
3			63	63	58	59	56	56	70	70	72	74	72	72
1*a*	300	33	77	78	61	59	58	57	74	75	76	76	76	74
1*b*		60	77	77	61	59	57	57	78	77	82	80	80	77
1*c*		70	77	77	61	61	60	57	77	77	78	82	80	77
2*a*	250	33	85	84	59	61	57	55	75	76	80	79	75	75
2*b*		60	84	84	61	61	60	58	74	75	78	80	80	78
2*c*		70	82	82	58	60	58	58	76	78	77	79	78	78
3*a*	200	33	90	89	58	59	58	58	70	70	75	75	73	71
3*b*		60	91	91	58	56	57	55	70	72	80	78	78	76
3*c*		70	90	90	57	57	57	57	75	75	78	80	80	78

breaking down at the high temperature. Cast material cracks immediately an attempt is made to press it at 200° C., and the same is true of material which has had only a small reduction at 380° C., though such material is forgeable at 250° C. In this condition, however, the properties obtained are not so good as those given by the alloys which have had over 50 per cent. reduction at 380° C., followed by a further forging at 200° C.

TABLE VIII.—*Effect of Annealing Temperature on the Brinell Hardness of a Magnesium Alloy Containing* 8·5 *Per Cent. Aluminium after being Reduced by Various Amounts at Various Temperatures. Brinell Hardness* (5/125/30).

No.	Forging Temperature, ° C.	Reduction, Per Cent.	As Forged. Position.		Annealed at 160° C., 18 Hrs. Position.		Annealed at 200° C., 1 Hr. Position.		Annealed at 250° C., 1 Hr. Position.		Annealed at 300° C., 1 Hr. Position.	
			1.	2.	1.	2.	1.	2.	1.	2.	1.	2.
1*a*	300	33	77	77	75	76	75	76	76	76	67	67
1*b*		60	75	73	74	74	74	74	73	73	69	68
1*c*		70	77	76	75	75	72	74	74	72	69	68
2*a*	250	33	86	86	84	84	80	78	80	78	70	79
2*b*		60	85	84	77	78	78	78	80	80	68	67
2*c*		70	83	83	79	81	77	77	78	80	66	66
3*a*	200	33	89	89	82	84	84	86	82	81	66	66
3*b*		60	90	90	83	83	84	84	80	82	69	69
3*c*		70	90	90	84	86	87	87	84	84	67	67

Hardness measurements were carried out on all the discs referred to above. Two series of tests were made. In the first series the hardness was measured on the same disc from each specimen: (*a*) as forged; (*b*) annealed at 350° C. for 1 hr. and air-cooled; (*c*) heat-treated at 400° C. for 1 hr. and quenched; and (*d*) aged at 160° C.

In the second series, the tests were carried out on separate discs cut from adjacent sections. These tests were on specimens: (*a*) as forged; (*b*) annealed for 18 hrs. at 160° C., and air-cooled; (*c*), (*d*), and (*e*) annealed for 1 hr. at 200°, 250°, and 300° C., respectively, and air-cooled. The tests were all carried out in duplicate.

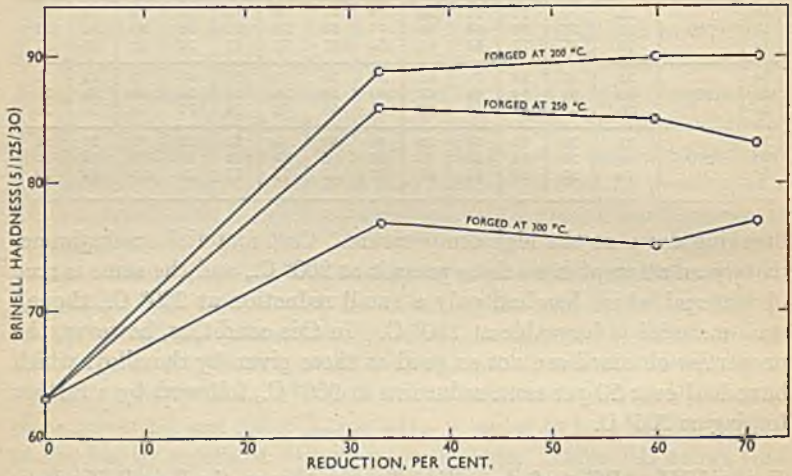

Fig. 6.—Effect of Forging Temperature and Percentage Reduction on a Magnesium Alloy Containing 8·5 Per Cent. Aluminium.

The results obtained for the first and second series are given in Tables VII and VIII, respectively.

The hardness values for the forged bars in the second series are plotted in Fig. 6, which shows that the material is completely work-hardened after 33 per cent. reduction at all three temperatures. This obviously only applies to material which has had the preliminary breaking down at 380° C. It is possible, of course, that the maximum hardness would be attained with even less reduction. It will also be seen that low-temperature forging results in a very great increase in hardness; thus for material forged at 200° C. the hardness increases from 63 to 90, and the alloy forged at 250° C. is nearly as hard. Annealing for 1 hr. at the forging temperature reduces the hardness by 4 to 6 units.

In view of these interesting results, it was decided to measure the tensile properties of material treated in this way. Much work was carried out on alloys containing from 4 to 10 per cent. aluminium with and without silver in amounts up to just over 4 per cent.,* the alloys being first broken down in the usual manner at 380° C. and then given reductions varying between 20 and 60 per cent. at 200° and 250° C. They were tested in the forged, annealed, and aged conditions. The material used for this purpose consisted in part of specially prepared alloys and in part of the middle sections (*CX*) of the bars referred to on p. 181 and in Table III.

In order to avoid overburdening this paper with tables, the properties of the more interesting alloys only are given, the rest of the results being summarized as follows:

1. In all the alloys examined, the properties obtained after 20 per cent. reduction at 200° C. (after breaking-down at 380° C.) were superior to those of heat-treated and aged alloys which had been pressed at 380° C. In general, some improvement was obtained by increasing the amount of work, though there seems to be little advantage in giving reductions greater than about 35 per cent.
2. The material produced by finishing at 200° C. is excellent in appearance, and forges very well without cracking, though the alloy containing 10 per cent. aluminium and 2·5 per cent. silver was very difficult to forge at this temperature, even with the full pressure available (120 tons). It forges readily, however, at 250° C.
3. The mechanical properties of the forged and of the annealed 9 per cent. aluminium alloy are given in Table IX, while the mechanical properties of a similar alloy (8·8 per cent. aluminium) in the annealed and in the aged states after forging at 380° C., as well as in the untreated state after forging at 200° C., are given in Table X.
4. The ultimate stress of alloys containing aluminium only, forged at 200° C., increases to a maximum value of about 27 tons/in.^{2} when the content is between 8 and 9 per cent., the elongation having a maximum value of 12 per cent. when the alloy contains 4–6 per cent. aluminium. The addition of 2·5 per cent. silver increases the ultimate stress by about 3·5 tons/in.^{2} for the 6 per cent. aluminium alloy and 6 tons/in.^{2} for the 10 per cent. aluminium alloy, the elongation values being 10·5 and 2·5 per cent., respectively (Fig. 7).

Special reference must be made to three series of alloys containing, respectively, 4, 6, and 8·5 per cent. aluminium. These were made to study the effect of the addition of silver, and were given a 60 per cent. reduction at 200° C. after the preliminary breaking-down at

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* To all the alloys 0·5 per cent. manganese was added.

TABLE IX.—*Mechanical Properties of a Magnesium Alloy Containing 9 Per Cent. Aluminium Forged at 380° C. and then Reduced by 33 and 60 Per Cent. at 300°, 250°, and 200° C.*

Forging Temperature, ° C.	Reduction, Per Cent.	As Forged.		Annealed for 1 hr. at 200° C.	
		Ultimate Stress, Tons/in.².	Elongation on $4\sqrt{A}$, Per Cent.	Ultimate Stress, Tons/in.².	Elongation on $4\sqrt{A}$, Per Cent.
300	33	22·3	11·0	...	...
	60	23·2	6·8	...	...
250	33	24·2	9·3	24·1	7·8
	60	24·1	8·5	...	...
200	33	26·1	8·9	25·5	8·8
	60	26·6	9·6	...	...

TABLE X.—*Mechanical Properties of a Magnesium Alloy Containing 8·8 Per Cent. Aluminium After Various Heat and Mechanical Treatments.*

Forging Temperature, ° C.	Reduction, Per Cent.	Heat-Treatment.	Ultimate Stress, Tons/in.².	Elongation on $4\sqrt{A}$, Per Cent.
380	75	Annealed at 350° C.	22·1	11·5
380	75	Heat-treated and aged	24·4	3·6
200	20	None	24·9	8·0
200	35	,,	24·9	8·0
200	60	,,	25·7	7·4

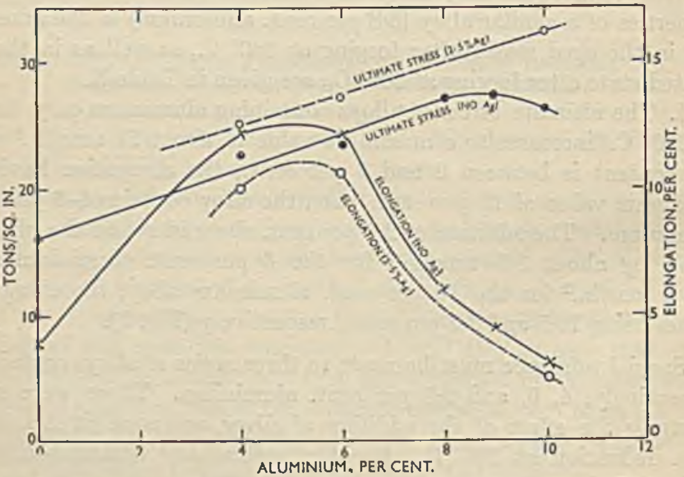

FIG. 7.—Mechanical Properties of Aluminium–Magnesium Alloys (With and Without 2·5 Per Cent. Silver) after 60 Per Cent. Reduction at 200° C.

380° C. The results are shown in Figs. 8, 9, and 10. It will be seen that silver increases the ultimate stress of the 4 per cent. aluminium-

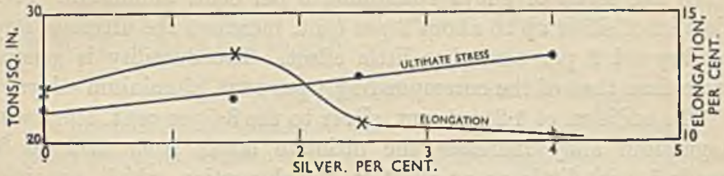

Fig. 8.—Effect of Silver on the Mechanical Properties of a Magnesium Alloy Containing 4 Per Cent. Aluminium, after 60 Per Cent. Reduction at 200° C.

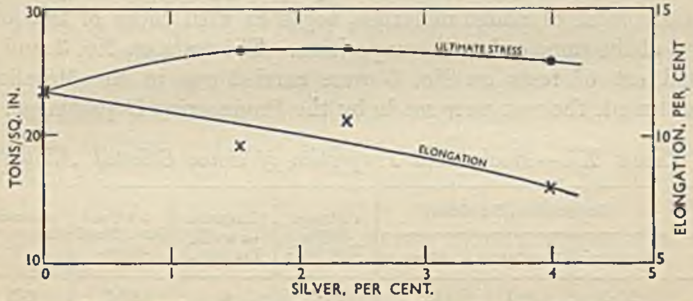

Fig. 9.—Effect of Silver on the Mechanical Properties of a Magnesium Alloy Containing 6 Per Cent. Aluminium, after 60 Per Cent. Reduction at 200° C.

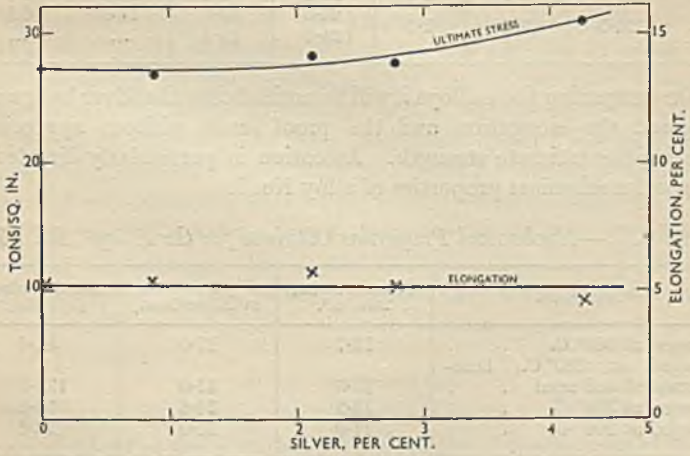

Fig. 10.—Effect of Silver on the Mechanical Properties of a Magnesium Alloy Containing 8·5 Per Cent. Aluminium, after 60 Per Cent. Reduction at 200° C.

magnesium alloy without very seriously reducing the elongation; the latter is in fact somewhat increased by the first additions of silver.

The curves (Fig. 8) suggest that little would be gained by increasing the silver beyond about 4 per cent.

In the series of alloys containing 6 per cent. aluminium (Fig. 9) addition of silver up to about 2 per cent. increases the ultimate stress, but beyond 2 per cent. has little effect. The ductility is generally lower than that of the corresponding 4 per cent. aluminium alloys.

The addition of 4·2 per cent. silver to the 8·5 per cent. aluminium–magnesium alloy increases the ultimate stress from 27·2 to 30·8 tons/in.², with little or no effect on the elongation, which remains at about 5 per cent. (Fig. 10).

Table XI shows the mechanical properties of three alloys having the same total of added materials, together with those of two other alloys of the same order of composition. The tests on No. 3 and the second set of tests on No. 5 were carried out in the Metallurgy Department, the rest were made by the Engineering Department.

TABLE XI.—*Mechanical Properties of Some Selected Alloys.*

No.	Composition, Per Cent.			Ultimate Stress, Tons/in.².	Elongation on $4\sqrt{A}$, Per Cent.	0·1 Per Cent. Proof Stress.	Modulus, Lb./in.² $\times 10^{-6}$.
	Magnesium.	Aluminium.	Silver.				
1	91·9	8·1	...	27·2	4	16·7	6·5
2	92·0	6·5	1·5	27·3	11·5	21·3	6·5
3	91·8	4·1	4·1	26·7	10·3	...	...
4	91·4	6·1	2·5	27·1	8·5	20·1	6·6
5	94·7	3·8	1·5	24·5	10·0	18·4	6·5
				24·0	13·4	...	...

On comparing these alloys it will be noticed that the silver has greatly increased the elongation and the proof stress without appreciably affecting the ultimate strength. Attention is particularly directed to the good mechanical properties of alloy No. 2.

TABLE XII.—*Mechanical Properties Obtained for the Alloy "RR 56."*

Treatment.	Ultimate Stress, Tons/in.².	Elongation on $4\sqrt{A}$, Per Cent.	Brinell Hardness (5/125/30).
Forged at 380° C. . .	13·7	17·0	54·4
Forged at 380° C., heat-treated and aged . .	26·5	11·0	130·0
Forged at 300° C. . .	13·3	14·6	56·8
Forged at 200° C. . .	17·0	10·0	76·2

For purposes of comparison, a billet of the alloy "RR 56" was made and broken down in the press from $3\frac{1}{2}$ in. diameter to $1\frac{7}{16}$ in. diameter at 400°–450° C. It was then cut into three pieces, which were forged to 1 in. diameter at 380°, 300°, and 200° C., respectively.

Part of the piece forged at 380° C. was heat-treated and aged to give a Brinell hardness of 130, and tensile tests were carried out on all four pieces. Table XII shows the results obtained.

The specific gravity of "RR 56" is 2·8, while that of the alloys given in Table XI is 1·78 to 1·79.

RÉSUMÉ.

The mechanical properties of pressed magnesium alloys containing up to 10 per cent. aluminium have been investigated, and the effect of adding up to 4 per cent. silver has been studied. A maximum in the mechanical properties at about 9 per cent. aluminium which was suggested by earlier work, at the National Physical Laboratory and elsewhere, is shown not to exist, while little if any benefit, either in the aged or annealed state, is obtained at room temperature by the addition of silver to alloys which have been forged at 380° C.

The effect of varying the amount of reduction given to a forging has been studied, and it is shown that the work penetrates to the centre of a 3½ in. diam. ingot after a reduction of 40 to 50 per cent. has been given, and that no further hardening is obtained until a reduction of 90 per cent. is reached, when a definite increase of hardness takes place.

Forging alloys at a temperature of 200° C. (after a preliminary breaking down at 380° C.) causes an appreciable increase in the ultimate stress without much loss of ductility as compared with that of alloys which have been forged at 380° C. The tensile strength of alloys treated in this way is still further increased by the addition of silver. An alloy containing 8·5 per cent. aluminium and 4·2 per cent. silver has a tensile strength of over 30 tons/in.^{2} with an elongation of 5 per cent.; an alloy containing 6·5 per cent. aluminium and 1·5 per cent. silver has an ultimate stress of over 27 tons/in.^{2} and an elongation of 11·5 per cent., and one containing about 4 per cent. aluminium and 1·5 per cent. silver has an ultimate stress and elongation of 24 tons/in.^{2} and 13·4 per cent., respectively. The second of these alloys has a proof stress of 21·3 tons/in.^{2}. These values compared very favourably with those for a specimen of "RR 56" alloy in various conditions of forging and heat-treatment.

ACKNOWLEDGMENTS.

The authors wish to express their thanks to Dr. C. H. Desch, F.R.S., Superintendent of the Metallurgy Department of the National Physical Laboratory, for his interest and encouragement in the research, and to Messrs. W. H. Withey, B.A., and P. Ward, B.Sc., who undertook the numerous chemical analyses required by the work. Thanks are also due to members of the staff of the Engineering Department of the

Laboratory for mechanical tests on some of the alloys, in particular for the determination of the proof stresses. The authors also wish to record their indebtedness to Mr. J. W. West for his assistance in the work, in particular in connection with the casting of the alloys, and in the matter of the segregation difficulties which were encountered and which are dealt with in the appendix.

REFERENCES.

[1] J. L. Haughton and R. J. M. Payne (Ni–Mg), *J. Inst. Metals*, 1934, 54, 275.

[2] W. E. Prytherch, *J. Inst. Metals*, 1935, 56, 133.

[3] J. L. Haughton and R. J. M. Payne (Al–Cd–Mg), *J. Inst. Metals*, 1935, 57, 287.

[4] R. J. M. Payne and J. L. Haughton (Ag–Mg), *J. Inst. Metals*, 1937, 60, 351.

[5] J. L. Haughton and T. H. Schofield (Ce–Mg), *J. Inst. Metals*, 1937, 60, 339.

[6] J. L. Haughton (Ca–Mg), *J. Inst. Metals*, 1937, 61, 241.

[7] J. L. Haughton and W. E. Prytherch, "Magnesium and its Alloys," London: 1937.

[8] J. A. Gann and A. W. Winston, *J. Indust. Eng. Chem.*, 1927, 19, 1193.

[9] A. Dumas and F. Rockaert, *Rev. Aluminium*, 1932, 9, 1717.

APPENDIX.

Reference is made in the earlier part of this paper to the lack of uniformity in composition found in many of the billets, the bottom being invariably richer in aluminium than the top. Examples of this have been given in Table III. Some evidence had been obtained that the uniformity of the ingots was greater when the rate of pouring was very slow. This suggested that the trouble was due to gravity segregation of the lighter primary crystals in the liquid, and that with very slow pouring the metal would become completely solid at the bottom of the mould before there was much head of liquid above it. It was decided, therefore, to find whether the temperature of the mould and of the metal at the moment of casting had any effect on the uniformity, as cold metal, poured into a cold mould, would solidify almost as soon as it entered the mould, and there would therefore be little depth of liquid in which segregation could occur, whereas very hot metal in a very hot mould would give rise to a mould full of liquid metal, and afford every opportunity for segregation. Four billets of a 9 per cent. aluminium–magnesium alloy were therefore cast as shown in Table XIII, the metal being poured reasonably slowly.

It is obvious from Table XIII that the mould temperature has no effect on the segregation, while the results are certainly no worse, but rather better, with a high casting temperature.

In order to make certain that there was no want of homogeneity in the liquid metal, a crucible full was given the usual stirring, and kept liquid for some time. A heated iron tube, whose end could be closed by a valve operated from the top, was then gently lowered into the metal, the valve closed and the tube removed, and a sample of the

TABLE XIII.

Mould Temperature, ° C.	Casting Temperature, ° C.	Position.	Analysis. Aluminium, Per Cent.	Difference, Per Cent.
100	700	Top Bottom	8·63 9·02	0·39
100	750	Top Bottom	8·56 9·09	0·53
100	850	Top Bottom	8·80 9·05	0·25
250	850	Top Bottom	8·92 9·19	0·27

metal from top to bottom thus obtained. When the sample had solidified, the iron tube was removed and the composition of the cylinder was determined at the top and bottom. Analysis showed, as was to be expected, that the liquid was perfectly homogeneous.

It was then decided to try to pour the metal as slowly as possible, so as to allow it to solidify while filling the mould. Two billets were made to contain 6 per cent. aluminium and 10 per cent. aluminium + 2·5 per cent. silver, respectively, and cast by pouring with extreme slowness—a difficult operation, as the first lot of metal came out of the pot suddenly and the tilt had to be reduced to the smallest amount that would keep up a stream.

The analysis of these billets is shown in Table XIV, Nos. 1 and 2, from which it would appear that the slow pouring had been a perfectly satisfactory cure. Five more alloys were then cast in the same manner (Nos. 3 to 7 of Table XIV), and it will be seen that, while two of them were reasonably good, two were bad.

It seemed probable that the variations arose from the impossibility of accurately controlling the speed of casting, so some efforts were made to fill the mould by pouring through a tundish. Some satisfactory results were obtained in this way, but they could not be repeated with any certainty, as it was difficult to get a slow enough speed, partly owing to the stream solidifying in the spout of the tundish when this was made small. The method was therefore abandoned.

In the greater part of this work, a mould was used whose cross-sectional area was about equal to that of the ingot, and it was thought that this might promote segregation, as the relatively thin mould would heat up rapidly. Although the work mentioned above on the effect of mould temperature (Table XIII) would seem to contradict this, some experiments were carried out with mould to ingot ratios of 2 : 1, 2·5 : 1, and 3 :1, and it was found that the 2 : 1 ratio moulds gave better results

TABLE XIV.

No.	Position.	Composition, Per Cent.		Difference, Per Cent.	
		Aluminium.	Silver.	Aluminium.	Silver.
1	Top	6·06	...	0·07	...
	Bottom	6·13	...		
2	Top	10·18	2·67	0·03	0·03
	Bottom	10·15	2·64		
3	Top	5·44	2·32	0·70	0·22
	Bottom	6·14	2·54		
4	Top	8·62	0·87	0·16	0·01
	Bottom	8·78	0·88		
5	Top	8·19	1·93	0·45	0·22
	Bottom	8·64	2·15		
6	Top	8·74	4·32	0·06	0·07
	Bottom	8·80	4·25		
7	Top	9·81	2·23	0·97	0·53
	Bottom	10·78	2·76		

than the 1 : 1, while with the 2·5 : 1 and 3 : 1 moulds, completely satisfactory results were obtained, provided the metal was poured slowly. Table XV gives the analyses of some billets cast in this way. In all cases the mould was filled slowly.

TABLE XV.—*Effect of Mould Ratio on Segregation.*

No.	Ratio.	Position.	Composition, Per Cent.		Difference, Per Cent.	
			Aluminium.	Silver.	Aluminium.	Silver.
1	2 : 1	Top	8·89	...	0·18	...
		Bottom	9·07	...		
2	2·5 : 1	Top	5·98	2·36	0·01	0·08
		Bottom	5·99	2·44		
3	2·5 : 1	Top	4·02	2·41	0·02	0·03
		Bottom	4·04	2·38		
4	3 : 1	Top	4·01	...	0·05	...
		Bottom	4·06	...		
5	3 : 1	Top	4·04	...	0·03	...
		Bottom	4·07	...		

It will be seen that by the use of a suitable mould ratio the trouble can be completely overcome, but it must be admitted that the cause is not completely understood.

JOINT DISCUSSION.

(*Condensed.*)

Mr. W. E. Prytherch,* M.Sc. (Member): The paper by Professor Jones and Mr. Wolfe describes a continuation of their work on the copper–magnesium alloys, but, as was to be expected, the properties obtained are not very interesting from a practical point of view. Copper and nickel behave very similarly as alloying constituents in magnesium, and this is probably accounted for by the similarity in the constitutional diagrams, there being very little solid solubility of either of these constituents. The alloys are well known to be very corrodible, nickel being rather worse than copper in this respect.

There seems ground for criticism of the method adopted for forging, since it is fairly well established that the method of hammer-forging for magnesium is, in general, unsatisfactory, the reason being that the forging range is rather small, and the temperature to which the metal would have to be heated is above that temperature which produces rather a coarse grain. Very much better results are produced by swaging, which can be done at a lower temperature and which produces a finer grain, and therefore better alloys. Further, forging under the hammer tends to produce very much more cracking than does swaging.

The results obtained by Dr. Haughton and Mr. Tate are unexpected, because it was originally believed that to work magnesium satisfactorily a very high temperature is necessary—*i.e.* just below the eutectic temperature. That is only true, apparently, in the case of the initial breaking down, and it is found that superior results are obtained if the temperature is progressively decreased as the amount of work or deformation increases. In this investigation a definite amount of work (30 per cent.) has been applied at specific temperatures. I think that the application of cold-work can be considered in a much more general way. A smaller amount of work at a lower temperature will produce much the same effect. For instance, about 10 per cent. controlled cold-work at 170° C. will have much the same effect as 30 per cent. at 200° C. or, say, 50 per cent. at 250° C. The amount of work necessary to produce that effect will vary considerably, of course, with the alloy, and particularly with the composition.

The authors' work is almost entirely confined to the tensile strength and Brinell hardness in the longitudinal direction. It would have been interesting if fatigue and transverse tensile, and also compression, particularly transverse compression, test results had been given. It is difficult to carry out such tests on small bars, but had it been possible to carry out this work on bars of larger diameter, I think that it would have been found that the properties were highly directional, and considerable difficulty would have been found in producing these properties in the transverse direction.

It would also have been interesting if properties at high temperatures had been studied. This method of working might be detrimental when applied to alloys for use at high temperatures, owing to the finer grain produced and the possible reduction in creep characteristics.

Mr. W. C. Devereux † (Member): said he wished to associate himself with the previous speaker's remarks. He added that he felt that the work

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† Managing Director, High-Duty Alloys, Ltd., Slough; and of Magnesium Castings and Products, Ltd., Slough.

which was being done was opening up quite a new field in the working and forging of magnesium alloys, and that he felt that, particularly in regard to the nickel–copper–magnesium alloys, if any benefit were to come out of it, it must be from a study of the workability and the forgability.

Mr. W. **Freeman Horn** * (Member): What is the exact definition of "drawing" in the paper by Professor Jones and Mr. Wolfe? They state that the alloys were previously drawn down, and that one-half of the billet was "drawn down further to a diameter of ⅞ in." Do they mean ordinary drawing down through a fixed die or some form of hammer-drawing?

Dr. H. W. **Brownsdon**,† M.Sc. (Vice-President): The mechanical properties of wrought alloys depend largely on the manner in which they are worked, and with the magnesium alloys in question it would have been of interest to have carried out mechanical tests after extrusion, especially as this process is so frequently applied to these alloys in commercial fabrication. Speaking generally, extrusion is probably the most satisfactory means of converting metals and alloys from the cast to the wrought state, the extruded product being then made the basis material for the further development of improved mechanical properties by cold-working.

Dr. M. A. K. **Hansen** ‡ (Member): Have any forging experiments been carried out by Dr. Haughton and Mr. Tate on aluminium–magnesium alloys which have been extruded, instead of starting from the cast state? With aluminium alloys it is usual to start with extruded material, and the same is often the case with magnesium alloys.

Dr. H. **Sutton** § (Member): In the paper by Dr. Haughton and Mr. Tate, on p. 186, appears the remark "to obtain material with uniform mechanical properties by forging at 380° C." Before speaking of uniform mechanical properties, especially with reference to magnesium-rich alloys, it is very necessary to test for real uniformity of properties. There are methods of working magnesium-rich alloys which do tend to give uniform tensile strength and elongation, etc., in all directions, but some people may be misled by the use of the words "uniform mechanical properties" in this connection, especially in the absence of evidence that the properties in various directions were in fact reasonably uniform. Probably the authors mean this in reference to hardness.

A remarkable feature of the paper is the reference to the merits of low-temperature working at 200° C. There is need for information on the properties in various directions as influenced by the low-temperature working, and the properties in two transverse directions particularly. Those are of increasing importance in technical applications. We also want to know the influence of low-temperature forging on the proof stress and fatigue properties. It may be early to speak on that subject, but there are signs that low-temperature working may not be a real help in improving fatigue properties; it may, on the other hand, not be a serious disadvantage.

In Table XI, there is a reference to an alloy (No. 1) containing 91·9 per cent. magnesium and 8·1 per cent. aluminium, with an ultimate stress of 27·2 tons/in.^{2} and an elongation of 4 per cent. That value for elongation is rather low, as compared with that of commercial forgings and extrusions; on the other hand, it may be reasonably comparable with the authors' other

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§ Principal Scientific Officer, Royal Aircraft Establishment, South Farnborough.

results. I presume that the alloys were prepared in the same general way. Our skilled technologists are producing that alloy with substantially better elongation values, and I have examples of alloys of similar composition which have much better elongation values and perhaps only a little lower ultimate stress. The ultimate stress value given in the paper is admittedly very good.

Professor Jones and Mr. Wolfe melted their flux in an iron ladle. In our experience, it is an advantage to sprinkle dry flux as a powder on the surface of the metal; this seems to help it to work more uniformly over the surface, expecially when dealing with small quantities. I note that the authors left their metal undisturbed at 700° C. They might have benefited by superheating it before casting; that is proving of advantage in certain cases with magnesium-rich alloys, and it might be worth considering in the case of the alloys with which the authors have been dealing.

I see also that the metal was teemed by lifting a stopper in the bottom of the pot. In our experience that is not a convenient way to cast small quantities of magnesium-rich alloys melted with flux, because of the difficulty of fully eliminating the flux. After persistent endeavours in that direction, we abandoned the use of flux and resorted to melting the alloys in an argon atmosphere. Argon is now a commercial gas, purchasable in bottles.

The diagrams bring out a point of which experience has also been obtained elsewhere in the technology of magnesium-rich castings, but of which the authors make no special mention, namely that the rate of cooling after heat-treatment has surprisingly little effect on magnesium-rich alloys. It is interesting to obtain independent evidence of this fact in a new series of alloys.

In the heat-treatment experiments, I note that the alloys were soaked for 1 hr. at 450° C. That seems a very short period in which to get the best out of the alloys; the authors might have done better with much longer periods. In industrial practice, 16 hrs. is sometimes used for the heat-treatment of magnesium alloys at the higher of the two temperatures which are used.

The authors have not been very enthusiastic about their alloys. They point out that the effect of heat-treatment on tenacity is negligible, but they do say that it caused an increase in elongation and in the reduction of area, and these properties are most useful. We have examples in which castings made in magnesium alloys gave trouble until the stage was reached at which the ductility could be increased by heat-treatment, and I would particularly refer to aircraft wheels, where heat-treated alloys have proved really successful. There is some increase in tensile strength, but the main difference between the heat-treated casting and the as-cast material is probably in the ductility.

The authors state that the effect of nickel on alloys containing 4 per cent. copper is of no benefit. One cannot help feeling that it might be of benefit to the high-temperature properties, and that would be worth a few simple tests. In relation to heat-treatment, it is stated that the alloys do not age-harden at room temperature. That is true, and I think that it is true of all the other magnesium-rich alloys with which I am familiar. It would have been worth while to carry out some age-hardening tests at elevated temperatures. Have the authors done this?

Dr. J. L. HAUGHTON * (Member): Professor Jones and Mr. Wolfe refer to the breaking-in of the pot to stop it taking up iron. In an earlier paper Professor Jones said that he melted alloys several times in the pot so as to get a surface, presumably containing a certain amount of magnesium, which prevented the molten metal from taking up iron from the pot. Did the authors find this necessary when using "Elrasal" flux? It has been our experience that it is unnecessary to do any breaking-in when using this

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flux. We have found that we get a slight reduction of the amount of iron in our magnesium when we melt it in an iron pot. That sounds remarkable, but I am sure that it is due to the fact that the "Elrasal" flux takes out more iron than the pot puts in. It may be that the authors' earlier experiments were carried out with some flux which had not that purifying action on the material.

Professor W. R. D. JONES,* D.Sc. (Member): The results recorded in the paper by Dr. Haughton and Mr. Tate will prove most useful in the search for magnesium alloys having high tenacity combined with a reasonable ductility. The pre-treatment recommended is quite promising, and, although lengthy, is possibly cheaper for this purpose than the addition of expensive metals, such as silver, or the comparatively little-used metals, such as cerium.

What does the pre-treatment do? Is it a question of diffusion or merely a release of casting stresses and a recrystallization? Would a shorter time, say 1 hr. at 450° C., be equivalent to 12 hrs. at 370–380° C.? We must, however, admit that the forging temperature is still of paramount importance. Was there any particular reason for the temperature chosen for annealing and for ageing? Would not an ageing temperature of 200° C. have been more reasonable than one of 160° C.?

It seems to me that the maximum given in Figs. 1 and 2 and in Table II is due to the presence of zinc, or is possibly a freak result which cannot be repeated ordinarily. Mere variation in composition, as stated on p. 182, will scarcely be sufficient to explain such a pronounced kink in the curve in Fig. 2 at about 9 per cent. aluminium. The exploration of the forging properties of the 8·6 per cent. aluminium alloy is very interesting. In the case of steel it is considered that Brinell hardness numbers are not accurate to more than ± 2 numbers per 100. With soft materials such as magnesium alloys, and also in view of the possibility that the indentations may not be perfectly symmetrical, it is doubtful whether it is legitimate to consider a difference of less than 3 numbers in the range reported. Consequently, in Tables VI–VIII, in which single tests are mainly reported, care must be taken in making deductions. From Table VIII it seems that variations in forging temperature and in the amount of reduction are eradicated by annealing at 300° C. In Fig. 6, if the forging temperature had been about 450° C., and if the forging had been stopped before the temperature had dropped below 350° C., probably there would have been no work-hardening.

Such pronounced segregation as was found is unexpected with two metals whose densities are not far apart, like magnesium and aluminium, but is not the diameter of 3½ in. rather wide for a comparatively short ingot? It seems definitely a matter covering the transference of the metal from the pot to the mould and its solidification. Ordinarily we find that unless the mould is very hot there is danger of a cold shut, and with a mould temperature of 450° C. (approximately) no segregation is found in alloys of magnesium with copper and/or nickel in casting an ingot 18 in. long and 2½ in. diameter, although admittedly there is rapid solidification. Pouring into a cold mould is accompanied by the risk of a cold shut, unless the utmost care is taken with the teeming.

Mr. W. R. BARCLAY,† O.B.E. (Past-President): Professor Jones and Mr. Wolfe described to some extent their forging technique, but Dr. Haughton and Mr. Tate give very little information on that point. Can they give a little more detail?

I am interested in the difference between the technique of forging in

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mechanically-worked presses as compared with those operated hydraulically. On the face of it, it does not seem that there should be any difference, but in other branches of industrial metallurgy we have found considerable differences between the properties of materials worked under the comparatively smooth operation of an hydraulically-controlled forging press and those of materials for which a mechanical press has been used. Mechanical presses, of course, differ amongst themselves, and it would be interesting to have as full a description as the authors can give of that particular section of their technique.

I am in entire agreement with Dr. Brownsdon that it is important to ascertain how any of these alloys, and particularly those of industrial promise, behave under extrusion.

Professor JONES (*in reply*): Mr. Prytherch referred to corrosion. When this work was commenced many years ago, we did try to carry out some work on corrosion, but I soon concluded that experiments on corrosion should be carried out by those who have great experience of corrosion testing, and that they should not merely be carried out as routine work, because we obtained some results which were not easily explained, and, as we could not afford time to investigate the matter thoroughly, we decided that it would be better to leave it alone.

I am very interested in the remarks made on forging, and I shall take heed of them. It would be advantageous to use better ways of forging and of carrying out the work (we could easily think of better methods), but in the metallurgical department of a University one has to make use of the facilities which are available.

The use of the word " drawing " has been referred to; perhaps it is used rather loosely in the paper. In our own case the ingot was hammered down and not drawn through a die. As regards swaging, I favour swaging down round and not hammering flat and then finishing off round. Even in the case of brasses, I have found that by forging in this manner there is less liability to corner cracking, and the bar is thoroughly forged down before it gets to the final size.

When this investigation was started, we used a different flux, and not " Elrasal." We thought to avoid any pick-up of iron by " breaking-in " the crucible thoroughly, and it acted well; so that when we resumed the work we used the same procedure to avoid iron pick-up. A crucible will last for a long time, and there is usually a good deal of scrap metal available which can be melted to " break-in " the crucible. We found that if we melted the flux just before putting it into the pot it acted perfectly; if we sprinkled it into the metal it tended to drop to the bottom of the pot and foul the stopper.

Regarding heat-treatment, a point raised by Dr. Sutton, some exploratory work was carried out, and we tried a longer time at 450° C. and various other temperatures, and found that, using the Brinell hardness figure as an indicator, 1 hr. at 450° C. suited our purpose very well, with bars of 1 in. cross-section.

Dr. HAUGHTON (*in reply*): Mr. Prytherch suggested that it is possible to get equal results by a smaller amount of work at a low temperature and a greater amount at a high temperature; that by varying the ratio of the high- to the low-temperature work it is possible to obtain similar results. I think that that is perfectly true, and there is one point which I should like to mention. It is necessary in the first place to do some breaking down in order that the material can be worked at all at the lower temperatures, and the lower the temperature at which the work is done the more power is required in the press, so that there is some advantage in giving a considerable amount of work at the high temperature and a rather less amount at the low temperature. Mr. Prytherch is correct in saying that there is a great deal more work to be done; that we should have transverse, fatigue, and compression tests. Fatigue and compression tests are in hand and fairly good results have been obtained from the former. We cannot carry out transverse tests on our bars, because we have not a large enough press to give us material of sufficient size when it is pressed down to make a transverse test-piece. On sheet, of course, we can carry out transverse tests, and the mechanical properties are probably quite different in the transverse from the longitudinal direction.

Dr. Brownsdon asked about extruded material. In industry, magnesium alloys are extruded to a very large extent, and they give excellent results. We do not possess an extrusion press, so that we cannot carry out extrusion tests. Dr. Hansen asked whether we had carried out tests on materials which had been extruded and then forged. Some bars have been extruded for us and we have carried out tests on rolled material on those bars, but so far we have done nothing on extruded and forged material.

Dr. Sutton mentioned that we carried out no transverse tests, and criticized the use of the word "uniform." He is right; we should not have used the word "uniform." We meant that it was uniform in one direction; that the hardness measured on a particular surface was the same on the outside as on the inside, but we do not know whether tests carried out longitudinally and transversely would be the same, though we are fairly sure that they would not be, so that the material is not uniform in that way.

In reply to Professor Jones, I do not think that the zinc is the cause of the maximum of 9 per cent. found, because it was found in other alloys, and has been referred to by other investigators. We have shown, I think, that it is spurious and that there is no maximum. We used the large 3½-in. mould because we wanted a big reduction and to have material of reasonable size when we had finished the tests. We should have liked to have used a much larger mould; with a larger press we might then have been able to carry out transverse tests.

Mr. Barclay asked about the press; it is a 120-ton hydraulic press, worked off a pump with two pistons, so that the motion is fairly uniform. There is a slight visible motion at each stroke of the pump. The dies in which the material was forged are illustrated in the monograph on magnesium and its alloys to which reference has been made in the paper. The dies had a ring of burners round them with little flames which played on them all the time; a thermocouple was embedded in the die, and the temperature measured all the time they were in use.

I will deal in writing with any other points which have arisen.

CORRESPONDENCE.

Dr. Haughton and Mr. Tate (*in further reply to the discussion*): Dr. Sutton asked for information about the effect of low temperature forging on the proof stress and fatigue properties of magnesium alloys. So far as proof stress is concerned, we would refer him to Table XI, where the 0·1 per cent. proof stress of four alloys is given. If these are compared with those obtained in practice for alloys forged or extruded in the ordinary way, it will be seen that the low temperature treatment gives considerably higher values. Unfortunately, no direct comparisons are available, as the proof stress was not determined on any of the alloys forged at 380° C. Work is now being carried out on the fatigue properties of these materials after low-temperature forging.

Dr. Sutton also directed attention to the low elongation value obtained for alloy No. 1 of Table XI. As he suggests, the alloys were all prepared in the same way, so that they should be reasonably comparable with each other, though higher values for all of them may well be obtained in industry.

Professor Jones asked for information on the mechanism of the annealing before forging. It was carried out mainly to help to produce a more homogeneous alloy as a result of diffusion. We do not think the release of casting stresses is of much importance, and though there is undoubtedly a certain amount of recrystallization, the exact mechanism is not clear and more work is required on this subject.

Professor Jones doubted whether it is legitimate to consider as significant a difference of less than 3 units in the Brinell hardness. A very large number of our results are from the mean of two measurements which were worked out to one place of decimals (and rounded off afterwards for publication). The majority of these duplicates agree to closer than one unit, while the greater number of the remainder are less than 2 units apart, so it would appear that, in spite of the risk of the impression not being perfectly symmetrical, the results are more accurate than might have been expected.

With reference to Mr. Prytherch's remarks and the verbal reply to them, Dr. Haughton regrets that he misunderstood the reference to the ratio of high- and low-temperature forging. While it is true, as stated in the reply, that if a large amount of breaking down at 380 ° C. is given, a lesser amount of forging at 200° C. will (within limits) give similar results to those obtained with more low-temperature forging and less breaking down; it is not true that a small amount of work at 170° C. will have much the same effect as a larger amount at 200° C. In general, a temperature of 200° C. was found to be the most effective (see Table IX). Forging at temperatures below 200° C. was found to be impracticable, owing to the extreme hardness and liability to cracking shown by the material at these temperatures. Incidentally, about 60 per cent. of deformation was in general applied in the case of the alloys discussed in the latter part of the paper, not 30 per cent., as suggested by Mr. Prytherch.

SOME PROPERTIES OF ROLLED MOLYBDENUM SHEET.[*]

By C. E. RANSLEY,[†] M.Sc., MEMBER, and H. P. ROOKSBY,[†] B.Sc.

(Communication from the Staff of the Research Laboratories of The General Electric Company, Ltd., Wembley, England.)

SYNOPSIS.

An X-ray examination of rolled molybdenum sheet has shown that rolling in only one direction produces an orientation of the crystals such that a set of (110) planes is perpendicular to the direction of rolling. There is, however, a considerable spread round the rolling direction, and the fully-preferred state, in which the cube face is brought into the surface of the sheet, is only attained by subsequent rolling in a direction at right angles to the original direction. Sheet so rolled exhibits cleavage-plane brittleness at 45° to the direction of rolling, and is very susceptible to penetration (*a*) by surface impurity, such as iron, which markedly increases the 45° brittleness, and (*b*) by hydrogen, when the metal is made the cathode in an electrolytic bath.

INTRODUCTION.

THE effect of cold-rolling on the crystal orientation of metals of the body-centred cubic system has been the subject of many investigations,[1, 2, 3] and it has been shown that, in general, the crystals tend to assume an orientation such that one (110) plane is perpendicular to the direction of rolling. In the final stable position, a (100) plane is, in addition, brought into the plane of rolling, and the material is then in what will be termed the completely-preferred state. The development of preferred orientation in rolled molybdenum foil has been particularly noted by Jeffries,[4] Konobejewsky,[5] and Fujiwara.[6] Jeffries showed, by X-ray examination, that molybdenum rolled first hot and then cold from 0·375 to 0·004 in., became oriented in the usual way, the reflections from the (110) planes showing a deviation of 10°, and those from the (100) planes a deviation of 13°, from the preferred positions. Fujiwara also found a spread of 10° round the rolling direction. In a more recent paper by Burgers and van Amstel,[7] on an electron-diffraction study of the orientation in very thin rolled tungsten

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[*] Manuscript received August 31, 1937.

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foil, mention is made of cleavage-plane brittleness at 45° to the direction of rolling after the metal has been recrystallized at a very high temperature.

The question of crystal orientation in rolled molybdenum sheet was first brought to the notice of the present authors by the incidence of a remarkable form of brittleness in some molybdenum blanks which had to be subjected to a forming and sand-blasting operation. These blanks developed cracks which were perpendicular to each other and accurately at 45° to the direction of rolling, as is shown in Fig. 1 (Plate XVIII). It was found that such brittleness could only be observed in sheets which had been rolled successively in two directions at right angles, and not when the rolling had been confined to one specific direction. Since in none of the papers quoted above is the rolling history of the material made clear, the present authors have repeated some of the work on crystal orientation from this point of view, and have also carried out some qualitative mechanical tests on sheets prepared by different rolling procedures. The only reference that has been found to mechanical tests on molybdenum sheet is in a paper by Kioka,[8] who showed that in sheet presumably rolled in one direction only, the tensile strength was approximately 10 per cent. less at 45° to the direction of rolling than in directions perpendicular to or parallel to it.

MATERIAL AND ROLLING PROCEDURE.

The material used for the experiments to be described in this paper was in the form of electrically-sintered bars, more than 99·9 per cent. pure. The bars were rolled sideways, at a temperature of 1200° C., from 12 mm. to 1·5 mm. in thickness. After a sand-blasting operation, to remove oxide scale, the metal was annealed in hydrogen at 970° C., rolled cold to 0·85 mm. (still in the same direction), and again annealed. Subsequent cold-rolling to a thickness of 0·10 mm. was continued either (*a*) in the same direction, or (*b*) in a direction at right-angles to the original direction; material will be referred to as "straight-rolled" and "cross-rolled," respectively, according to the method of finishing.

Anneals were introduced at suitable stages during the final rolling to prevent blistering of the metal owing to overwork. It has been shown [4] that annealing at 1000°–1100° C. has no effect whatever on the X-ray orientation pattern; after annealing at 1600° C. the grains are large enough to show characteristic individual diffraction, but any preferred orientation developed by working still persists.

Since it is the authors' experience that photomicrographs of incompletely-recrystallized molybdenum are of a very indecisive nature, and add no valuable information to the X-ray results, no such photographs of sections of the various specimens have been included in the paper.

X-Ray and Mechanical Tests.

For the X-ray examination of the samples, Cu K_a radiation from a 45 kV. tube was used, the beam having a cross-sectional area of about 1 mm.^{2}. The usual method adopted for obtaining the diffraction patterns was to bend a small piece of the sheet in the form of a U, and to set this up so that the X-radiation impinged at a glancing angle on the curved surface. This was found to give results similar to those obtained when the more usual flat specimens were used, but ensured that the whole of the diffraction pattern required was obtained in every case. By examining one specimen cut in the direction of rolling, and another cut at right angles to this, information as to the orientation in two perpendicular directions was readily obtained. On the X-ray patterns reproduced, the rings, starting from the origin, are the (110), (200) and (112) diffractions.

The method of determining crystal orientation by means of X-ray reflection in two perpendicular directions was first used by Davey, Nitchie, and Fuller[9] and was developed by Post[10]; each used diffraction from flat specimens.

All specimens used for X-ray examination had been annealed at 1050° C., and were previously etched to remove the surface layer and to ensure that the structure obtained was representative of the body of the material.

Since this investigation was undertaken primarily to determine the directional properties of molybdenum sheet, mechanical testing was confined to bend-tests on specimens cut in specific directions in the sheet. A standard Jenkin's bend-test machine was used, in which a strip of metal about ½ in. wide is bent backwards and forwards through 180° over a pair of steel jaws ground to an accurate radius. A complete bend is specified as a bend through 180°. In this paper, the "direction of bend" is the direction in which the test-piece was cut; the actual line of bend will, of course, be perpendicular to this.

Preferred Orientation Developed by "Straight" and "Cross" Rolling.

Figs. 2*a* and 2*b* (Plate XIX) show reflections from specimens of 0·85 mm. sheet, set so that the direction of the X-ray beam was perpendicular to, and parallel to, the direction of rolling, respectively. Whilst Fig. 2*b* suggests a considerable spread of orientation of all planes round the direction of rolling, the maxima on the (200) and (110) diffraction rings in Fig. 2*a* show marked development of preferred orientation; in other words, a (110) plane is assuming an orientation perpendicular to the direction of rolling. Continued rolling in the same direction results in further development of this orientation, as will be seen from Figs. 3*a* and 3*b* (Plate XIX), which show the patterns obtained from 0·10 mm. sheet, using the same convention as above. It is apparent that at this thickness (equivalent to 93 per cent. reduction cold) the orientation such that a (110) plane is perpendicular to the direction of rolling is comparatively well-developed. The completely-preferred state has been defined above as that in which there is in addition a face of the lattice cube in the plane of the sheet. This second condition is clearly not fulfilled, for the continuity of the rings of Fig. 3*b* suggests a considerable spread round the rolling direction; this has been found for other metals, *e.g.* silver.[11]

If, instead of continuing the rolling in the same direction, the sheet is " cross-rolled " from 0·85 mm. to 0·10 mm. thick, there is a marked difference in the orientation developed. Figs. 4*a* and 4*b* (Plate XX) are the X-ray patterns obtained from annealed " cross-rolled " sheet when the direction of the beam is perpendicular and parallel, respectively, to the *original* direction of rolling. It appears that the orientation developed approaches much more closely that defined as completely-preferred than does the orientation in straight-rolled material of the same thickness. For considering the figures which reveal the greatest spread in each case, Figs. 3*b* and 4*a*, the spread is considerably less for the cross-rolled sheet as indicated by the maxima on the (200) rings.

Briefly, what has happened is that the first rolling to 0·85 mm. resulted in one of the (110) planes approximating to an orientation perpendicular to the rolling direction; a further reduction to 0·1 mm. by rolling in the same direction only resulted in a more accurate alignment of this plane. Cross-rolling from 0·85 mm. has not changed the orientation of this plane, as will be seen from a comparison of Figs. 4*a* and 2*a*, but has caused a second (conjugate) (110) plane to be perpendicular to the new rolling direction. This means that a (100) plane is brought into the plane of the sheet, two other (100) planes lying at 45° to the rolling direction, and perpendicular to the surface of the sheet.

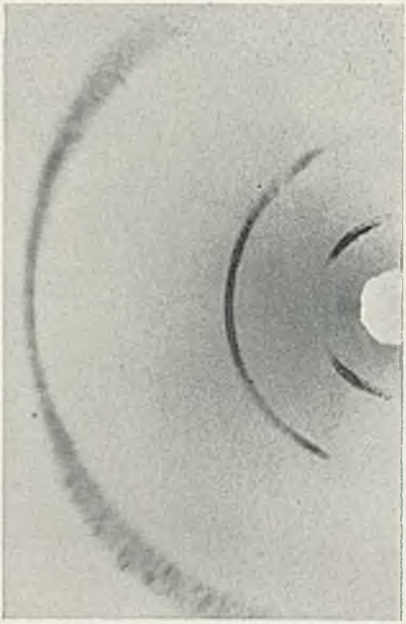
MECHANICAL TESTS.

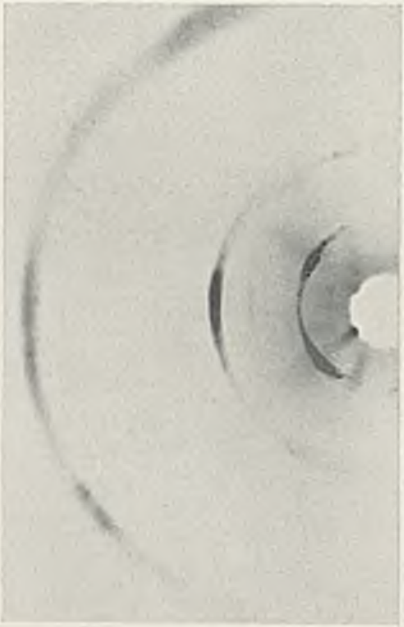
Fig. 5 shows the bend-test results obtained on 0·10 mm. straight-rolled sheet after annealing at different temperatures. The annealing treatments were carried out in a silica-tube furnace, in an atmosphere of dry hydrogen, for a standard time of 15 minutes. The tests were made using jaws with a radius of 1 mm., and the values plotted are the

FIG. 1.—Sample of Cross-Rolled Molybdenum Sheet Showing 45° Brittleness. (Natural Size.)

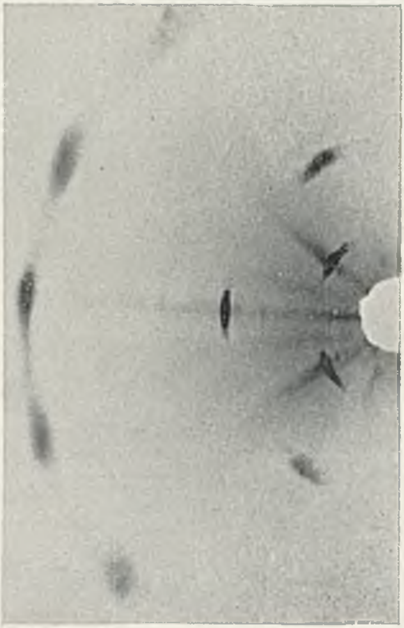
2b

3b





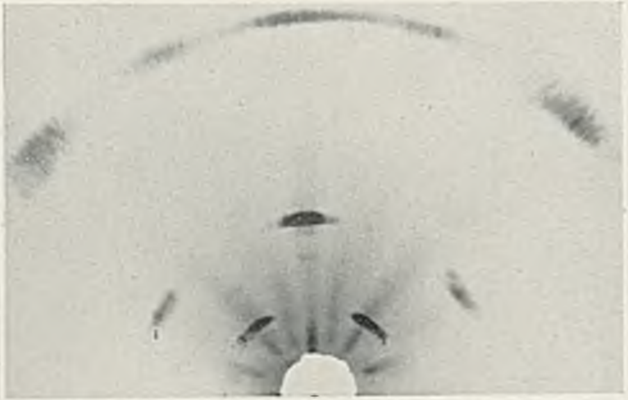
2a

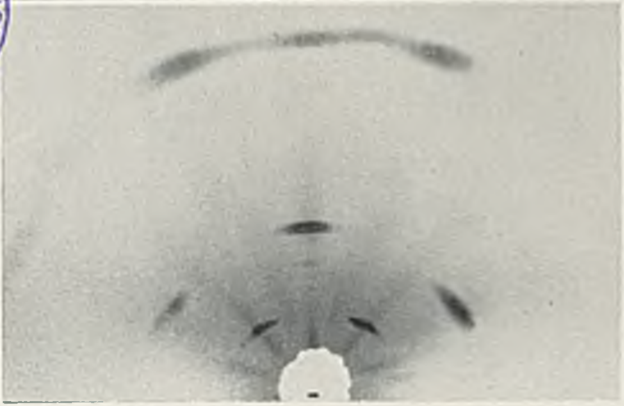


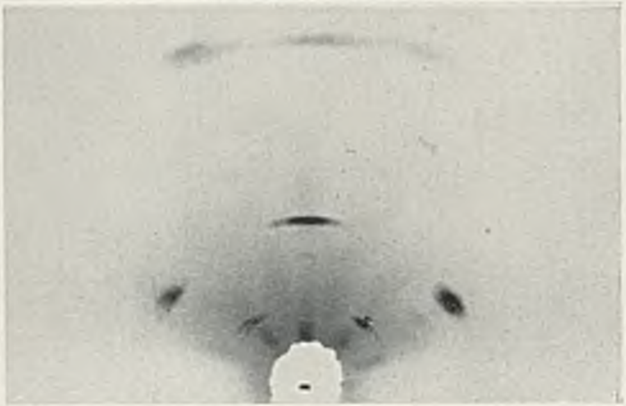
3a

PLATE X


4*a*


4*b*


9*a*


9*b*

X-Ray Beam Perpendicular to Original Rolling Direction.

X-Ray Beam Parallel to Original Rolling Direction.

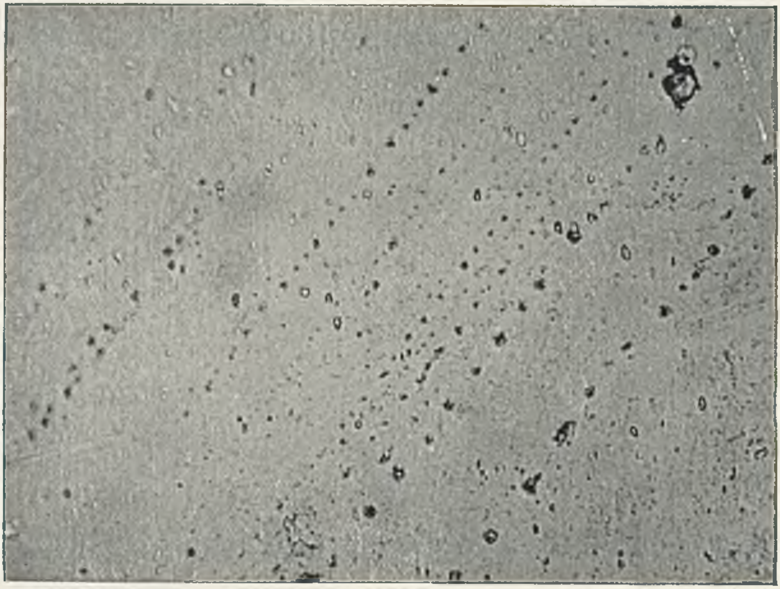


FIG. 10.—Pattern Developed on Cross-Rolled Sheet by Cathodic Charging. × 500.

averages of a large number of results. Test-pieces were cut at 0°, 45°, and 90° to the direction of rolling, and the values obtained show that, in common with other metals, the fibrous structure developed by rolling results in a much higher bend-test value at 0° than at 90°, whilst the values at 45° are intermediate.

A more complete determination of the distribution of ductility with respect to the rolling direction was made on a sample of straight-rolled sheet annealed at 1050° C.; the results are plotted in Fig. 6. It will be seen that the bend-test value changes continuously with the angle to the direction of rolling at which the test-piece is cut, and the metal shows no signs of brittleness other than the normal inter-fibre weakness.

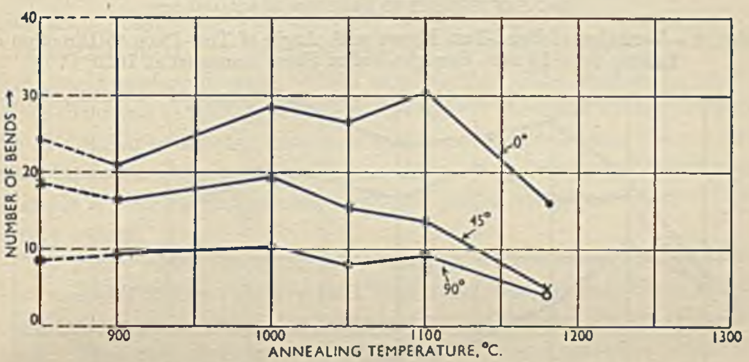


Fig. 5.—Effect of Annealing Temperature on Bend-Test Figures for 0·10 mm. Straight-Rolled Sheet.

Fig. 7 shows the results of bend-tests on cross-rolled sheet, 0·10 mm. thick, annealed at different temperatures; in this case 0° indicates that the specimen was cut parallel to the last direction of rolling. The effect of cross-rolling has been to eliminate the inter-fibre weakness, but has resulted in a definite reduction in the bend-test value at 45°, particularly at the higher annealing temperatures. This is shown more clearly in Fig. 8, which gives the results of bend-tests at various angles on sheet annealed at 1050° C. The number of bends at 45° is approximately 6·5, as compared with 15·0 for straight-rolled sheet similarly annealed.

If molybdenum sheet be annealed at a temperature as high as 1600° C., the metal is brittle in all directions, owing to lack of cohesion at the grain boundaries. To illustrate this, some bend-test values for cross-rolled sheet annealed at this temperature are included in Fig. 7, and it will be seen that the number of bends is equally low in the three directions of test.

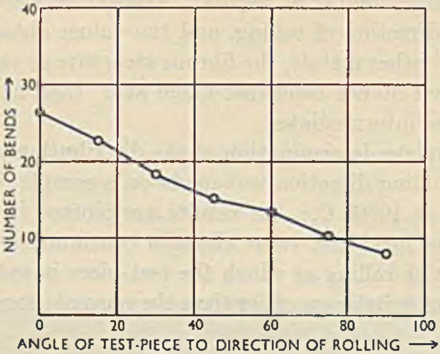


Fig. 6.—Variation of Bend-Test Figure with Angle of Test-Piece to Direction of Rolling for 0·10 mm. Straight-Rolled Sheet Annealed at 1050° C.

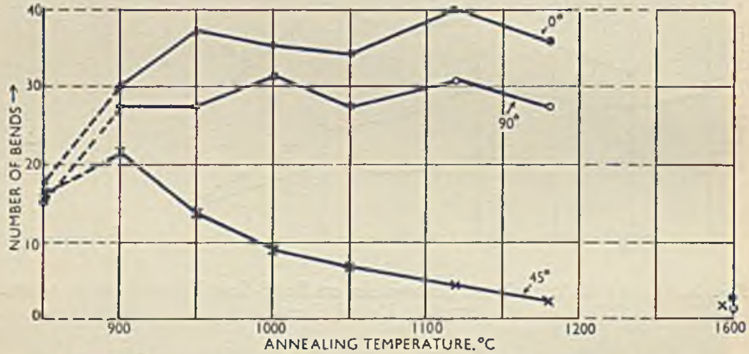


Fig. 7.—Effect of Annealing Temperature on Bend-Test Figures for 0·10 mm. Cross-Rolled Sheet.

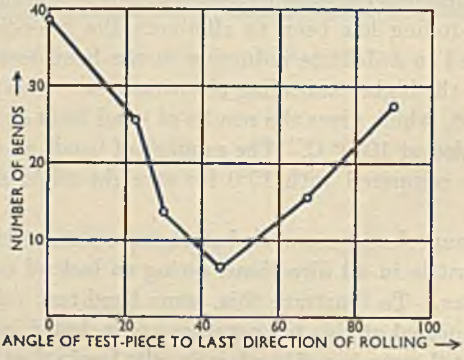


Fig. 8.—Variation of Bend-Test Figure with Angle of Test-Piece to Direction of Rolling for 0·10 mm. Cross-Rolled Sheet Annealed at 1050° C.

CLEAVAGE-PLANE WEAKNESS IN MOLYBDENUM SHEET.

The X-ray results show that the rolling of molybdenum in one direction only results in an orientation of the crystals such that one set of (110) planes lies perpendicular to the direction of rolling, but that the orientation round this direction is still comparatively random. Continuation of straight-rolling to a thickness of 0·01 mm. did not alter appreciably the spread round the rolling direction. The mechanical tests show that, apart from the normal inter-fibre weakness, there are no preferentially brittle directions in straight-rolled sheet.

The bend-tests on cross-rolled sheet give values for specimens cut both with and across the direction of rolling which are nearly equal, but disclose a greatly reduced ductility at 45°. The X-ray results show that in this sheet the orientation of the crystals approximates to the completely-preferred state, which is such that (100) planes lie at 45° to the direction of rolling, and perpendicular to the sheet surface. Since the (100) planes are the cleavage planes in molybdenum, their alignment in cross-rolled sheet would seem to account for the 45° brittleness. There is a possibility that the cleavage planes are riven in some way during rolling.

An X-ray examination of both straight- and cross-rolled sheet at a thickness of 0·35 mm., showed that at this stage the orientation produced was intermediate in character between that at 0·85 and that at 0·10 mm. thick. This suggested that, by adjustment of the amount of reduction in the two rolling directions, it should be possible to obtain an even better development of the completely-preferred state than is shown by the 0·1 mm. sheet hitherto considered, *e.g.* sheet straight-rolled to 0·10 mm. and then cross-rolled to 0·04 mm. gave the orientation patterns shown in Figs. 9*a* and 9*b* (Plate XX).

PENETRATION OF CLEAVAGE PLANES.

Cross-rolled material exhibits several peculiarities which have not, as yet, been fully investigated. Two examples will be given, however, to illustrate the ease with which the cleavage planes are penetrated in sheet having the preferred orientation.

(a) *Effect of Iron.*

In order to investigate the effect on the mechanical properties of impurities picked up in rolling, some sheets were put through with a special acid-pickling treatment before each of the intermediate and final anneals. Some of the bend-test values obtained on these sheets are given in Table I, and are compared with those obtained on sheet rolled from the same bar, but by the normal procedure.

TABLE I.—*Effect of Surface Cleaning.*

Material.	Annealing Temperature, °C.	Bend Test at		
		0°	45°	90°
Straight-rolled : normal	1000	28·8	20·2	10·6
,, ,, cleaned	,,	23·7	18·5	8·7
,, ,, normal	1100	30·4	14·7	9·4
,, ,, cleaned	,,	26·6	13·0	8·0
Cross-rolled : normal	1000	35·7	9·0	31·7
,, ,, cleaned	,,	33·7	12·0	23·7
,, ,, normal	1100	40·0	4·5	30·9
,, ,, cleaned	,,	34·9	6·2	24·2

It will be seen that in straight-rolled sheet, the effect of surface cleaning has been to reduce the bend-test value in all cases, whether the test-piece is cut in or across the rolling direction or at 45° to it. In cross-rolled sheet, tests in or across the rolling direction show a similar reduction, but at 45° there is an appreciable increase in ductility. Chemical tests showed that there was a small, but definite, amount of iron picked up during cold-rolling, and some experiments were carried out to determine whether the presence of iron as an impurity at the surface of the sheet had a positive effect on the ductility. For this purpose, some 0·10 mm. sheets as-rolled were flashed with a very thin coating of iron in a ferrous sulphate bath. The iron was subsequently removed from one half of each sheet by pickling in dilute hydrochloric acid, and the sheets were then annealed in hydrogen at 1050° C. for ½ hr. A comparison of the bend tests on the clean and the iron-contaminated halves of the sheet (Table II), showed that this treatment resulted in a remarkable increase in the 45° brittleness of the cross-rolled sheet, but had no very marked effect on the straight-rolled sheet.

TABLE II.—*Effect of Iron Penetration on* 0·10 *mm. Sheet Annealed at* 1050° *C.*

Material.	Bend Test at		
	0°	45°	90°
Straight-rolled : clean	29·3	16·4	8·8
,, ,, contaminated with iron	26·5	11·3	7·6
Cross-rolled : clean	34·3	7·7	27·0
,, ,, contaminated with iron	32·0	$<0·5$	21·4

The same result was obtained after annealing *in vacuo* instead of in hydrogen, and hence the effect could not be attributed to the absorption of hydrogen during annealing. X-ray analysis on the iron-plated and annealed material failed to show any change in the lattice such as would result from iron in solution. Moreover, the deliberate addition of 0·10 per cent. of iron to the metal prior to sintering and working produced no unusual characteristics, beyond a slight reduction in the 45° bend. It is presumed, therefore, that the effect is due to penetration of the surface iron down flaws in the cleavage planes during annealing.

(b) *Effect of Electrolytic Hydrogen.*

A few experiments have also been carried out on the penetration of hydrogen into the metal during cathodic charging in an electrolytic bath. Some interesting results have been obtained by Smith and Derge[12] on the effect of cold-rolling on palladium and nickel, using this method of investigation. In the experiments now described, samples of straight- and cross-rolled molybdenum sheet were charged at 4 amp./dm.^{2} in a dilute sodium bicarbonate solution, using a platinum anode. The electrolysis was continued for periods of 24 hrs. or more.

It was found that this treatment produced a considerable amount of surface-blistering on cross-rolled sheet, but very little on the straight-rolled sheet, indicating that the former is much more readily penetrated by hydrogen. If the sheet were subjected to a previous anneal at 900° C., the cross-rolled sheet developed patches with a regular pattern of black dots, very similar to etching pits, in straight lines at 45° to the rolling direction, and these are assumed to be collapsed blisters, similar to those observed by Smith and Derge. An example of this effect is shown in Fig. 10 (Plate XXI). It appears, therefore, that when molybdenum is charged cathodically, the hydrogen enters the metal preferentially on the cleavage planes.

BRITTLENESS IN MOLYBDENUM SHEET.

The results which have been obtained indicate that rolled molybdenum foil may exhibit three types of brittleness:

(*a*) Normal inter-fibre weakness, due to lack of cohesion between the fibres developed in the direction of rolling. This is only shown in straight-rolled sheet; cross-rolling results in a spreading of the fibres, and consequent elimination of this effect.

(*b*) Transcrystalline cleavage at 45° to the rolling direction. This is only appreciable when the crystals are in the completely-preferred condition, and, as has been shown, this condition is only approached if the metal has been rolled successively in two perpendicular directions.

When the crystals are so oriented, the metal is particularly susceptible to attack and penetration on the cleavage planes.

(*c*) Intercrystalline brittleness due to lack of cohesion between the grains of the fully-recrystallized metal. Sheet which has been annealed at a high temperature (1600° C. or higher) is brittle in all directions.

REFERENCES.

[1] W. Boas and E. Schmid, *Z. tech. Physik*, 1931, **12**, 71.
[2] F. Wever, *Trans. Amer. Inst. Min. Met. Eng.*, 1931, **93**, 51.
[3] C. S. Barrett, *Trans. Amer. Inst. Min. Met. Eng.*, 1937, **124**, 29.
[4] Z. Jeffries, *Trans. Amer. Inst. Min. Met. Eng.*, 1924, **70**, 303.
[5] S. T. Konobejewsky, *Z. Physik*, 1926, **39**, 415.
[6] T. Fujiwara, *World Eng. Congress, Tokyo, 1929, Proc.*, 1931, **36**, 179.
[7] W. G. Burgers and J. J. A. P. van Amstel, *Physica*, 1936, **3**, 1064.
[8] H. Kioka, *World Eng. Congress, Tokyo, 1929, Proc.*, 1931, **36**, 183.
[9] W. P. Davey, C. C. Nitchie, and M. L. Fuller, *Trans. Amer. Inst. Min. Met. Eng.*, **1930**, 557.
[10] C. B. Post, *Z. Krist.*, 1935, **90**, 330.
[11] C. B. Hollabaugh and W. P. Davey, *Metals and Alloys*, 1931, **2**, 246, 302.
[12] D. P. Smith and G. J. Derge, *J. Amer. Chem. Soc.*, 1934, **56**, 2513.
[13] G. A. Moore and D. P. Smith, *Trans. Electrochem. Soc.*, 1937, **71**, 545.

THE CREEP OF TIN AND TIN ALLOYS.—PART II.*

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Synopsis.

A description is given of results of creep tests on alloys of tin with 2 to 7 per cent. cadmium and 3 to 9 per cent. antimony. The influence of annealing at 170° and at 200° C. is discussed. After cold-rolling and self-annealing, the best alloy is that containing 7 per cent. cadmium and 9 per cent. antimony; it withstands a stress of 1200 to 1400 lb./in.^{2} for many years. After annealing at 170° C., the most beneficial composition is 2 per cent. cadmium and 7 per cent. antimony; a safe stress for this alloy is 3500 lb./in.^{2}. Annealing at 200° C. produces optimum creep properties at a composition of 3 per cent. cadmium and 7 per cent. antimony; a safe stress in this case is 3700 lb./in.^{2}. It is shown that grain-size is an important factor in determining creep-resistance, and therefore, as the tensile strength is not greatly influenced by grain-size, no relationship is found between these two properties in the annealed alloys investigated. The effect of additions of 1 and 2 per cent. silver, 1 per cent. copper, or 0·3 per cent. nickel is discussed. The silver and copper alloys show similar creep properties, but the nickel alloy is inferior. An alloy containing 1 per cent. cadmium and 3·5 per cent. silver has great creep-resistance when cold-rolled and self-annealed; it is superior to the alloy containing 7 per cent. cadmium and 9 per cent. antimony.

Introduction.

In a previous paper [1] dealing with the creep of tin containing additions of silver, bismuth, antimony, or cadmium, it was shown that antimony or cadmium conferred the greatest beneficial effects. The present paper, therefore, deals with the influence of additions of these two elements together.

Hanson and Pell-Walpole [2] investigated the constitution and mechanical properties of the ternary alloys, and showed that, by suitable heat-treatment, stable tensile strengths up to 7 ton/in.^{2} can be obtained. The alloys now under consideration contain from 2 to 7 per cent. cadmium and from 3 to 9 per cent. antimony. All have been tested in the form of strip, 0·1 in. thick, cold-rolled from ingots 0·5 in. thick, the tests having been carried out after three heat-treatments: (*a*)

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self-annealed for at least 2 months after cold-rolling; (*b*) heat-treated at 170° C. for 2 days and cooled in the furnace; and (*c*) heat-treated at 170° C. for 5 hrs., then at 200° C. for 1 day, and cooled in air. The heat-treatment (*c*) will be referred to as "annealing at 200° C." Throughout the paper, reference numbers have been used. Cadmium and antimony are referred to as C and S, respectively, each followed by a number representing the addition in per cent. (*e.g.* C2S5 = 2 per cent. cadmium + 5 per cent. antimony). The suffixes "SA," "A170," and "A200" are used to denote the heat-treatments *a*, *b*, and *c*, respectively, *e.g.* C3S7.A170 = 3 per cent. cadmium + 7 per cent. antimony, annealed at 170° C. Each series of alloys will be described separately. The method of testing has already been described.[1] The results are given as graphs showing the variation in life against the initial stress, while further results not amenable to graphical treatment are shown in tables.

RESULTS OF CREEP TESTS.

Self-Annealed Alloys.

Table I gives a list of the alloys investigated, and their identification numbers, tensile strengths, and elongation, while Table II shows the results of creep tests on these alloys. Fig. 1 shows the stress–duration curves for these alloys. They have the same general trend as was found for other alloys of tin, but they require, nevertheless, a much greater

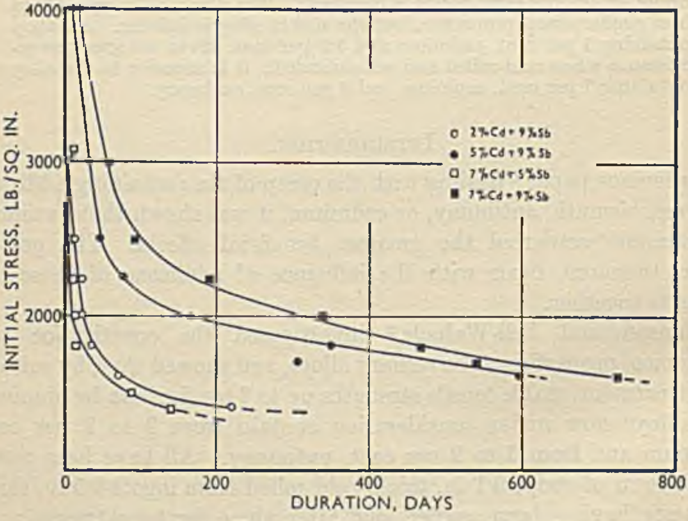

FIG. 1.—Stress–Duration Curves; Self-Annealed Alloys.

TABLE I.—*Tensile Properties of Self-Annealed Cadmium–Antimony–Tin Alloys.* (*Rate of testing* = 0·1 *in./in./minute.*)

Cadmium, Per Cent.	Antimony, Per Cent.	Reference Number.	Ultimate Tensile Strength, Lb./in.^{2}.	Elongation, Per Cent. on 2 in.
2	5	C2S5.SA	11,460	53
2	9	C2S9.SA	12,910	58
5	5	C5S5.SA	12,520	55
5	9	C5S9.SA	17,000	40
7	5	C7S5.SA	12,500	74
7	9	C7S9.SA	17,730	35

TABLE II.—*Results of Creep Tests on Self-Annealed Cadmium–Antimony–Tin Alloys.*

Stress, Lb./in.^{2}.	2% Cadmium + 9% Antimony.		5% Cadmium + 9% Antimony.		7% Cadmium + 5% Antimony.		7% Cadmium + 9% Antimony.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
4000			7	40			14	48
3000	4	23	32	54	2	79	56	80
2500	13	41	47	64·4	6	100	90	76·0
2240	23	52	78	50·4	10	139	189	80·4
2000	23	35	165	81·6	12	77	338	56·8
1800	34	31	350	54·8	14	63	465	78·2
1700			307	64·8			540	78·4
1600	70	34	598	57·6			724	68·2
1500			(592)	(40·6)	86	100	(592)	(20·6)
1400	219	71			139	98		

2% Cadmium + 5% Antimony—5 days' duration at 3000 lb./in.^{2}.
5% Cadmium + 5% Antimony—6 days' duration at 3000 lb./in.^{2}.
The figures in parentheses are for specimens which have not fractured.

stress to cause failure in the same time than did the alloys previously investigated; thus, pure tin withstands a stress of 250 lb./in.^{2} for 1 year, while alloy C7S9.SA will sustain 1950 lb./in.^{2} for the same duration. This is nearly an eight-fold increase in stress, and corresponds closely to the increase in tensile strength, which is 6½ times greater. Previous work had shown that the heat-treated cadmium–tin alloys had the best creep properties, but these ternary alloys are better even without heat-treatment. After quenching from 168° C. and tempering at 120° C., the alloy containing 6 per cent. cadmium withstands a stress of 1350 lb./in.^{2} for one year, a result which is inferior to that obtained with alloy C7S9.SA. Nevertheless, the marked improvement in these alloys is not obtained at the expense of ductility, as is the case with the heat-treated cadmium–tin alloys, which extend 1 or 2 per cent. only before failing with an intercrystalline fracture. The cadmium–antimony–tin alloys extend 50 to 100 per cent. before failure, and have an appearance typical of that of a fine-grained metal. Fig. 11 (Plate XXIII) shows several specimens after fracture.

The alloys containing 9 per cent. antimony with 2, 5, and 7 per cent. cadmium are superior to those containing less antimony, but the alloy having the greatest amount of additions (C7S9.SA) is the best. Furthermore, the sequence of increasing creep-resistance is the same as the sequence of increasing tensile strength. This will be discussed later.

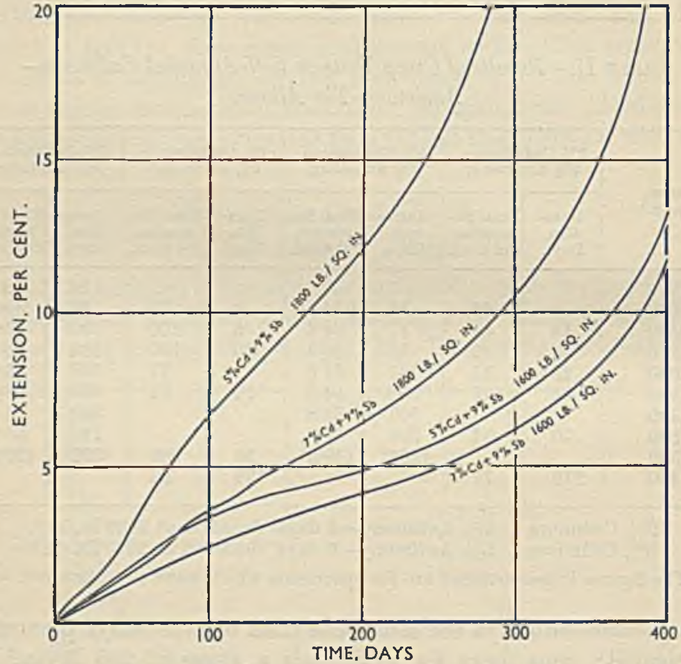

Fig. 2.—Time–Extension Curves; Self-Annealed Alloys.

Fig. 2 shows the initial portion of some time–extension curves for the alloys C5S9.SA and C7S9.SA at various stresses. These curves conform to the usual pattern; there is, at first, a period in which the creep rate is rapid, but decreasing; then a period during which the rate is a minimum, after which it increases until fracture occurs. With alloys C7S9.SA and C5S9.SA, the minimum is not reached until 4 to 5 per cent. extension has occurred.

Heat-Treated Alloys.

A series of creep tests was carried out to investigate the effect of heat-treatment on the cadmium–antimony–tin alloys. A number of specimens was cut from cold-rolled strip, and ten of each alloy were heat-treated by annealing at 170° C. for 2 days and cooling in the furnace, over a period of 8 hrs. This treatment had been found by Hanson and Pell-Walpole to give stable tensile properties. All the specimens of one composition were heat-treated together at the same time. Table III gives a list of the alloys investigated, their reference numbers, tensile strengths, and elongations. Tables IV to VII give the results of creep tests on these alloys, while Figs. 3 and 4 show several stress–duration curves. Some results have been obtained in duplicate.

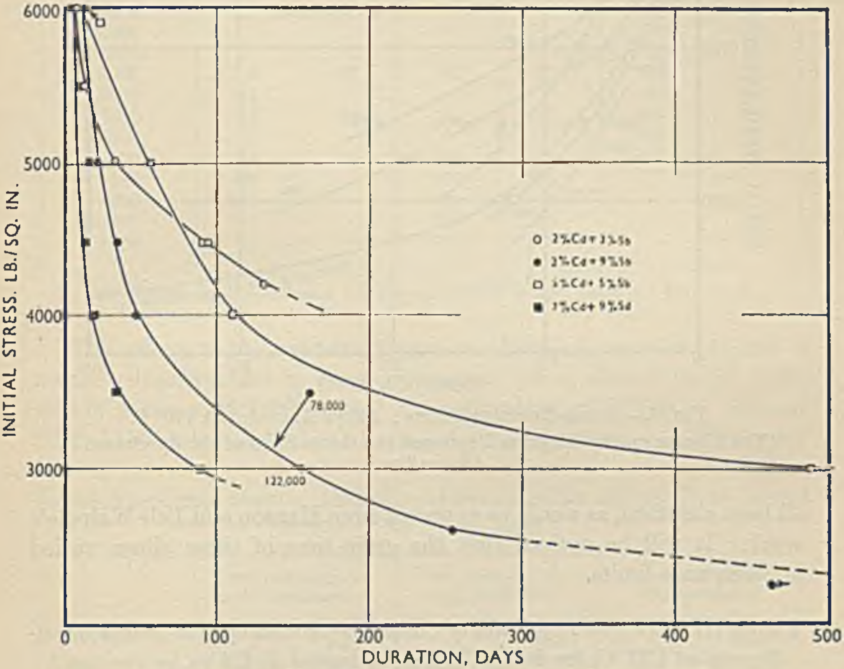

Fig. 3.—Stress–Duration Curves; Alloys Annealed at 170° C.
(The Figures on the Diagram Represent the Grain-Sizes of the Specimens in Grains/Cm.².)

Some of these alloys were examined microscopically, in order to elucidate any possible connection between creep strength and microstructure, and also as a check on the composition. Photomicrographs are shown in Figs. 5 to 10 (Plate XXII). This investigation showed that the compositions of the alloys were in close agreement with the intended compositions, but that the time of annealing was not quite sufficient to produce equilibrium. In some cases, the β phase had not all been absorbed, as would be expected from Hanson and Pell-Walpole's work. It will be noticed that the grain-sizes of these alloys varied between wide limits.

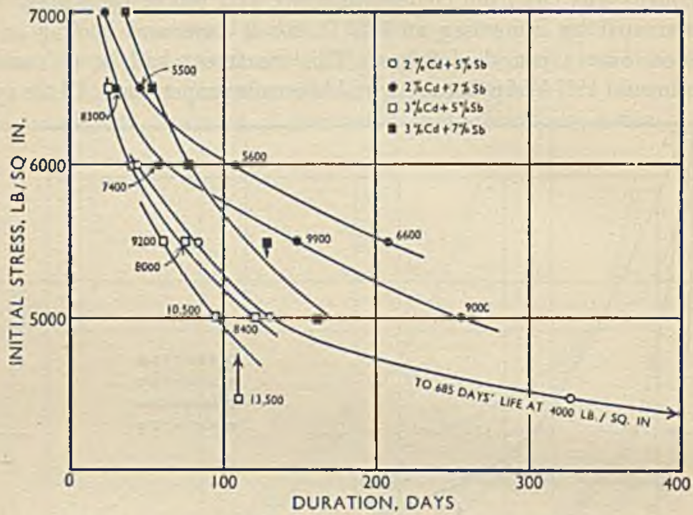

Fig. 4.—Stress–Duration Curves; Alloys Annealed at 170° C.
(The Figures on the Diagram Represent the Grain-Sizes of the Specimens in Grains/Cm.^{2}.)

Table III.—*Tensile Properties of Cadmium–Antimony–Tin Alloys, Heat-Treated at* 170° *C. for* 2 *days.* (*Rate of testing* = 0·1 *in./in./minute.*)

Cadmium, Per Cent.	Antimony, Per Cent.	Reference Number.	Ultimate Tensile Strength, Lb./in.^{2}.	Elongation, Per Cent. on 2 in.
2	3	C2S3.A170	10,800	38
2	5	C2S5.A170	10,500	38
2	7	C2S7.A170	11,600	29
2	9	C2S9.A170	12,800	53
3	5	C3S5.A170	14,700	38
3	7	C3S7.A170	14,200	33
4	7	C4S7.A170	14,000	28
4	9	C4S9.A170	12,900	30
5	5	C5S5.A170	15,000	32
5	7	C5S7.A170	15,100	31
5	9	C5S9.A170	13,600	36
7	5	C7S5.A170	14,200	36
7	9	C7S9.A170	14,400	35

Table IV.—*Creep Results, Cadmium–Antimony–Tin Alloys, Heat-Treated at* 170° *C. for* 2 *days.*

Stress, Lb./in.^{2}.	2% Cadmium + 3% Antimony.		2% Cadmium + 5% Antimony.		2% Cadmium + 7% Antimony.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
7000					22	23
6500					46	15
6500					30	27
6000	8	27	43	25	108	18
6000	11	25			58	19
5500	14	25	84	27	209	23
5500					149	24
5000	34	30	130	24	257	25
4480	93		327	21		
4200	131					
4000			685	19		
3000			(791)	(3·44)		

The figures in parentheses are for specimens which have not fractured.

The effect of the heat-treatment on these alloys is to produce a marked improvement in creep resistance; thus, alloy C2S9.SA withstands a stress of 1400 lb./in.^{2} for a duration of 200 days, whereas C2S9.A170 withstands 2800 lb./in.^{2} for the same time. With alloy

Table V.—*Creep Results, Cadmium–Antimony–Tin Alloys, Heat-Treated at* 170° *C. for* 2 *days* (*cont.*).

Stress, Lb./in.^{2}.	2% Cadmium + 9% Antimony.		3% Cadmium + 5% Antimony.		3% Cadmium + 7% Antimony.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
7000					33	28
6500			23	17	52	37
6000	12	46	39	24	78	35
5500			77	23	129	30
5500			61	28		
5000	22	42	122	20	162	34
5000			100	22		
4480	35	32	109	22		
4000	46	50				
3500	161	45				
3000	155	37				
2600	254	46				
2240	(466)	(25·6)				
2000	(736)	(27·8)				

The figures in parentheses are for specimens which have not fractured.

TABLE VI.—*Creep Results, Cadmium–Antimony–Tin Alloys, Heat-Treated at* 170° *C. for* 2 *days* (*cont.*).

Stress, Lb./in.².	4% Cadmium + 7% Antimony.		4% Cadmium + 9% Antimony.		5% Cadmium + 5% Antimony.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
6000	24	33	16	40	13	20
5500	40	17	28	33		
5000	37	46	33	41	55	26
5000	70	43	64	37		
4480	41	39	47	31	92	28
4000	106	34	91	34	109	30
3000					488	28
2240					(448)	(5·80)
2000					(930)	(9·92)
1600					(930)	(3·14)

The figures in parentheses are for specimens which have not fractured.

TABLE VII.—*Creep Results, Cadmium–Antimony–Tin Alloys, Heat-Treated at* 170° *C. for* 2 *days* (*cont.*).

Stress, Lb./in.².	5% Cadmium + 7% Antimony.		5% Cadmium + 9% Antimony.		7% Cadmium + 5% Antimony.		7% Cadmium + 9% Antimony.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
6000	16	35	10	28	7	22	5	33
5500	29	41	18	32	11	28	10	36
5000	49	37	26	34	18	28	15	33
4480	30	58	24	41	19	32	14	31
4000			49	42	28	26	18	34
3500					58	25	34	38
3000					161	28	89	68

C7S9.SA (the best of the self-annealed alloys), however, the improvement is not so marked. The best of the annealed alloys is seen to be C2S7.A170, which has a duration of 200 days at a stress of 5200 lb./in.². This is a great improvement on pure tin (300 lb./in.² for an equal duration), on the best of the heat-treated cadmium–tin alloys (6 per cent. cadmium, 1600 lb./in.²), and on alloy C7S9.SA (2200 lb./in.²). This improvement, however, is not achieved at the expense of ductility, since these alloys all extend 20 per cent. or more before fracture. Several fractures are shown in Fig. 12 (Plate XXIII). Those alloys having small amounts of additions show a rumpled surface, typical of a coarse-grained material.

Some results on these alloys have been obtained in duplicate and, while in some cases close agreement is found, in others wide discrepancies are apparent. This is particularly noticeable in the alloy C2S7.A170, where two curves have had to be drawn to connect all the results. For the further elucidation of this point, the grain-sizes of several specimens have been measured by the intercept method; the results are shown on Figs. 3 and 4.

With alloy C2S7.A170, the grain-sizes fall into two groups, one between 5500 and 6600 grains/cm.^{2} and the other between 7400 and 9900 grains/cm.^{2}. The alloys having the larger grain-size (fewer grains) have a longer duration than those of smaller grain-size. With alloy C2S9.A170, the result at 3500 lb./in.^{2} shows a duration greater than would be expected; the grain-size of this specimen, however, is larger than that of the specimen tested at 3000 lb./in.^{2}. With alloy C3S5.A170, two groups of grain-size are again apparent; here, also, the larger grain-sizes show longer duration. It seems certain, therefore, that the duration of a creep test depends not only on the composition and constitutional changes produced by any heat-treatment, but also on the grain-size; the larger the grain-size the better is the creep resistance. This statement is only meant to be applied to the alloys in question.

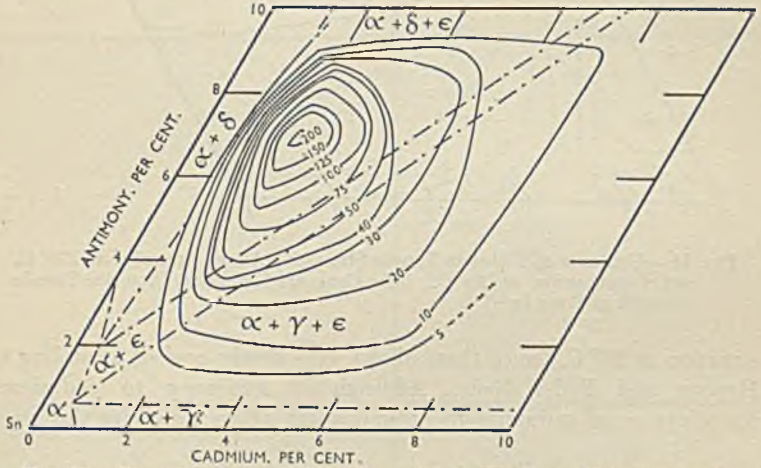

FIG. 13.—Creep Strength of Alloys Annealed at 170° C. and Constitution at 20° C. (The Contours Represent Durations in Days at a Stress of 5500 Lb./In.^{2}.)

A comparison of the relative merits of these alloys is made simpler by Fig. 13, in which the creep results at 5500 lb./in.^{2} are plotted as contours connecting alloys having equal duration. For the construction of this diagram, extra alloys were tested at 5500 lb./in.^{2}; the results are shown in Table VIII. Superimposed on this diagram is the constitution at 20° C. (since these alloys were slowly cooled) according t Hanson and Pell-Walpole. Addition of antimony to cadmium-tin alloys or of cadmium to antimony–tin alloys improves the cree

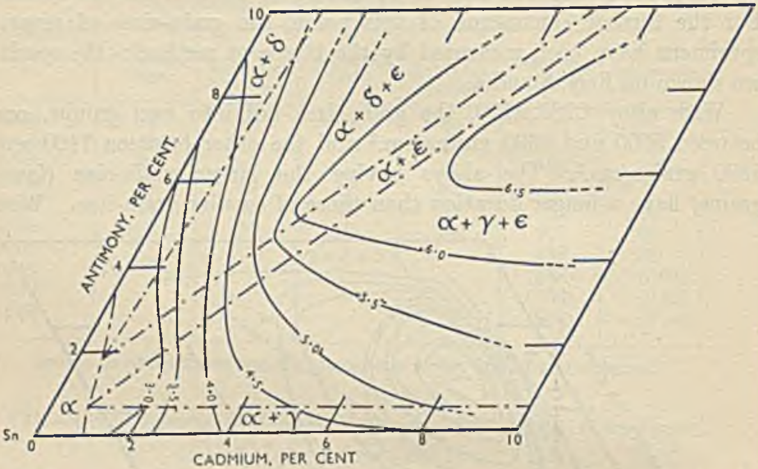

FIG. 14.—Contours of Ultimate Tensile Strength; Alloys Annealed at 170° C. and Constitution at 20° C. (The Contours Represent Ultimate Tensile Strength in Tons/In.^{2}.)

TABLE VIII.—*Results Used in the Construction of Figs.* 13 *and* 15.

Composition.		Duration at 5500 Lb./in.^{2}.	Grain-Size, Grains/cm.^{2}.
Cadmium, Per Cent.	Antimony, Per Cent.		
0	3	8 seconds	
0	5	2 minutes	5,200
0	7	23 minutes	19,000
0	9	39 minutes	
1	3	42 minutes	1,650
1	5	12 hrs.	2,400
1	7	7 days	6,500
1	9	4 days	13,000
2	1	5 hrs.	16,000
5	1	30 hrs.	
5	3	12 days	
7	1	2 days	
7	3	20 days	

6

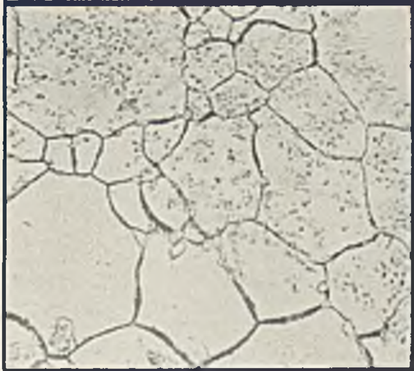

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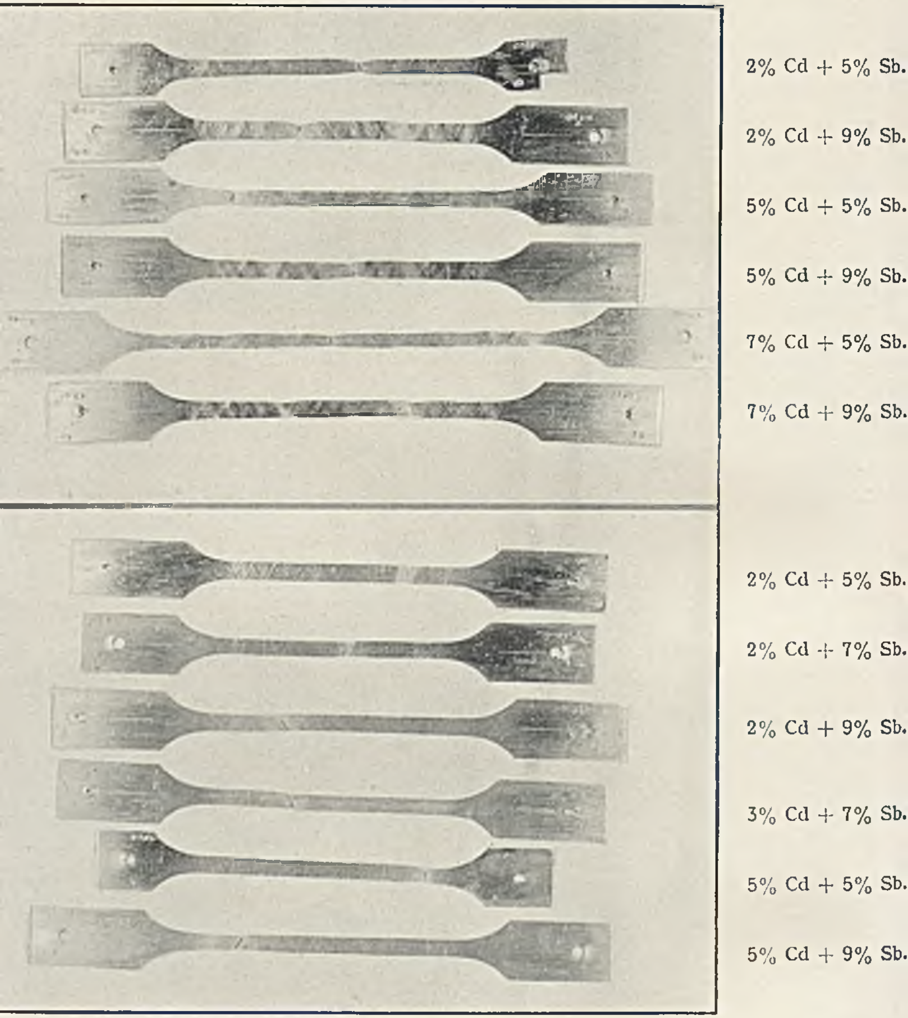
FIG. 5.—2% Cd + 7% Sb. Annealed at 170° C. α + δ + ε (δ and ε not shown). × 60.
FIG. 6.—3% Cd + 5% Sb. Annealed at 170° C. α + ε + eutectoid. × 250.
FIG. 7.—3% Cd + 7% Sb. Annealed at 170° C. α + δ + ε. × 250.
FIG. 8.—4% Cd + 9% Sb. Annealed at 170° C. α + ε. × 250.
FIG. 9.—7% Cd + 5% Sb. Annealed at 170° C. α (light) + ε + eutectoid. × 250.
FIG. 10.—7% Cd + 9% Sb. Annealed at 170° C. α (light) + ε + eutectoid. × 250.

All Specimens Etched in a Solution of 2% Nitric Acid in Alcohol.

[*To face p.* 224.

PLATE XXIII.



Figs. 11–12.—Fractured Creep Specimens of Cadmium–Antimony–Tin Alloys. × ⅓. Fig. 11.—Self-Annealed. Fig. 12.—Annealed at 170° C.

resistance up to a maximum, which occurs at 2 per cent. cadmium plus 7 per cent. antimony. Further addition of either element produces a deterioration in creep properties. The contours form roughly a parallelogram, one diagonal of which lies approximately along the $\alpha + \varepsilon$ phase field. The maximum lies in the $\alpha + \varepsilon + \delta$ field. The addition of up to 2 per cent. cadmium to antimony–tin alloys effects a sudden increase in duration from a few minutes to over 200 days at 5500 lb./in.^{2}, but the effect of antimony on cadmium–tin alloys is not so marked, since 7 per cent. of antimony is needed to reach the maximum.

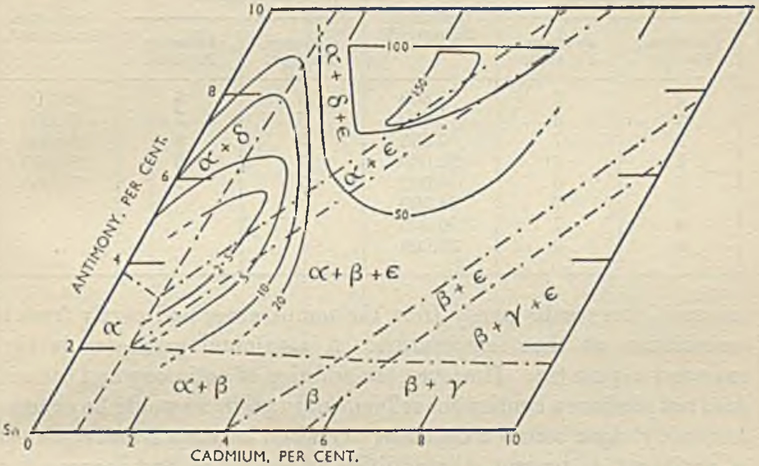


Fig. 15.—Grain-Size Contours; Alloys Annealed at 170° C. and Constitution at 170° C. (The Contours Represent Grain-Size in Thousands of Grains/Cm.^{2}.)

Fig. 14 shows the contours of equal tensile strength of these alloys according to Hanson and Pell-Walpole. Here, a maximum is found around 8 per cent. cadmium and 7 per cent. antimony. The contour lines show a change of direction which lies along the $\alpha + \varepsilon$ field, indicating that the addition of cadmium to antimony–tin alloys increases the tensile strength until the $\alpha + \gamma$ eutectoid (β at 170° C.) appears, whereupon a decrease in tensile strength is found. Referring to Fig. 13, in alloys with up to 4 per cent. antimony, the addition of cadmium effects an improvement in creep properties until the eutectoid appears, but with more than 4 per cent. antimony the ridge slopes away into the $\alpha + \varepsilon + \delta$ field, *i.e.* at any concentration of antimony above 4 per cent., optimum creep properties are produced by the addition of less cadmium than is required to reach the $\alpha + \varepsilon$ phase field; deterioration is found before the cadmium content is sufficient to cause the formation of the eutectoid. Here, then, some other factor appears to be operating to produce a decrease in creep properties which cannot be ascribed to the presence of the eutectoid.

Fig. 15 shows contours connecting alloys of equal grain-size. The results used in the construction of this diagram are given in Tables VIII and IX. Superimposed is the constitution at 170° C., since the grain-size results partly from the temperature and partly from the constitution at that temperature. A maximum grain-size is to be expected in pure tin. However, the addition of antimony and cadmium does not produce a continuous refinement in grain, as would be expected. Antimony alone causes a decrease, but when between 5 and 8 per cent. of antimony is present, the addition of cadmium first increases and then decreases the grain-size. The maximum lies approximately on the boundary between the $\alpha + \delta$ and $\alpha + \varepsilon + \delta$ phase fields. Thus, the tendency of the ε phase is to decrease the grain-size. This is further shown by the minimum at 4·5 per cent. cadmium and 8 per cent. antimony, almost on the $\alpha + \varepsilon$ phase field.

TABLE IX.—*Results Used in the Construction of Fig.* 15.

Composition.		Grain-Size, Grains/cm.^{2}.	Composition.		Grain-Size. Grains/cm.^{2}.
Cadmium, Per Cent.	Antimony, Per Cent.		Cadmium, Per Cent.	Antimony, Per Cent.	
2	3	5,800	5	5	50,000
2	5	600	5	7	47,000
2	7	6,600	5	9	180,000
2	9	90,000	7	5	29,000
3	5	8,000	7	9	70,000
3	7	78,500			
4	7	176,000			
4	9	99,000			

Here, then, are the two factors which determine the creep properties. The addition of cadmium and antimony tends to produce stronger alloys up to a maximum at 8 per cent. cadmium and 7 per cent. antimony, ε being the phase most beneficial to strength. However, ε tends to produce a small grain-size, which, as has been shown, is detrimental to creep properties. Therefore, a balance is formed between the increase in strength and the decrease in grain-size due to ε, the balance occurring at 2 per cent. cadmium and 7 per cent. antimony.

That grain-size is an important factor in determining creep properties explains why creep is not always proportional to tensile strength. In a series of alloys of uniform grain-size, these two properties would bear an approximate relationship to each other, but where the grain-size varies considerably between different alloys, no such relationship will be found. An example of the former case is seen in the self-annealed alloys, which have a small but uniform grain-size, while the annealed alloys are typical of the second case.

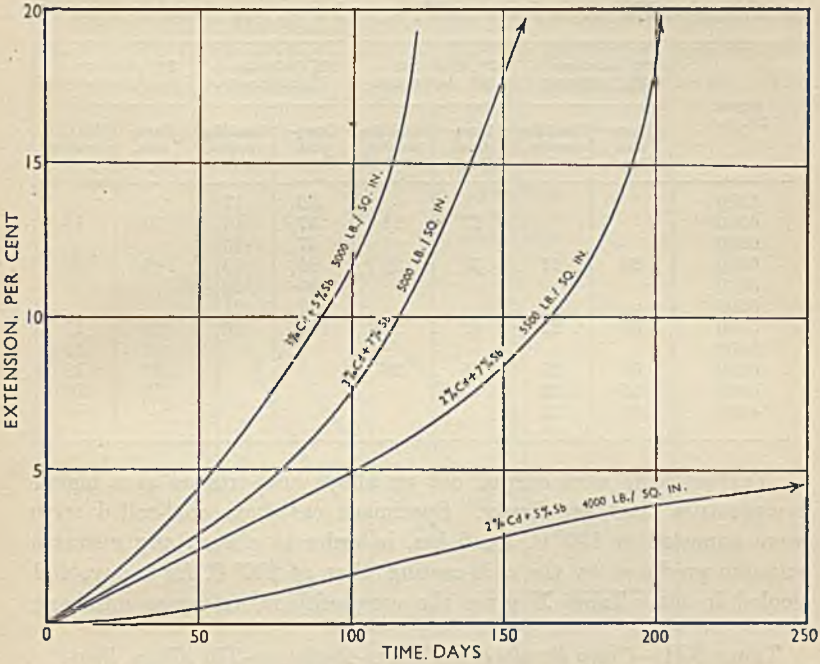


Fig. 16.—Time–Extension Curves; Alloys Annealed at 170° C.

Several time–extension curves for these alloys are shown in Fig. 16.

Table X.—*Tensile Properties of Cadmium–Antimony–Tin Alloys, Heat-Treated at* 170° *C. for* 5 *Hrs.*, 200° *C. for* 1 *Day, and Cooled in Air.*

Cadmium, Per Cent.	Antimony, Per Cent.	Reference Number.	Ultimate Tensile Strength, Lb./in.².	Elongation, Per Cent. on 2 in.
2	3	C2S3.A200	11,100	34
2	5	C2S5.A200	10,700	32
2	7	C2S7.A200	11,200	30
2	9	C2S9.A200	14,500	38
3	7	C3S7.A200	14,700	19
4	7	C4S7.A200	16,800	22
4	9	C4S9.A200	15,500	35
5	9	C5S9.A200	16,300	38

They show no unusual feature, except that the rate of extension increases continuously practically from the beginning of the test.

TABLE XI.—*Creep Results, Cadmium–Antimony–Tin Alloys, Heat-Treated at* 170° *C. for* 5 *Hrs.*, 200° *C. for* 1 *Day, and Cooled in Air.*

Stress, Lb./in.^{2}.	2% Cadmium + 3% Antimony.		2% Cadmium + 5% Antimony.		2% Cadmium + 7% Antimony.		2% Cadmium + 9% Antimony.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
7000					26	17		
6500			27	24	57	19	19	19
6200					67	16		
6000	20	21	51	29	91	16	46	20
5800					105	20		
5600					117	21		
5500	33	22	92	21	133	26	69	17
5500							66	15
5000	63	27	86	26			94	16
5000	55	23					88	16
4480	64	22						

Further tests were carried out on alloys heat-treated at a higher temperature than previously. Specimens cut from cold-rolled strip were annealed at 170° C. for 5 hrs. in order to absorb any unstable eutectic produced by the chill-casting, then at 200° C. for 1 day, and cooled in air. Table X gives the compositions, reference numbers,

TABLE XII.—*Creep Results of Cadmium–Antimony–Tin Alloys, Heat-Treated at* 170° *C. for* 5 *Hrs.*, 200° *C. for* 1 *Day, and Cooled in Air* (*cont.*).

Stress, Lb./in.^{2}.	3% Cadmium + 7% Antimony.		4% Cadmium + 7% Antimony.		4% Cadmium + 9% Antimony.		5% Cadmium + 9% Antimony.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
8000	22	20						
7500	40	17						
7000	82	24	18	17				
6500	128	24	44	29	31	26		
6500	129	19			14	27		
6000	140	24	48	21	24	37	20	29
5700	176	20						
5500	238	20	82	28	49	23	13	31
5500			77	25			41	30
5000			70	29	34	26	28	26
5000							23	30
4480					60	32	24	28
4000					130	28		

tensile strengths, and elongations of the alloys investigated. Tables XI and XII give the results of creep tests. Some results have been obtained in duplicate. Discrepancies in these will be discussed later.

The results of the heat-treatment at 200° C., when compared with those at 170° C., show that in some alloys little improvement is effected, but in others considerably improved creep properties result. The alloys C2S3, C2S5, C2S7, C5S9 show little improvement; alloy C4S9 is slightly improved; and alloys C2S9, C3S7, C4S7 are greatly improved. Alloy C2S9.A170 withstands 3500 lb./in.^{2} for 100 days, whereas C2S9.A200 withstands 5000 lb./in.^{2} for the same time. Alloy C3S7.A170 breaks in 200 days at 4800 lb./in.^{2}, whereas with C3S7.A200 5600 lb./in.^{2} is required to cause fracture in this time. This alloy is so improved by the heat-treatment at 200° C. that it now becomes better than alloy C2S7.A170, which previously was the best. Several stress-duration curves for these alloys are shown in Fig. 17. That for alloy C3S7

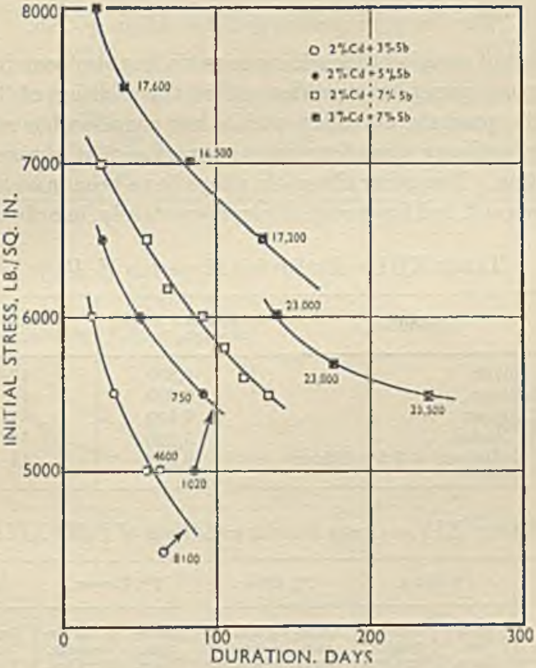


Fig. 17.—Stress-Duration Curves; Alloys Annealed at 200° C.
(The Figures on the Diagram Represent the Grain-Sizes of the Specimens in Grains/Cm.^{2}.)

indicates that a stress of 5000 lb./in.^{2} will not produce fracture in less than 1 year.

Certain results which do not agree are connected with the grain-size, figures for which are given in Fig. 17. With alloy C3S7.A200 three specimens having grain-sizes between 16,500 and 17,600 grains/cm.^{2} fall on one curve, and three between 23,000 and 23,500 fall on another; the latter show shorter durations than the former.

The Creep Properties of Other Alloys of Tin.

The effect of certain other additions to tin has also been investigated. In the previous paper,[1] it was shown that the addition of 3·5 per cent. silver to tin produces an alloy which has considerable resistance to creep, withstanding a stress four times as great as that of pure tin for the same duration. Two other silver–tin alloys have been investigated, containing 1 per cent. and 2 per cent. silver, respectively, in order to ascertain

TABLE XIII.—*Mechanical Properties of Alloys.*

Composition.	Ultimate Tensile Strength, Lb./in.^{2}.	Elongation, Per Cent. on 2 in.
1% Silver	4,800	40
2% Silver	6,200	40
1% Copper	7,100	31
0·3% Nickel	5,600	46
1% Cadmium + 3·5% Silver .	10,200	17

TABLE XIV.—*Creep Results on Alloys of Table XIII.*

Stress, Lb./in.^{2}.	1% Silver.		2% Silver.		1% Copper.		0·3% Nickel.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
2000					6	10		
1800	3	35	8	55	9	19		
1600	9	75	19	60	20	21	1	61
1400	21	55	45	42	56	8		
1300					61	25		
1200	48	64	98	69	119	18		
1100			119	54				
1000	130	41	219	59			7	42
900	203	50	282	59				
800	290	49	(577)	(42·2)			10	56
600							64	83
400							(464)	(42)
300							(421)	(2·5)
200							(389)	(0·42)

The figures in parentheses are for specimens which have not fractured.

Table XV.—*Creep Results, Alloy Containing* 1 *Per Cent. Cadmium* + 3·5 *Per Cent. Silver.*

Stress, Lb./in.².	Duration, Days.	Extension, Per Cent.	Stress, Lb./in.².	Duration, Days.	Extension, Per Cent.
3500	10	12	2240	349	2
3000	67	7	2000	(470)	(1½)
2500	145	3			

The figures in parentheses are for specimens which have not fractured.

whether a reduced silver content produces markedly inferior results. These alloys have been tested in the cold-rolled and self-annealed condition. Alloys containing 1 per cent. copper and 0·3 per cent. nickel have also been tested (cold-rolled and self-annealed). Lastly, the effect of cadmium (1 per cent.) and silver (3·5 per cent.) together has been investigated as a preliminary to more detailed work. The tensile strength and elongation values are shown in Table XIII, and the creep results in Tables XIV and XV.

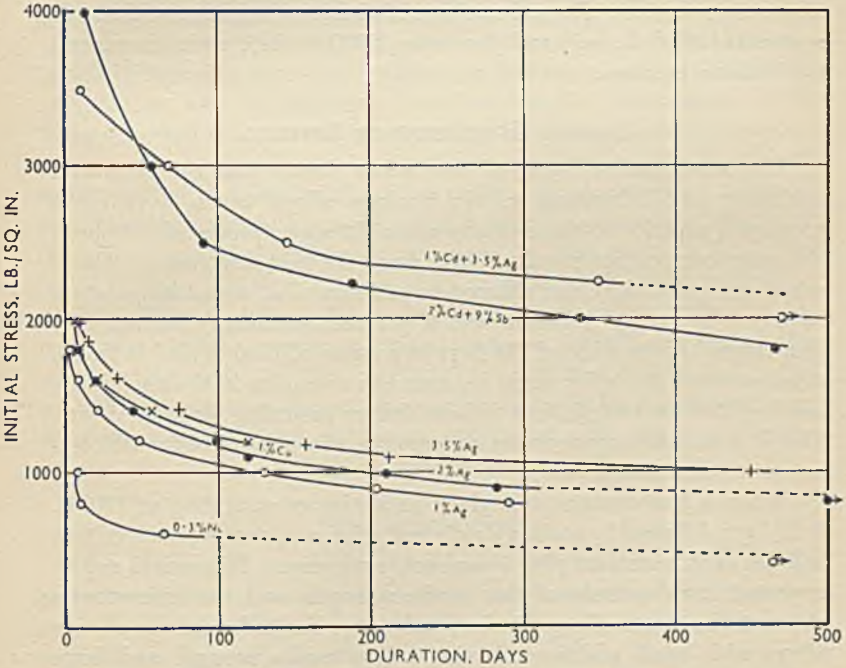


Fig. 18.—Stress–Duration Curves; All Alloys Self-Annealed.

In Fig. 18, these results are shown plotted as stress–duration curves; that for the alloy containing 3·5 per cent. silver is also included for comparison. The alloys containing 1 and 2 per cent. silver are little inferior to that having 3·5 per cent. silver; the stresses to cause fracture in 200 days are 900, 1000, 1100 lb./in.^{2}, respectively. The properties of the 1 per cent. copper alloy fall between those of the alloys with 2 and 3·5 per cent. silver; that with 0·3 per cent. nickel is definitely inferior. The alloy containing 1 per cent. cadmium plus 3·5 per cent. silver has a creep resistance which is remarkable for a self-annealed alloy. For completeness, the curve for the self-annealed alloy with 7 per cent. cadmium and 9 per cent. antimony is given in the figure. These curves illustrate that short-time tests are not always a true guide to creep properties, since they cross at a stress of 3100 lb./in.^{2}; above this, the cadmium–antimony–tin alloy is superior; below, the cadmium–silver–tin is better. For a duration of 200 days, the former withstands a stress of 2200 lb./in.^{2}, and the latter, 2350 lb./in.^{2}, which is a small but definite increase.

GENERAL DISCUSSION OF RESULTS.

The investigation described above has shown that cadmium and antimony added together to tin produce alloys which have creep properties superior to those of any other tin alloys previously studied; the exact composition required depends on the heat-treatment. Alloys which are cold-rolled and allowed to self-anneal at room temperature require 7 per cent. cadmium and 9 per cent. antimony for the best properties. Since a life of 724 days at a stress of 1600 lb./in.^{2} is found, it follows that this alloy could be stressed in practice in the neighbourhood of 1200 to 1400 lb./in.^{2} without failure occurring for many years. This is a marked improvement on pure tin, the safe stress for which is not more than 150 lb./in.^{2}.

When a heat-treatment is given consisting of annealing at 170° C. for 2 days, followed by cooling slowly in the furnace, the best composition is 2 per cent. cadmium plus 7 per cent. antimony. This would not be expected from a study of the tensile strength, and the difference is shown to be due to the grain-size; a balance has to be found between alloys with small additions, having a low tensile strength and large grain-size, and alloys with high additions, having a high tensile strength and small grain-size. The constitutional changes producing the alloy of optimum properties have been worked out. Tests on this alloy have not proceeded beyond a duration of 250 days, but an approximation to a safe working stress can be found by comparison with the alloy containing 2 per cent. cadmium plus 5 per cent. antimony, after annealing at 170° C. The latter extends 3·44 per cent. in 791 days at 3000 lb./in.^{2}, a stress which may be taken as safe. After annealing at 170° C., the alloy with 2 per cent. cadmium plus 7 per cent. antimony withstands a stress greater than the alloy with 2 per cent. cadmium plus 5 per cent. antimony for an equal duration; thus, a safe stress for the latter is around 3500 lb./in.^{2}. Among the alloys heat-treated at 200° C. for 1 day, followed by cooling in air, the optimum composition is about 3 per cent. cadmium plus 7 per cent. antimony. A safe stress for this alloy is slightly higher than that for the previous one, *i.e.* around 3700 lb./in.^{2}.

Although it has been shown that grain-size is an important factor in determining creep properties, the results and deductions given above are not vitiated by the objection that other results would have been obtained had the alloys used possessed grain-sizes different from those recorded. Grain-size is a property of an alloy depending, not only on history and heat-treatment, but also on composition and constitution; large differences in grain-size are likely to be found in alloys of different composition, even though they have had identical treatments. It is to be expected that, whenever any of the alloys used are subjected to the treatments described, the grain-sizes reported in this paper will result (within certain limits). It is justifiable, therefore, to compare alloys having different grain-sizes, but it must be remembered that any deviation from the treatments described in this paper is likely to influence the grain-size, and therefore to produce different results.

The addition of 1 or 2 per cent. silver is shown to produce creep properties slightly inferior to those produced by 3·5 per cent.; the safe working-stress for these alloys is not more than 600 lb./in.^{2}. Tin containing 1 per cent. copper gives results intermediate between those of alloys containing 2 and 3·5 per cent. silver; the alloy containing 0·3 per cent. nickel is considerably inferior.

ACKNOWLEDGMENTS.

The authors are greatly indebted to the International Tin Research and Development Council for financial assistance wherewith to carry out this investigation, and to Mr. D. J. Macnaughtan for his keen interest and helpful criticism.

REFERENCES.

[1] D. Hanson and E. J. Sandford, *J. Inst. Metals*, 1936, 59, 159.
[2] D. Hanson and W. T. Pell-Walpole, *J. Inst. Metals*, 1937, 61, 123, 265.

DISCUSSION.

(*Condensed.*)

Dr. **Bruce Chalmers** *: While appreciating the way in which the authors have shown the relation between constitution, heat-treatment, grain-size, and endurance, there are one or two points to which further attention might be directed. In the first place, a very definite distinction seems to be made between the "creep" tests and the tensile tests; and yet they should really be considered as the two extremes of the same process, namely, that of applying a load which breaks the test-piece. The reason why a test-piece will endure longer under a smaller load must surely be sought in the self-annealing that occurs if there is time before fracture. The factors which cause the crossing over of the curves in Fig 4, for example, must be those which control the self-annealing process. The effect of annealing at 170° C. is interesting in this connection, as it seems to influence the properties affected by self-annealing (*i.e.* creep tests) more than the rapid test.

I am not quite clear whether the grain-size is really the cause of the separation, for example, of the top two curves of Fig. 4, which relate to materials of nominally the same composition, treated in exactly the same way, but having different grain-sizes. It seems possible that there is some other variable that causes the difference in grain-size and the difference in creep endurance. If that were so, the rather unexpected way in which the creep endurance apparently varies with grain-size might be explained. It might be suggested, for example, that the distribution of shape and orientation of the crystals might influence both the measured grain-size and the creep properties.

Mr. D. J. **Macnaughtan** † (Member of Council): I think that the progress which has been made in this work has been due to the fact that work on constitution is carried out in the same laboratory as that in which the creep tests have been made. There has been collaboration in discussing matters in which the constitution of the alloys and their physical properties are concerned.

It may be said: "These tin alloys are self-annealed after working, or annealed; what interest have we in the creep properties of such materials?" Interest is naturally taken in the creep properties of cast tin alloys such as solders, which, of course, are chill castings, and a good deal of work is in progress on the creep properties of cast tin alloys of this kind. I had an interesting example of the need for information on the worked and subsequently self-annealed alloys some time ago. My attention was directed to a tin alloy pipe which had been introduced into a refrigerating unit employed in large numbers. There were special merits for this particular purpose in using a tin alloy pipe. Fluids circulated through the pipe, and there was external pressure. After some months, the pipe slowly flattened and put the mechanism out of order. An attempt was made to replace this by what appeared, from ordinary tensile tests, to be a stronger tin alloy pipe. Much to the surprise of the manufacturer, the result was that creep took place at a still greater rate and the pipe failed in a very short period of time. These investigations at Birmingham have shown how impossible it is to deduce the creep properties from a knowledge of the tensile properties.

Dr. J. **McKeown**,‡ M.Sc. (Member): We are now coming to realize that, in materials tested at temperatures above their temperature of recrystallization

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† Director, International Tin Research and Development Council, London.

‡ Investigator, British Non-Ferrous Metals Research Association, London.

after severe cold-working, grain-size is almost equal in importance to composition. Thus, it is not sufficient to say that the resistance to creep of alloy A is greater than that of alloy B when both have been treated in the same manner, *i.e.* have identical mechanical and thermal histories. It may be possible to improve the creep resistance of B by a different treatment—mechanical, thermal, or a combination of both—which will increase its grain-size.

The effect of grain-size on the resistance to creep of alloys of tin has been recognized by the authors, but such variations in grain-size as they have encountered have been obtained by accident, and not by design. Do the authors now propose to take the best of their alloys and see whether it is possible, by varying the methods of production and hence the grain-size of their specimens, to increase still further the resistance to creep?

The life of a creep specimen at a given stress may increase in two ways: (1) in which the rate of creep is decreased and a longer time is taken to reach the amount of extension required to produce failure; and (2) in which the rate of creep may be greater than in the previous case, but the amount of extension which may take place before failure occurs is much greater and this increases the life. In general, with materials and testing conditions such as are considered here, *i.e.* materials tested at temperatures above their temperature of recrystallization after severe cold-working, an increase in grain-size produces a reduction in the rate of creep and also a reduction in the permissible deformation before failure occurs. It would appear that at some stage in grain-size changes, brought about by thermal and mechanical treatment, a point will be reached at which a balance will be struck between decrease in life due to decrease in ductility, and increase in life due to decrease of rate of creep. Such a grain-size would appear to be the ideal to be aimed at.

The authors give no indication of possible practical applications of the alloys on which they have experimented. Are any such applications in view and in such applications is creep resistance an important factor which must be taken into account?

Dr. C. H. M. JENKINS,[*] A.R.S.M. (Member): Mr. Macnaughtan referred to the importance of cast alloys, to which the authors have omitted reference. This omission is to be regretted, as cold-rolled and annealed tin, which is a very soft material, is used as a basis for comparison. This omission has the effect of emphasizing the great difference between pure tin and some of the alloys dealt with in the paper.

The authors have noted certain constitutional changes in the alloys and have also pointed out a maximum in the resistance to creep. It appears that the two effects have been associated. This is understandable in binary and pseudo-binary systems of alloys, but it is difficult to account for in more complex systems. The association of constitutional changes with resistance to creep presumes, apparently, that there are age-hardening effects present which produce, in turn, increased resistance to creep. This last-named relationship is by no means certain.

The need for the study of cast alloys relates to their use as solders and as bearing metals whose condition corresponds more closely to that of cast metals than to that of worked material. As a point of immediate application, the addition of cadmium to tin–antimony bearing metals is worthy of study as a means of strengthening the tin base.

A passage on p. 226 appears open to doubt. The text states: "That grain-size is an important factor in determining creep properties explains why creep

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is not always proportional to tensile strength. In a series of alloys of uniform grain-size these two properties would bear an approximate relationship to each other, but where the grain-size varies considerably between different alloys, no such relationship would be found." The generalization that there is a relationship between creep and tensile strength in other materials is difficult to accept. The authors may have, in this particular series of alloys, an increase in the tensile strength more or less corresponding to an increase in creep properties, but they do not appear to be justified in attributing any discrepancies to grain-size differences. It should be remembered that, even in a pure metal, two samples of similar grain-size do not necessarily show the same resistance to deformation under creep conditions. This discrepancy may arise from self-annealing effects in cold-worked material which do not give rise to grain-size differences. Fortunately, such self-annealed materials are capable of examination after heat-treatment experiments at slightly elevated temperatures at which the response to grain growth and recrystallization provides a means of unravelling the changes in the material.

Mr. E. H. Bucknall,* M.Sc. (Member): The authors seem to have managed to avoid a dilemma in which workers on other alloys have found themselves, as a result of regarding the matter from the point of view of the reduction of creep rate. It is easy to arrive at an alloy which is very resistant to creep, but which breaks with a very small elongation and is for that reason unattractive industrially. The authors do not seem to have worried over much about creep rates, and have succeeded in obtaining alloys which break with large elongations of the order of 20 per cent.

The character of the creep curves of materials stiffened by heat-treatment at 170° C. seem to differ rather markedly from that of those softened by self-annealing at room temperature. The heat-treated alloys show a continuously increasing creep rate, rather like that found by Pearson for solders.

The authors' work shows the need for a specific type of treatment to develop the best creep-resistance. In service conditions, where vibration and repeatedly applied stress may be involved, as well as steady stress, it seems possible that a compromise might have to be effected between the treatment which yields the best creep-resistance and that which improves most the fatigue resistance.

The correlation between microstructure and creep life in these alloys seems to be much more complete than in the case of steels, where materials of similar microstructure, or microstructures which do not differ much, can have creep rates differing by as much as 100 : 1, and possibly 1000 : 1. This "abnormality," as it is termed, does not seem to have been found in any non-ferrous metal or alloy.

CORRESPONDENCE.

The Authors (*in reply*): We agree with Dr. Chalmers that the difference between a tensile and a creep test is probably due to the self-annealing which occurs during the creep test. However, it is for future work to settle this point. Dr. Chalmers raised the question whether grain-size is the deciding factor or whether some other variable influences the grain-size and the creep simultaneously. We would point out that all the specimens of one composition were cut from the same piece of strip, and were annealed in the furnace at the same time. It is difficult, therefore, to see what other variable

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* Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

could be operating when every specimen received the same treatment. There may have been slight differences in the machining of the specimens (*e.g.* in the amount taken off at each cut) which produced slight differences of strain and therefore variations in the grain-size.

We are glad that Mr. Macnaughtan emphasized the importance of correlating constitutional work with mechanical tests, since it is only when this is done that any knowledge of the factors influencing mechanical properties can be had.

In reply to Dr. McKeown, we are hoping to effect further improvements to these alloys by controlling the grain-size. It is generally agreed that increasing the grain-size of these and similar alloys decreases the creep rate, and also the total extension before fracture. However, little work has been carried out in cases where the grain-size is very much larger than usual. It may be that the continued increase of the grain-size eventually causes the creep rate to increase.

We would point out to Dr. Jenkins that, since all the alloys are in the rolled condition, it is reasonable to compare them with pure tin also in the rolled condition. In a future paper we hope to present results obtained with cast materials; these results will be compared with those of cast tin. We fail to see how it can be presumed that age-hardening effects are present in these alloys, since we have stated on p. 219 that the heat-treatment was that which gave stable tensile properties. In associating the constitutional changes with the creep properties, we have only stated that the best properties are obtained when certain phases are present in certain proportions, and that other phases are deleterious to creep. The passage on p. 226 which Dr. Jenkins criticizes is meant to be applied to these alloys only, *i.e.* to alloys of one system. This statement is obviously not true when comparisons are made between alloys of different systems or between alloys of different basic metals. We have always found that creep results may be repeated with good agreement so long as the constitution and grain-size of the specimens remain the same; we have had no evidence that any other factor is influencing creep.

We are glad that Mr. Bucknall has noted that these alloys have good elongations and do not suffer from brittleness. Mr. Bucknall points out that the extension–time curves indicate that there is less strain-hardening in the heat-treated than in the self-annealed specimens. This seems to indicate that grain-size also influences strain-hardening. We are investigating this point. We have no figures for the fatigue strengths of these alloys, nor does the influence of grain-size on fatigue seem to have been studied. It is quite likely that the grain-size which gives the best creep results will not give the best fatigue properties, in which case a compromise will have to be effected, as Mr. Bucknall points out. An investigation on the effects of the distribution of the phases, as distinct from the quantity present, might help to explain the widely differing results found in steels of almost identical microstructures.

SINTERED ALLOYS. PART I.—COPPER–NICKEL–TUNGSTEN ALLOYS SINTERED WITH A LIQUID PHASE PRESENT.*

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By G. H. S. PRICE,† B.Sc., Member, C. J. SMITHELLS,† M.C., D.Sc., Member of Council, and S. V. WILLIAMS,† B.Sc., Member.

(Communication from the Staff of the Research Laboratories of The General Electric Company, Ltd., Wembley, England.)

Synopsis.

Factors which influence the preparation of alloys made by mixing, pressing, and sintering metal powders in an atmosphere of hydrogen have been investigated with particular reference to the copper–nickel–tungsten system. The distinctive character of the work is that sintering has been carried out at temperatures sufficiently high to ensure the presence of a liquid phase during the formation of the alloy.

The effect of time and temperature of sintering has been investigated with a copper 2, nickel 5, and tungsten 93 per cent. alloy. Alloy formation, determined by density measurements and microexamination, does not progress uniformly as the sintering temperature is increased, but shows a rapid increase at a temperature of about 1300° C. Although considerable solid diffusion may occur at lower temperatures, it is essential that this temperature should be exceeded if alloys of "theoretical" density are to be obtained.

The time for which the alloys must be held at the sintering temperature to reach equilibrium is largely dependent on the composition. An alloy having a high percentage of the liquid phase reaches its "theoretical" density sooner than one in which the amount of liquid phase present is small.

The effect of composition has been investigated for a series of alloys containing from 80 to 97 per cent. tungsten. With copper only, the tungsten particles are merely wetted and cemented together; there is no grain-growth and much porosity. With nickel only, the full density is obtained after sintering above 1500° C. When both copper and nickel are present, two factors are important: the ratio of nickel to copper, and the total percentage of these metals. Maximum density is obtained when the nickel–copper ratio is about 2 : 1 and the tungsten content lies between 89 and 93 per cent.

A fourth fundamental variable is the fineness of the metal powders, a longer time, or a higher temperature, being required for complete sintering when the tungsten grains are coarse. Fully-sintered alloys prepared in this way have no porosity, densities equal to the "theoretical" values, and a tensile strength up to 40 tons/in.^{2}. Microexamination reveals the presence of large, rounded tungsten grains, whose diameter

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† Research Laboratories of The General Electric Company, Ltd., Wembley.

is about 100 times that of the original particles, embedded in a continuous matrix of copper–nickel phase saturated with tungsten.

An explanation of the changes which take place during sintering, based on the abnormal solubility of particles less than 1 μ in diameter, accounts satisfactorily for all the observations. This hypothesis has been confirmed by results obtained with sintered silver–copper and copper–iron alloys.

INTRODUCTION.

IN a previous paper from the authors' laboratories [1] changes in structure during the sintering of pressed tungsten powder were described. The mechanism of sintering in compressed powders of various metals has been intensively studied by Sauerwald [2] and his collaborators, who have also measured the changes in certain physical properties that accompany the sintering process. Papers by Hedvall [3] and Trzebiatowski [4] have also appeared on the same subject. The effect of pressure and of annealing on the hardness of pressed metal powders has been investigated by Kikuchi,[5] but since reducing atmospheres were not employed during annealing, the results were complicated by the presence of oxide films. The formation of alloys by annealing compressed mixtures of metal powders at temperatures below their melting points was studied in 1909 by Masing.[6] References to other papers dealing with various phases of powder metallurgy will be found in the books on this subject by Jones,[7] and Skaupy.[8] The present paper describes an investigation of the preparation of alloys by sintering mixed metal powders at temperatures at which a small quantity of a liquid phase is present. So far as the authors know, no previous investigation has been carried out under these conditions. The investigation has mainly been confined to mixtures of tungsten with small amounts of copper and nickel, although certain conclusions regarding the mechanism of the sintering process have been checked by making up alloys of other metals.

THE COPPER–NICKEL–TUNGSTEN SYSTEM.

Short accounts have already appeared [9] of some of the properties of a series of copper–nickel–tungsten alloys prepared by pressing and sintering the mixed metal powders. These alloys were developed, on account of their high density, for use as shields in radium beam therapy. The copper–nickel–tungsten ternary system has not previously been investigated. Tungsten is said to be insoluble in molten copper, and tungsten and copper form no alloys. On the other hand, in an atmosphere of hydrogen, molten copper "wets" tungsten, and when tungsten contacts are brazed on to steel screws in this way a strong joint is obtained. This is, perhaps, a little surprising if copper is completely insoluble in tungsten. The nickel–tungsten equilibrium diagram of Vogel is reproduced in Fig. 1. Molten nickel can dissolve up to 52 per cent. tungsten at 1510° C., and the solubility increases at higher temperatures. 47 per cent. tungsten can be held in solid solution above 900° C., but the solubility decreases at lower temperatures. Nickel is insoluble in solid tungsten. The copper–nickel equilibrium diagram is reproduced in Fig. 2, and is too well known to need comment.

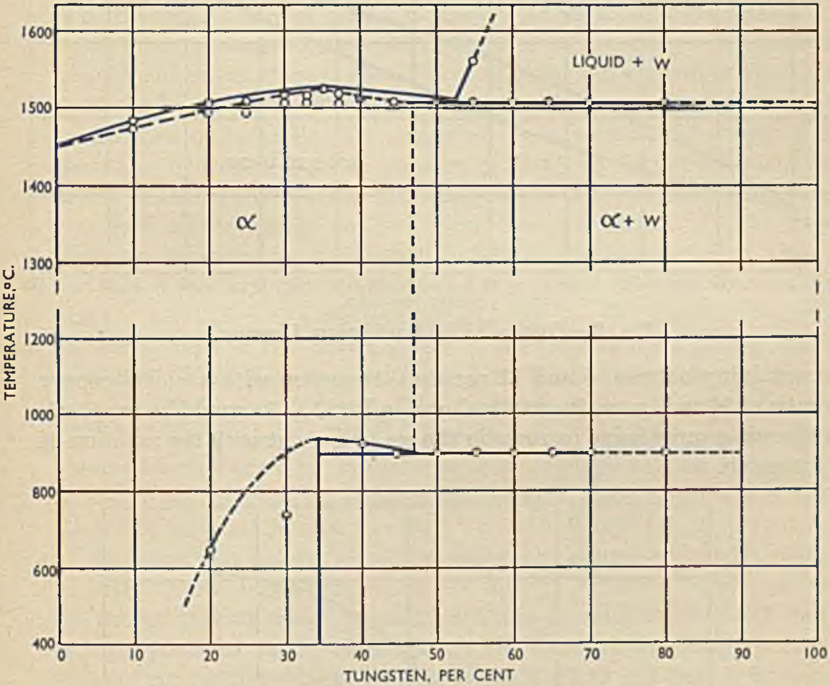


Fig. 1.—Nickel–Tungsten Equilibrium Diagram (Vogel).

The solubility of tungsten in copper–nickel alloys has not previously been determined. The present authors have made an approximate determination of the solubility of tungsten in an alloy containing nickel 66·6 and copper 33·3 per cent. Some pieces of tungsten rod were added to the molten alloy held at 1600° C. in an induction furnace in an atmosphere of hydrogen for ½ hr. On cooling, the undissolved tungsten remained at the bottom of the crucible. The upper part of the melt, which had a typical cored structure, was found on analysis to contain nickel 55·4, copper 27·6, and tungsten 16·8 per cent. This value for the solubility is confirmed by data given later in the paper.

It is clear that the presence of copper decreases the solubility of tungsten in nickel.

An approximate determination of the melting points of alloys containing between 5 and 17 per cent. tungsten, with a nickel-copper ratio of $2\frac{1}{2}$ to 1, gave the results shown in Fig. 3. As would be expected, there is a progressive increase in the melting point with the addition of tungsten.

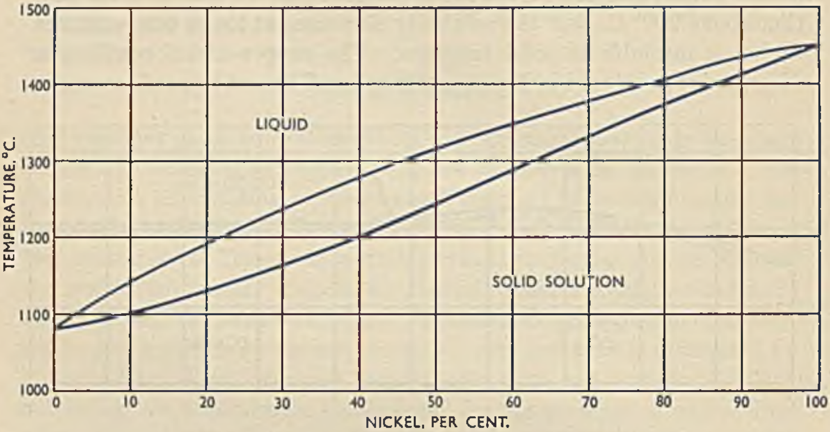


Fig. 2.—Copper-Nickel Equilibrium Diagram.

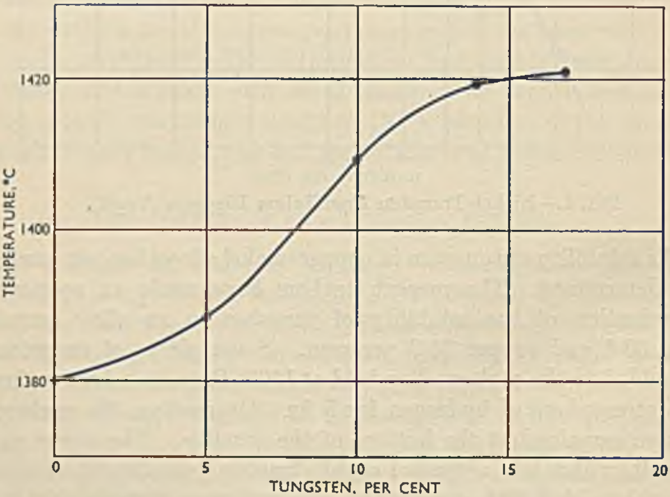


Fig. 3.—Melting Points of Copper-Nickel-Tungsten Alloys. Nickel-Copper Ratio $2\frac{1}{2}:1$.

Preparation of Alloys.

The standard method of preparation, which has been arrived at as the result of two or three years' experience in the production of these alloys, is essentially as follows. The metal powders, after screening or otherwise obtaining the required particle size, are weighed and thoroughly mixed together. The mixture is then moistened with a solution of wax in benzol, and the benzol evaporated whilst stirring is continued. The wax makes it possible to press coherent masses at much lower pressures than would otherwise be necessary. A weighed quantity of the mixture is placed in a steel die, and a pressure of about 5 tons/in.^{2} is applied. The pressed pieces, which are strong enough to be handled quite easily, are supported on a suitable refractory and heated in hydrogen to a temperature of 1400° C. It is convenient to divide the firing process into two stages, since the temperature must be increased rather slowly until the wax has evaporated. In the first stage, the temperature is increased to 950° C., during a period of 3 hrs., and the pieces are then transferred for a period of 1 hr. to another furnace maintained at a temperature of 1400° C. For the experimental work described in this paper, pieces in the form of discs were pressed in a die 1 in. in diameter, and were $\frac{1}{4}$ in. thick after pressing. Each piece weighed about 30 grm. The size of the piece, however, has no effect on the properties of the material, and identical results were obtained with discs 6 in. in diameter and weighing several kilograms. Although at the sintering temperature a liquid phase is present in the alloy, the material retains its shape perfectly if suitably supported.

An important feature of the process is the accurate reproducibility of both structure and properties, not only in different samples from the same batch of mixed powders, but also in samples from different batches prepared in the same way. The density, for example, of a series of similar pieces does not vary by as much as ± 1 per cent., even though a linear shrinkage of 17–20 per cent. occurs during sintering. On the other hand, small changes in composition or procedure are immediately reflected in the properties of the finished product, and may be readily correlated. Alloys may be prepared in this way which are entirely free from porosity and have the "theoretical" density, provided that the composition is suitably chosen. They have all the properties usually associated with alloys prepared by more conventional methods.

The effects of particle size, pressure, sintering temperature and time, composition, and the substitution of other elements for copper and nickel, on the density and microstructure of the alloys were examined. Over 100 different mixtures were investigated. The microstructure, density, and Brinell hardness were determined in each case, and other physical properties are given for one of the most useful alloys.

Effect of Temperature and Time of Sintering.

The changes in density and microstructure which take place during sintering have been followed for a number of alloys of different compositions. The general character of these changes will be described with reference to a typical alloy containing copper 2, nickel 5, and tungsten 93 per cent. A series of specimens was prepared by the standard process, except that the final sintering was carried out for 1 hr. at temperatures varying from 950° to 1400° C. The tungsten powder used had passed a 200-mesh sieve, and its particle size distribution was:

Particle diameter	0–1 μ	1–2 μ	2–5 μ	>5 μ
Number of particles, per cent.	11	29	42	18

The copper and nickel powders had passed the same sieve, but had a much smaller proportion of fine particles.

TABLE I.—*Effect of Sintering Temperature on Percentage Shrinkage and Density.* (*Copper* 2, *Nickel* 5, *Tungsten* 93 *Per Cent. Alloy.* "*Theoretical*" *Density* 17·8 *grm./c.c.*)

Sintering Temperature, ° C. (Time: 1 hr.).	Linear Shrinkage, Per Cent.	Density, Grm./c.c.
950	0	10·5
1050	0·3	10·7
1150	1·3	11·1
1250	3·0	12·0
1300	6·6	12·8
1350	12·7	16·1
1400	16·2	17·2

The densities of the alloys were measured after sintering, and are recorded in Table I. In the case of specimens sintered at high temperatures, the density was determined by weighing in air and in water. Alloys sintered at low temperatures are sufficiently porous to absorb water, and the density was calculated from the weight and dimensions. The alloys shrink during sintering, but, owing to unequal distribution of pressure in the die, the shrinkage is not quite uniform in all directions. The linear shrinkage recorded in Table I was measured across the flat face of the disc. For an alloy of this composition, assuming it to be a simple mixture, the calculated, or "theoretical," density is 17·8 grm./c.c., taking the density of both copper and nickel as 8·9 grm./c.c. and that of tungsten as 19·25 grm./c.c.

No measurable shrinkage takes place on sintering at 950° C., but at higher temperatures there is a progressive increase in density, although below 1300° C. the alloys are still porous. A little above this temperature there is a very marked increase in density, as seen from Fig. 4, and at 1400° C. the porosity is reduced to about 3 per cent. The "theoretical" value is actually reached by the alloy sintered at 1400° C. for 6 hrs. Sections of these alloys show that there is also a marked change in structure at about 1300°–1350° C., corresponding to the observed changes in density.

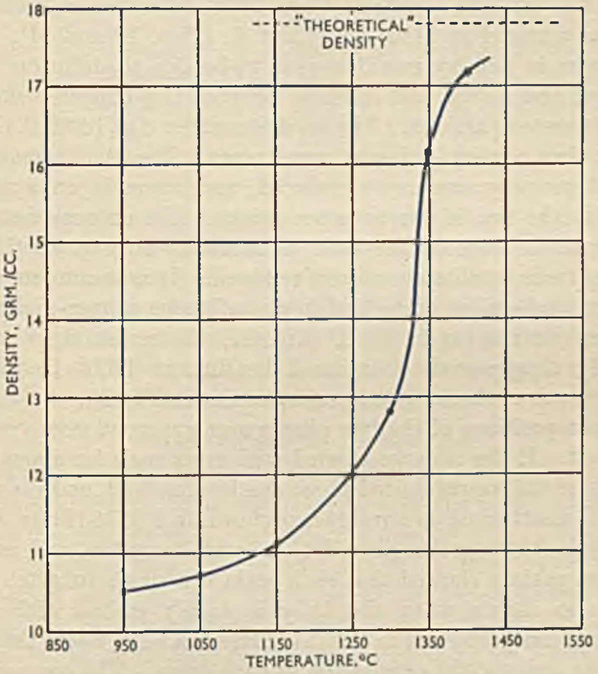


Fig. 4.—Effect of Sintering Temperature on Density. Alloy: 2% Copper, 5% Nickel, 93% Tungsten. Time of Sintering: 1 Hr.

The specimens were prepared for microexamination by polishing in the usual way, although some difficulty was experienced with those sintered at low temperatures, owing to the breaking away of grains from the surface. Certain changes in structure can be observed without etching, but other features are revealed by a light etch. The most suitable etching reagents are either boiling hydrogen peroxide, which etches tungsten but does not attack the copper–nickel phase, or acetic–nitric acid reagent, which attacks the copper–nickel phase and leaves the tungsten unaltered. The specimens, of which photomicrographs are shown in Figs. 8–15 (Plates XXV and XXVI), were etched for 15 seconds in boiling hydrogen peroxide, and the following changes can be seen. After sintering at 950° C., the original components can still be identified by colour, and have been marked in Fig. 8. There is some evidence of solid diffusion between the copper and nickel grains, which has progressed sufficiently at 1050° C. (Fig. 9) for the copper to be entirely decolourized. At the same time this copper–nickel phase has become rather more continuous around the tungsten grains. The latter show no change, and the size of the tungsten particles still corresponds to that of the original powder. Very little difference is seen in the specimens sintered at 1150° and 1250° C. (Figs. 10 and 11). So far, the changes in density would appear to be due to diffusion between the copper and nickel, and cohesion between this copper–nickel phase and the tungsten particles. The specimen sintered at 1300° C. (Fig. 12), however, has a very different appearance. The dark areas, which represent porosity, are much reduced, and there is an appreciable increase in the size of the tungsten grains. The copper–nickel phase still appears in more or less isolated patches. In Fig. 13 (1350° C.) the structure is much more clearly resolved. It now consists of large, rather rounded grains, embedded in a continuous copper–nickel phase, and after sintering at 1400° C. (Fig. 14) the remaining voids have practically disappeared. Continued heating at 1400° C. results in further growth of the tungsten grains, as seen in Fig. 15.

The compositions of the two phases now apparent were very easily determined. If the alloy be treated with aqua regia for about 24 hrs., the whole of the copper–nickel phase can be dissolved, and the rounded grains left unattacked as a residue, as shown in Fig. 16 (Plate XXVII). On analysis, these grains proved to be pure tungsten, and an X-ray diffraction pattern showed that each grain is a single tungsten crystal. This is also shown when the alloy is deeply etched with alkaline potassium ferricyanide, as in Fig. 17 (Plate XXVII), where the etching pits clearly indicate the orientation of each grain. The composition of the matrix was determined from the X-ray diffraction pattern of the alloy, which gave a lattice parameter corresponding to that of a copper–nickel alloy containing 17 per cent. tungsten. If the alloy be etched with acetic–nitric acid reagent, the matrix shows the heavily-cored structure seen in Fig. 18 (Plate XXVII).

The structure of the fully-sintered alloy therefore consists of rounded single-crystal grains of tungsten, with diameters from 50 to 100 times those of the original tungsten grains, embedded in a matrix which consists of a copper–nickel alloy saturated with tungsten. This type of structure is unusual in ordinary alloys, but may be obtained by quenching from a temperature at which a liquid phase is present. Such a structure in an antimony–cadmium–tin alloy quenched from 212° C., is shown in Fig. 78 of a recent paper by Hanson and Pell-Walpole.[10]

TABLE II.—*Effect of Sintering Time on Percentage Shrinkage and Density.* (*Copper* 2, *Nickel* 5, *Tungsten* 93 *Per Cent. Alloy.* "*Theoretical*" *Density* 17·8 *grm./c.c.*)

Time at 1400° C.	Linear Shrinkage, Per Cent.	Density, Grm./c.c.
5 seconds.	9·7	13·9
1 minute.	10·0	14·1
5 minutes.	11·9	15·0
¼ hr.	14·1	16·3
½ hr.	15·3	16·7
1 hr.	16·2	17·2
6 hrs.	17·2	17·8

Further specimens of the same alloy were sintered at 1400° C. for various periods of time, and their densities are recorded in Table II. It will be seen that a considerable time is required to attain equilibrium at this temperature. If the sintering is carried out at a higher temperature, or if the alloy contains a larger proportion of the copper–nickel phase, equilibrium may be attained more rapidly, and in certain alloys may be complete in 15 minutes, at 1450° C.

Effect of Tungsten Particle Size.

It will be shown later in the paper that an essential factor in the elimination of voids during sintering is that the liquid phase should not only wet the tungsten, but actually dissolve it. It would be expected, therefore, that the process would be more rapid the finer the tungsten particles, and this is confirmed by experiment. Three portions of a sample of tungstic oxide were reduced, the conditions being varied so as to produce a wide variation in the particle size of the resulting metal powders. Measurements of particle diameter gave the distributions recorded in Table III.

TABLE III.

Tungsten Powder.	Particles Within the Limits, Per Cent.			
	0–1 μ.	1–2 μ.	2–5 μ.	> 5 μ.
Fine	98	2	0	0
Medium	13	54	33	0
Coarse	1	11	27	61

1 μ = 0·001 mm.

TABLE IV.—*Effect of Tungsten-Particle Size on Density.* (*Copper* 4, *Nickel* 6, *Tungsten* 90 *Per Cent. Alloy.* "*Theoretical*" *Density* 17·2 *grm./c.c.*)

Time and Temperature of Sintering.	Density, Grm./c.c.		
	Fine.	Medium.	Coarse.
1 hr. at 1300° C.	16·4	15·8	13·2
½ „ 1400° C.	17·0	16·9	15·6
1 „ 1400° C.	17·2	17·0	16·4
3 hrs. at 1500° C.	17·2	17·2	16·7

Alloys containing copper 4, nickel 6, and tungsten 90 per cent. were prepared from each of these powders and sintered under the conditions indicated in Table IV, in which their densities are also recorded. The alloy made from the fine powder, whose particles are nearly all less than 1 μ, has practically the "theoretical" density after 1 hr. at 1400° C.; the medium powder, with a maximum in the distribution curve at 1½ μ, takes rather longer. With the coarse powder, whose particles are nearly all greater than 2 μ, the alloy is still porous after 3 hrs. at 1500° C.

Effect of Pressure.

The pressure employed determines the density of the pressed block, but has little effect on the final density, since with low pressures the shrinkage is greater. The effect of pressure on both shrinkage and final density is shown in Table V for a mixture containing copper 2, nickel 5, and tungsten 93 per cent., sintered for ½ hr. at 1400° C. A pressure of 5 tons/in.^{2} is sufficient to make the pressed pieces easily handled, the density being then about 10 grm./c.c.

TABLE V.—*Effect of Pressure on Percentage Shrinkage and Density.* (*Copper* 2, *Nickel* 5, *Tungsten* 93 *Per Cent. Alloy. Sintered for* ½ *hr. at* 1400° C.)

Pressure, Tons/in.^{2}.	Linear Shrinkage, Per Cent.	Density, Grm./c.c.
2·5	17·9	16·7
10	15·7	16·9
15	14·7	16·9
20	13·1	17·0

PLATE XXIV.

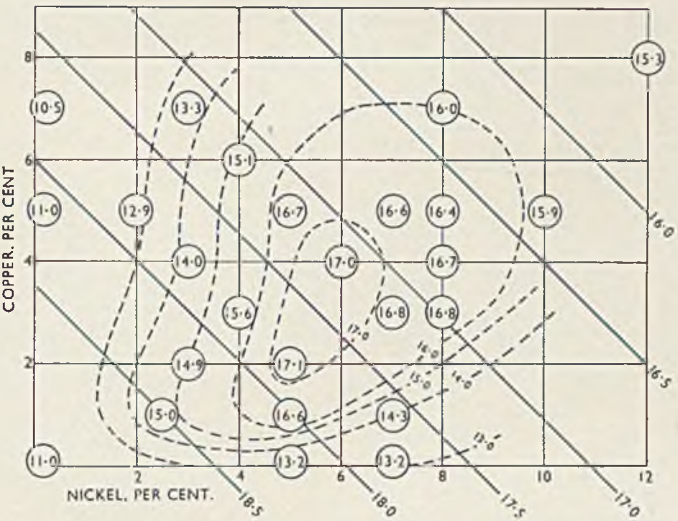


FIG. 6.—Effect of Composition on Density of Copper–Nickel–Tungsten Alloys.

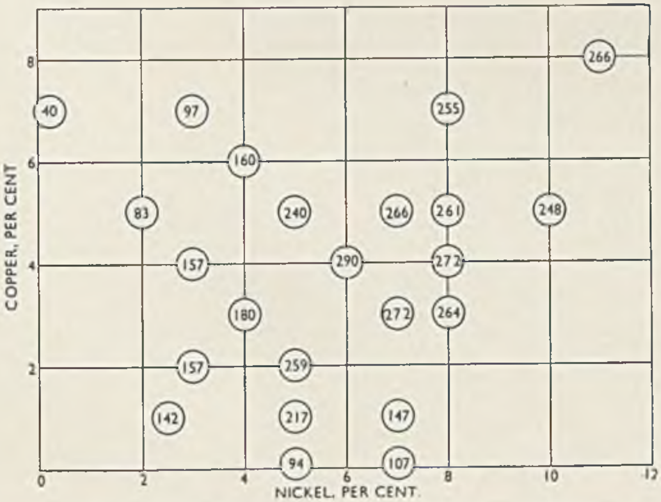
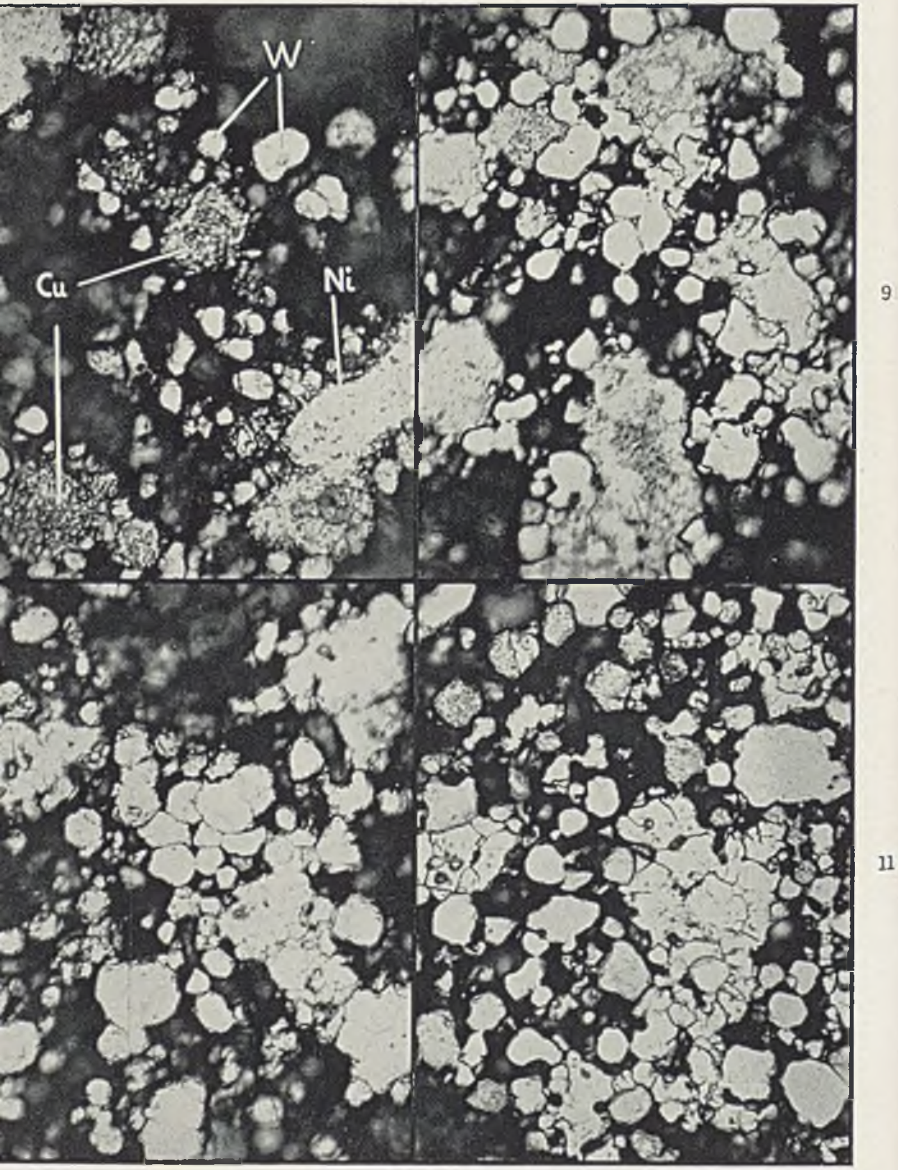


FIG. 7.—Effect of Composition on Brinell Hardness of Copper–Nickel–Tungsten Alloys.

[*To face p.* 24

PLATE XXV.



s. 8–11.—Copper 2, Nickel 5, Tungsten 93% after Sintering at the Temperatures Indicated Below. Etched Hydrogen Peroxide. × 500.

FIG. 8.—1 hr. at 950° C.
FIG. 9.—1 hr. at 1050° C.
FIG. 10.—1 hr. at 1150° C.
FIG. 11.—1 hr. at 1250° C.

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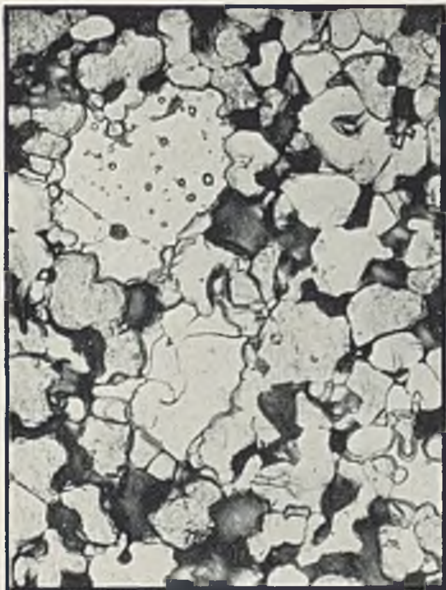

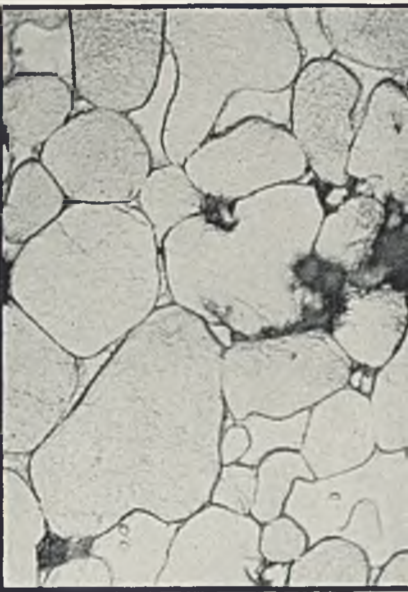

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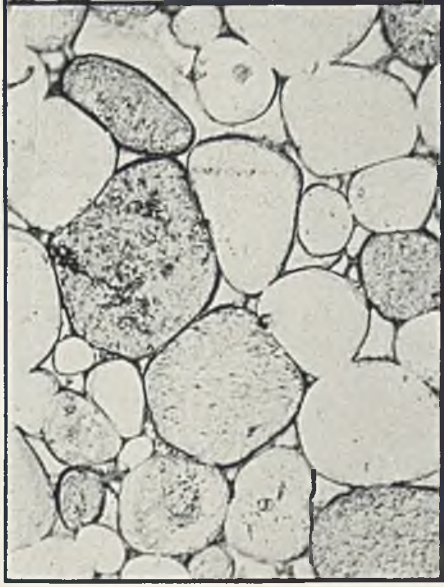

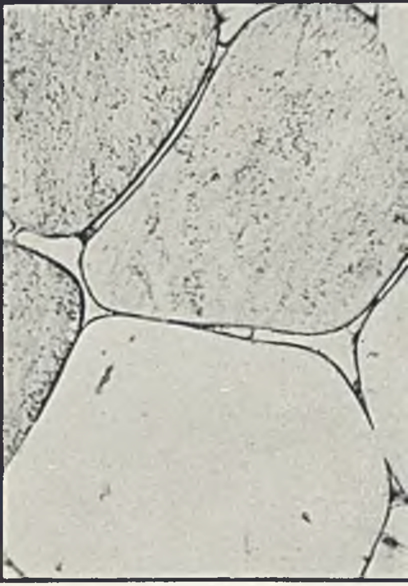

FIGS. 12-15.—Copper 2, Nickel 5, Tungsten 93% after Sintering at the Temperatures Indicat
Below. Etched Hydrogen Peroxide. × 500.

FIG. 12.—1 hr. at 1300° C.
FIG. 13.—1 hr. at 1350° C.
FIG. 14.—1 hr. at 1400° C.
FIG. 15.—6 hrs. at 1400° C.

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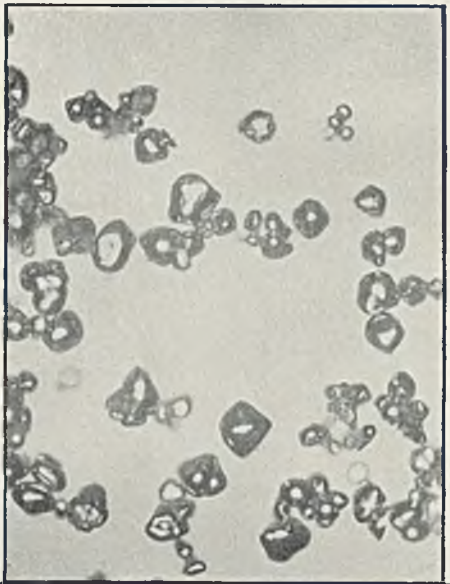

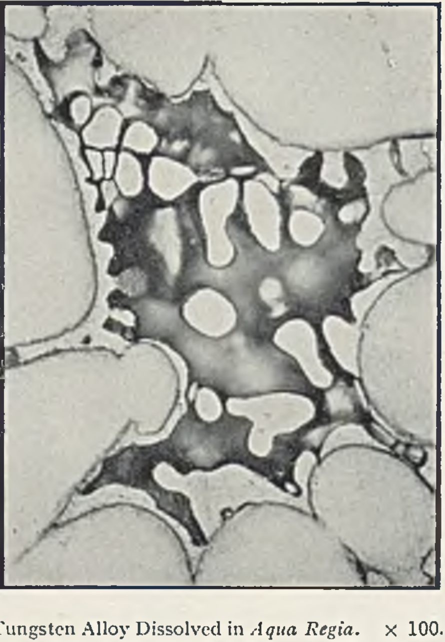

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s. 16.—Tungsten Grains from Copper–Nickel–Tungsten Alloy Dissolved in *Aqua Regia*. × 100.
s. 17.—Copper 2, Nickel 5, Tungsten 93% Alloy. Etched Alkaline K_3FeCy_6. × 500.
. 18.—Copper 8, Nickel 12, Tungsten 80% Alloy, Showing Cored Structure of Solid Solution. Etched Acetic-Nitric Acid. × 1000.

PLATE XXVIII.

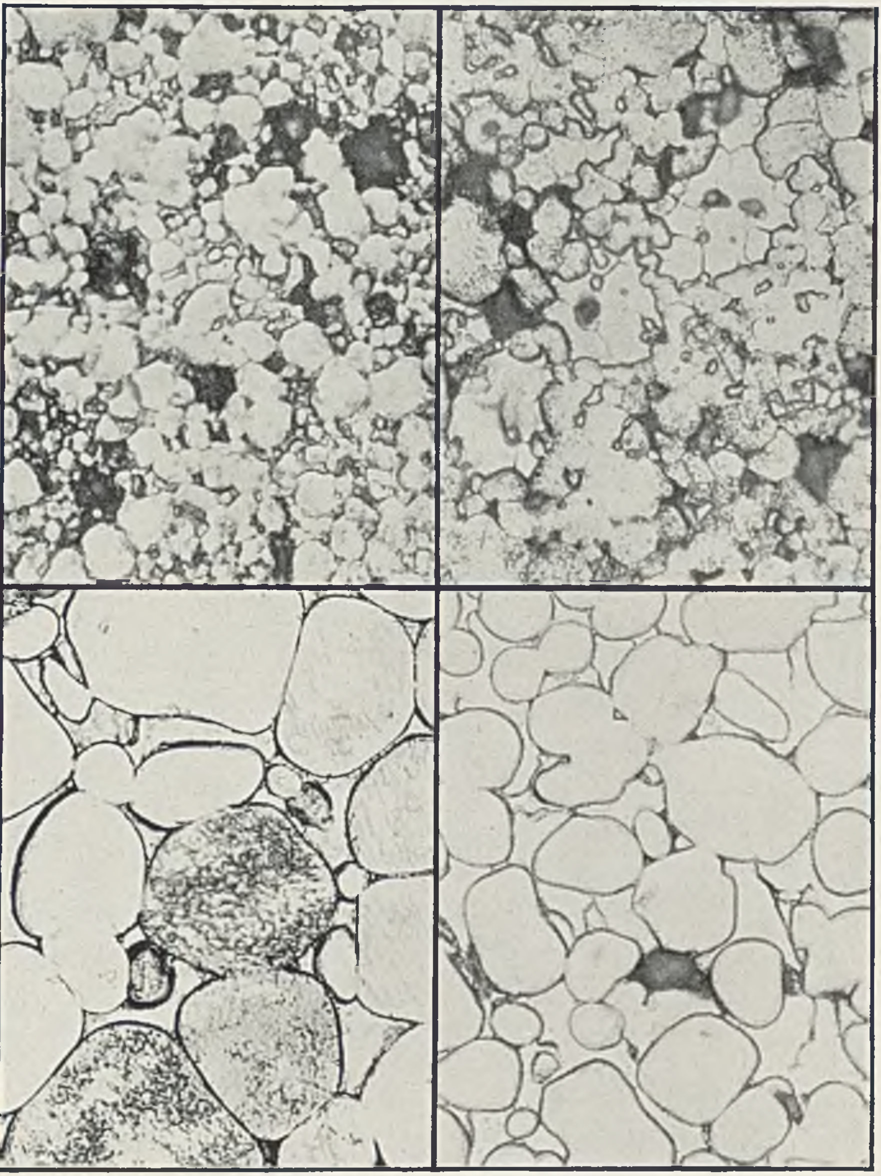
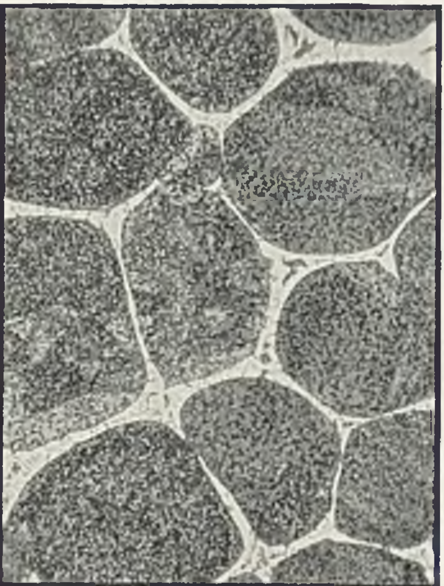


FIG. 19.—Copper 7, Tungsten 93%. Etched H_2O_2. × 500.
FIG. 20.—Nickel 7, Tungsten 93%. Etched H_2O_2. × 500.
FIG. 21.—Copper 1, Nickel 5, Tungsten 94%. Etched H_2O_2. × 500.
FIG. 22.—Copper 8, Nickel 12, Tungsten 80%. Etched H_2O_2. × 500.

PLATE XXIX.



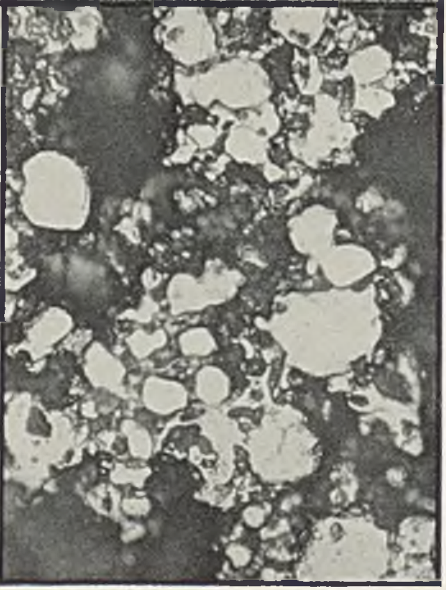


FIG. 23.—Copper 5, Nickel 2, Tungsten 93%. Etched H_2O_2. × 500.
FIG. 24.—Silver 20, Copper 80%, Sintered ½ Hr. at 900° C. Etched Chromic-Sulphuric Acid. × 500.
FIG. 25.—Copper 20, Iron 80%, Sintered 3 Hrs. at 1400° C. Etched $FeCl_3$. × 500.
FIG. 26.—Silver 4, Cobalt 6, Tungsten 90%. Etched H_2O_2. × 500.

Effect of Composition.

In the case of a simple mixture consisting of x per cent. of a metal of density d_1 and y per cent. of a metal of density d_2, the "theoretical" density, d_t, is given by:

$$d_t = \frac{100}{\frac{x}{d_1} + \frac{y}{d_2}}$$

The "theoretical" densities of mixtures containing various amounts of tungsten are shown in Fig. 5. Since the lowest value of density of practical interest is about 16 grm./c.c., only alloys containing more than 80 per cent. tungsten have been investigated. A series of alloys was made up under the standard conditions—that is, sintering for 1 hr. at 1400° C.—and the results of density measurements are shown in Fig. 6 (Plate XXIV). The numerals represent the measured densities, and curves have been drawn to show compositions of approximately equal density. The lines marked at 45° show the "theoretical" densities.

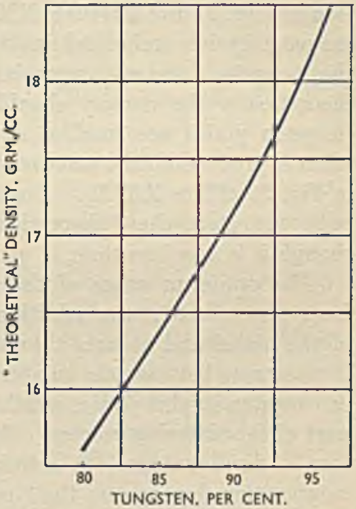


Fig. 5.—"Theoretical" Densities of Copper–Nickel–Tungsten Alloys.

Certain generalizations can be made from these results when considered in conjunction with the microstructures. The alloys containing tungsten and copper only do not shrink during sintering and show no change in density, although they become appreciably stronger. The only effect of sintering is that the molten copper wets the tungsten particles and cements them together, but there is practically no change in the size of the tungsten particles and no reduction in porosity, as shown in Fig. 19 (Plate XXVIII). Alloys containing tungsten and nickel only, show a small shrinkage, and with 3–10 per cent. nickel the density increases to about 13 grm./c.c. After polishing, these alloys have a more metallic appearance than those containing copper only. The microstructure of the 5 per cent. nickel alloy (Fig. 20, Plate XXVIII), shows a considerable increase in the size of the tungsten particles. The nickel has segregated into comparatively large areas, so that the tungsten particles are not completely wetted by it, and a large amount of porosity is apparent. This seems to be due to the melting point of the nickel phase being raised above the sintering temperature by solution of tungsten in the nickel, so that no liquid phase is present, for if the sintering is carried out at 1500° C., these alloys have the same structure as fully-sintered copper–nickel–tungsten alloys and densities up to 17 grm./c.c.

In alloys containing both copper and nickel, two factors appear to be of importance : the ratio of nickel to copper, and the total percentage of these metals present. Fig. 6 (Plate XXIV) shows that the maximum density is obtained when the nickel–copper ratio is about 2 to 1, and the tungsten content is between 89 and 93 per cent. The microstructures of alloys in this range are similar, and typical examples are seen in Figs. 21 and 22 (Plate XXVIII). These show the usual rounded tungsten grains embedded in the copper–nickel–tungsten matrix. If the tungsten content appreciably exceeds 95 per cent., although theoretically the density should be higher, it is actually less. The tungsten grains are smaller, and there is more porosity. The same effect is produced if the amount of copper exceeds that of nickel, as seen in Fig. 23 (Plate XXIX). On the other hand, with less than 89 per cent. tungsten, the "theoretical" density is more nearly attained, though it is now less than 17 grm./c.c.

The optimum value of the nickel–copper ratio appears to result from two effects : the addition of copper lowers the melting point of the nickel and ensures the presence of a liquid phase which is able to penetrate between the tungsten grains ; and it reduces the solubility of tungsten in this phase, which, as will be shown later, is an essential part of the sintering process. Too high a proportion of copper is therefore a disadvantage. It should be pointed out that the optimum composition depends on the choice of sintering conditions, and would be nearer the tungsten corner of the ternary diagram if the time or the temperature were increased.

The Brinell hardness of each alloy was measured, and the results are shown in Fig. 7 (Plate XXIV). It will be seen that there is a very close parallel between hardness and density. The hardness is mainly determined by the porosity, but when the latter is low it would appear to be an additive property of the hardness of the components. The Brinell hardness number of a copper–nickel alloy saturated with tungsten (tungsten 17, copper 28, and nickel 55 per cent.) is about 150, whilst that of annealed tungsten is 400.

Mechanism of Sintering.

From the data given in the previous paragraphs, it appears that sintering, in alloys within the range of optimum composition, involves the following stages : Between 1000° and 1100° C., the copper and nickel particles become alloyed by diffusion, and some cohesion with the tungsten grains takes place. Very little further change occurs until the temperature reaches the melting point of the copper–nickel alloy, but above this temperature a very remarkable change takes place. The tungsten particles are rapidly dissolved by the liquid phase, but tungsten is re-precipitated on certain nuclei, which develop into the characteristic large, rounded grains. This process continues until all the original fine tungsten particles have disappeared, and are replaced by fairly uniform grains with diameters about 100 times those of the original particles. At the same time all the remaining voids are eliminated.

That the tungsten grains grow by this process of solution and precipitation is confirmed by the behaviour of alloys containing copper only. Here there is no doubt of the presence of a liquid phase which "wets" the tungsten, but there is no solubility and no growth. With nickel only there is the necessary solubility, but, unless the temperature is above 1450° C., there is no liquid phase and the process of growth is slow and incomplete. When the ratio of nickel to copper greatly exceeds 2 to 1, the solubility is so much reduced that the process is again very slow.

At first it is not obvious why the tungsten grains should dissolve, only to be thrown out of solution again. The explanation is to be found in the surface energy of the system. It has been well established that for very small crystals the interfacial tension between the crystals and their saturated solution is greater than that for large crystals.[11] This is the reason why small crystals are more soluble than large ones. The surface tension is related to the solubility by the equation[12] :

$$\sigma = \frac{RT\Delta r}{2M} \cdot \log \frac{L_w}{L}$$

where σ is the interfacial tension, Δ is the density and M the molecular weight of the solid, L is the normal solubility, and L_w the solubility of small particles of radius r. Measurements made in different ways and with different materials agree in demonstrating that this effect is only shown by crystals whose diameters are less than 1 μ, and that below this size it increases very rapidly as the diameter decreases. For example, the solubility in water of gypsum crystals 0·6 μ in diameter is 18 per cent. greater than that of crystals 4 μ in diameter, which have the normal solubility.[13]

These facts offer a simple explanation of the changes observed in the alloys under investigation. The fine tungsten particles dissolve in the copper–nickel phase to give a solution which is supersaturated with respect to the larger tungsten grains, which therefore act as nuclei for precipitation and develop into the large, rounded grains. The observed effect of the size of the tungsten powder used is in remarkable agreement with this hypothesis. The data given in Table IV show that the density is only slightly less when the mean particle size is increased from ½ to 1½ μ. On the other hand, with the coarse powder containing very few particles less than 1 μ, comparatively little growth takes place, even after prolonged heating at 1500° C. This must be attributed to the fact that as soon as all the small particles have been dissolved there is no longer the difference in solubility essential to growth. If this picture is correct, we should expect that the peculiar type of structure shown by the copper–nickel–tungsten alloys would also be obtained with other alloy systems which fulfil the same equilibrium conditions, and would not be found among those which do not. A few other systems have therefore been examined from this point of view.

OTHER ALLOY SYSTEMS.

The essential features of binary systems that would be expected to behave in the same way as the nickel–tungsten system are:

(*a*) An appreciable difference in melting point of the two components, and

(*b*) The higher melting metal (*B*) should be soluble in the lower melting metal (*A*), but *A* should be insoluble, or have a very small solubility, in *B*.

Very few binary systems fulfil these conditions, but the silver–copper and copper–iron systems appear to do so.

Silver–Copper Alloys.

The solid solubility of copper in silver, and of silver in copper, is about 9 per cent. at the eutectic temperature, but less than 1 per cent. at room temperature. An alloy containing 20 per cent. silver should therefore provide the necessary liquid phase capable of dissolving copper at 900° C. Such a mixture was made up and sintered for ½ hr. at 900° C. A shrinkage of 15 per cent. took place and the density was found to be 8·8 grm./c.c., the "theoretical" value being 9·2 grm./c.c. The microstructure of the alloy is seen in Fig. 24 (Plate XXIX). It has the typical appearance of the copper–nickel–tungsten alloys. The large, rounded grains of copper (saturated with silver) are embedded in a matrix of silver from which a little excess copper has been precipitated as eutectic. The change in density and the structure are therefore typical of the solution-precipitation process.

Copper–Iron Alloys.

At 1400° C. liquid copper can hold about 20 per cent. iron in solution. The solid solubility of copper in iron at this temperature is about 9 per cent. A mixture was made up containing copper 20 and iron 80 per cent., and sintered for 3 hrs. at 1400° C. The density increased to 7·3 grm./c.c. ("theoretical" density being 7·85 grm./c.c.), and the structure, seen in Fig. 25 (Plate XXIX), again has the typical form.

Silver–Cobalt–Tungsten Alloys.

This system was selected because, in spite of the similarity between nickel and cobalt, and between copper and silver, the silver–cobalt and copper–nickel systems are entirely different, silver and cobalt being immiscible even in the liquid state. Moreover, cobalt, unlike nickel, is soluble in tungsten, with which it forms a series of intermetallic compounds. The necessary conditions for the solution-precipitation type of growth do not therefore exist in the ternary alloy. A mixture containing silver 4, cobalt 6, and tungsten 90 per cent. was sintered for 1 hr. at 1500° C. Very little shrinkage took place, the final density being 10·7 grm./c.c., compared with the "theoretical" value of 17·5 grm./c.c. The rather confused structure seen in Fig. 26 (Plate XXIX) is quite unlike that of the corresponding copper–nickel alloy.

PHYSICAL PROPERTIES OF THE COPPER–NICKEL–TUNGSTEN ALLOYS.

The physical properties of the copper–nickel–tungsten alloys, within the range of composition considered, are very similar, provided that the "theoretical" density is closely approached. In Table VI are given the results of measurements made on a typical alloy containing copper 4, nickel 6, and tungsten 90 per cent. The high values of tensile strength and yield-point obtainable in a pressed and sintered material may be noted particularly.

TABLE VI.—*Physical Properties of Copper* 4, *Nickel* 6, *Tungsten* 90 *Per Cent. Alloy.*

Tensile strength, tons/in.^{2}	40
Yield-point, tons/in.^{2}	37
Elongation, per cent. on 1 in.	4
Elastic modulus, lb./in.^{2}	32×10^6
Brinell hardness number	290
Density, grm./c.c.	17·1
Coefficient of expansion	$5{\cdot}6 \times 10^{-6}$
Thermal conductivity, C.G.S. units	0·25
Specific resistance, ohm. cm.	$1{\cdot}16 \times 10^{-5}$
Electrical conductivity, ohm.$^{-1}$ cm.$^{-1}$	$0{\cdot}86 \times 10^5$

REFERENCES.

[1] C. J. Smithells, W. R. Pitkin, and J. W. Avery, *J. Inst. Metals*, 1927, **38**, 85.
[2] F. Sauerwald, *Z. anorg. Chem.*, 1922, **122**, 277.
F. Sauerwald, *Z. Elektrochem.*, 1923, **29**, 79.
F. Sauerwald, *Z. Metallkunde*, 1924, **16**, 41.
F. Sauerwald and E. Jaenichen, *Z. Elektrochem.*, 1924, **30**, 175.
F. Sauerwald and G. Elsner, *Z. Elektrochem.*, 1925, **31**, 15.
F. Sauerwald and J. Hunczek, *Z. Metallkunde*, 1929, **21**, 22.
F. Sauerwald and St. Kubik, *Z. Elektrochem.*, 1932, **38**, 33.
F. Sauerwald and L. Holub, *Z. Elektrochem.*, 1933, **39**, 750.
[3] J. A. Hedvall, *Z. physikal. Chem.*, 1926, **123**, 33.
[4] W. Trzebiatowski, *Z. physikal. Chem.*, 1934, [A], **169**, 91; and 1934, [B], **24**, 75, 87.
W. Trzebiatowski, *Naturwiss.*, 1933, **21**, 205.
[5] R. Kikuchi, *Sci. Rep. Tôhoku Imp. Univ.*, 1937, [i], **26**, (1), 125.
[6] G. Masing, *Z. anorg. Chem.*, 1909, **62**, 265.
[7] W. D. Jones, "Principles of Powder Metallurgy," London: 1937.
[8] F. Skaupy, "Metallkeramik," Berlin: 1930.
[9] J. C. McLennan and C. J. Smithells, *J. Sci. Instruments*, 1935, **12**, 159.
C. J. Smithells, *Nature*, 1937, **139**, 490.
L. G. Grimmett and J. Read, *Brit. J. Radiology*, 1935, [N.S.], **8**, 661.
[10] D. Hanson and W. T. Pell-Walpole, *J. Inst. Metals*, 1937, **61**, 265.
[11] For summary of evidence see Freundlich, "Colloid and Capillary Chemistry," (English Edn.), London: 1926, p. 155.
[12] W. Ostwald, *Z. physikal. Chem.*, 1900, **34**, 495.
[13] G. A. Hulett, *Z. physikal. Chem.*, 1901 **37**, 385; and 1904, **47**, 357.

DISCUSSION.

(*Condensed.*)

DR. W. D. JONES,* M.Eng. (Member): The authors have used three different powders, tungsten, nickel, and copper, and they have given a considerable description concerning particle size and pressures used in manufacture, but there are many properties which have to be stated before it is possible to define what a powder is like, and some of these are not mentioned. For example, in using a metal powder it is necessary to know something about the particle shape, the density, the flow factor, hardness, etc., and these necessitate knowledge of the process of manufacture of the powder. None of these details has been reported by the authors.

The basis of the manufacture of this alloy depends on the shrinkage during sintering, and this shrinkage does not seem to be very well understood. The factors which control shrinkage are rather complex, and require more statement than is given in this paper. In point of fact, no real attempt has been made by the authors to explain why shrinkage occurs during sintering of their alloy. I have found that shrinkage can be dependent to some extent on purity; there is nothing in the paper about the analysis of the powders. It is quite customary to say something about the analysis and purity of an alloy when describing it.

The principle of solution of very fine particles and reprecipitation in the form of large particles, has been familiar for many years in connection with

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* Sir John Cass Technical Institute, London, E.C. 3.

the recrystallization of alloys, but I have never before seen it demonstrated so clearly.

The authors, however, should not allow themselves to believe that this theory explains in any way the shrinkage that occurs. Mr. Price has shown that after 1 hr. at 1400° C., the tungsten particles are the size of golf balls, and after 6 hrs. they look like Rugby footballs. Does that mechanism which the authors describe, the solution of particles less than 1 μ, also explain that change between 1 and 6 hrs.? Does this represent the continued precipitation from the supersaturated liquid phase?

There are two statements in the paper which might have been better expressed. It is stated on p. 240 that "The effect of pressure and of annealing on the hardness of pressed metal powders has been investigated by Kikuchi, but, since reducing atmospheres were not employed during annealing, the results were complicated by the presence of oxide films." Why should they not have been complicated by the presence of oxide films? I feel that that is not a satisfactory justification for dismissing the work of Kikuchi. In view of the fact that he obtained very good physical properties, I feel that, on the contrary, he is to be congratulated on carrying out his work in the presence of oxide films. Will the authors say whether the use of hydrogen is absolutely essential to the manufacture of this alloy, and whether attempts have been made to make it in less reducing or neutral atmospheres? By the combined use of a certain amount of pressure, could it be done in an oxidizing atmosphere?

The values for tensile strength which the authors obtained (40 tons/in.^{2} and 4 per cent. elongation) are very good indeed, but it is stated that "the high values of tensile strength and yield-point obtainable in a pressed and sintered material may be noted particularly." That might have been better put. It gives the impression that in the authors' opinion it is very unusual to obtain good physical properties with a sintered material, which is quite incorrect. I have obtained tensile strength values of between 30 and 40 tons/in.^{2} with ordinary nickel- and iron-base alloys. The authors could have mentioned the elongation, which is good. In general, sintered alloys have rather low elongation, unless special care is taken in their manufacture.

In discussing this paper, I am under a slight disadvantage in not knowing what is coming next. I may have criticized some things which will be satisfactorily explained in Part II of the paper. For example, will the physical properties of this alloy with respect to radium emanation be dealt with subsequently, or should that be included in this paper?

Dr. W. J. P. Rohn [*] (Member): It might be well to emphasize how wonderfully this material can be machined. It behaves in a manner which one would expect only from tough steel. I am sure that these alloys not only arouse much interest in the scientific field, but will find large uses in industry.

Mr. E. H. Bucknall,[†] M.Sc. (Member): In its title the paper is limited to sintering in the presence of a liquid phase, and the importance of the liquid in the process is rightly emphasized. I differ somewhat from the authors regarding the interpretation of the microstructure of the final product at 1400° C., to which they refer as a peculiar type of structure, and which one gathers they regard as a quenched (solid plus liquid) structure. I submit that almost any two-phase system obtained by sintering will have a reticulated structure, in which the second phase surrounds grains of the first and equilibrium conditions apply at the interface. The suggestion that the

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[†] Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

second phase was liquid at 1400° C. seems to be discounted by the evidence that an X-ray study indicated that it contained 17 per cent. tungsten. From Fig. 3, which shows the melting points (or are they really freezing points ?) of alloys containing copper, nickel, and tungsten, with a nickel–copper ratio of 2½ : 1, it will be seen that at 1400° C. the greatest amount of tungsten possible in the liquid is 8 per cent. Combining this information with that given in Figs. 1 and 2, it seems possible to make a sketch-map of the equilibrium relations of copper, nickel, and tungsten at 1400° C. Fig. A indicates the phase ultimately produced in equilibrium with tungsten in the 5 : 2 alloys to be the solid α phase.

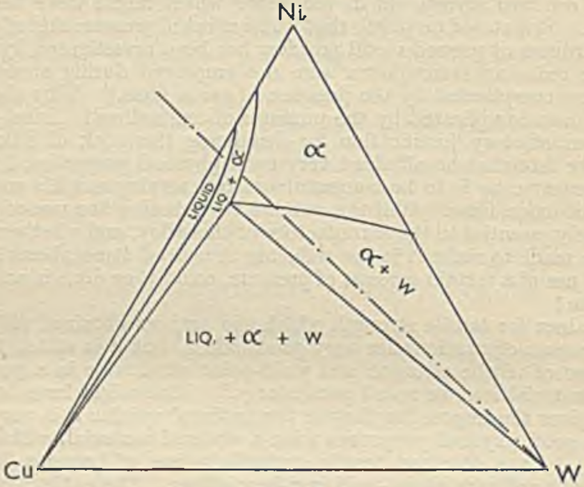

Fig. A.

When the pressed copper–nickel–tungsten powder mixture is heated, some copper probably melts at 1083° C., without diffusion of nickel in the solid state, and this liquid dissolves nickel and becomes solid. At a higher temperature, more nickel is dissolved in the liquid, which then takes up tungsten and again solidifies. In this sense, sintering is accompanied by the presence of liquid. The low temperature liquid has its effect in the results shown in Table I, and especially those obtained at 1300° C., when the authors state that only the copper and nickel have been involved in the structural changes. After sintering at 1300° C., the material had shrunk 6 per cent. of a total 18 per cent. This is in contrast with the proportion of copper and nickel present, 7 per cent., which might be expected to be associated with $7/100 \times 18 = 1{\cdot}3$ per cent. shrinkage if the liquid did not have a specific effect on the shrinkage.

It would be interesting to have the results of similar experiments conducted with tungsten and a copper–nickel alloy, so that initial liquid would appear only, say, above 1340° C. It seems to me that the mechanism of shrinkage probably involves mainly the solution of corners of the tungsten granules and the pulling together of the tungsten by surface tension forces. I feel that the explanation involving differential solubility of large and small pieces is less happy here, where there is a solubility of 17 per cent., than in cases of very small solubility, where use has often been made of it by chemists.

Dr. J. C. Chaston,* B.Sc., A.R.S.M. (Member): I am not at all happy about the evidence which has been brought forward to support the theory that grain growth occurs in these pressed compacts owing to the difference in solubilities of a small particle and a large particle. An opportunity has been lost here, for it seems that in powder metallurgy there is an ideal method of obtaining conclusive experimental evidence of this hypothesis. Have the authors thought of making up a compact in which all the tungsten particles were of very nearly the same size, and seeing whether in that grain growth occurs?

There is also mention of 1 μ as a limiting size, below which this differential solution pressure really becomes important. In Table III details are given of coarse powders in which only 1 per cent. was less than 1 μ in average diameter; yet, according to the table, while complete compaction and sintering were not obtained, there was quite a large amount of shrinkage and, presumably, grain growth. If it is only the particles less than 1 μ which come into play in this connection, one would not expect any grain growth at all to take place.

I am sure that the authors would not suggest that grain growth in a pressed compact occurs only when there is a liquid present. However, the manner in which this paper is worded in parts might lead one to believe that for grain growth to take place it is essential that there should be present a liquid in which the tungsten particles are soluble. I would like to put it the other way, that grain growth in a pressed compact always occurs on heating, provided that there are not between the grains some materials which act as barriers to prevent grain growth. If there is present a liquid phase in which the tungsten particles are not soluble, the liquid acts as a barrier to grain growth; but if the tungsten is soluble in the liquid, or, alternatively, if there is no liquid present so that the particles are in intimate contact, grain growth occurs.

Dr. E. Voce,† M.Sc. (Member): Does the presence of the combined phase do anything to mitigate the attack of oxygen on the tungsten; would the alloy as a whole be more resistant to oxidation than ordinary tungsten for high-temperature service? Have the authors considered the addition of any other material which might enhance resistance to oxidation, such, for instance, as a comparatively small amount of aluminium to the copper and nickel, or possibly of beryllium? It seems possible, but I do not know whether in fact it is, that sufficient protection of the tungsten might be gained to permit the exploitation of its high refractoriness without the necessity for special atmospheres. For such purposes the density would be of secondary consideration.

The President (Dr. Desch): It will be remembered that in the very first work of Ewing and Rosenhain an attempt was made to explain grain growth in such a metal as lead by the presence of low melting material in thin films between the grains. It was afterwards found not to be essential that there should be any thin film between the grains, and that grain growth could occur without it. Here, however, is an instance of grain growth being brought about at temperatures far below those at which grains of tungsten will grow by themselves, and that has been brought about by material between the grains. The explanation given is exceedingly interesting. There are certain cases in non-metallic systems in which recrystallization does go on by the presence of a very small quantity of solvent between the grains, namely

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† Investigator, British Non-Ferrous Metals Research Association, London.

in the setting of cements and plasters, but there is the difference there that the substance which goes into solution is a different modification from that which comes out. The hemihydrate of calcium sulphate goes into solution and comes out as the dihydrate, but it takes only a small quantity of water between the grains to bring about complete recrystallization. Here we have, at temperatures of 1400° C. or so, an extremely complete recrystallization in which the original nuclei of the tungsten disappear altogether, giving perfect single crystals, as shown by the etch-figures. Whether that is to be attributed to the difference in solubility between small and large particles is, of course, not proved, but it is an interesting suggestion and suggests further lines of research.

Dr. Smithells (*in reply*): Our object in presenting this paper is to bring forward problems of metallurgical or scientific interest, and not to discuss what is only of technical interest. We have used commercial powders and also prepared them ourselves by hydrogen reduction. The results described in the paper will be substantially obtained with any powders, but the best results will only be obtained with the finest and purest powders.

With regard to shrinkage and density, there is an interesting fact which is not immediately obvious, namely, that the presence of only 2 per cent. of an impurity with a density like that of aluminium or silicon will reduce the theoretical density from, say, 17·8 to 16·4, owing to the enormous difference in the volume of the same weight of tungsten and of such an impurity. If commercial powders are used they must therefore be fairly pure.

I am glad that Dr. Jones supports our explanation of the recrystallization process. We feel very satisfied from all our observations that it is correct. As the President pointed out, tungsten at 1400° C. is practically cold, and, though in a hard-drawn wire it is possible to obtain recrystallization at that temperature, there would be very little increase in grain-size in a pressed and sintered bar of pure tungsten. Another fact which supports it is the extraordinary speed with which the structure develops. In certain compositions it is possible to grow these enormous grains from fine powders in 5 minutes, whereas with pure tungsten grain growth would not take place in that time.

With regard to Dr. Jones's question, I would say that we had not intended to submit anything about the application of these alloys to radium beam therapy to this Institute, since it is merely a particular application in the medical profession. These alloys are used far more extensively in engineering, and some information has been published elsewhere.* As Dr. Jones said, from a description it sounds easy to carry out these processes, but in practice there are a great many difficulties.

The curve to which Mr. Bucknall refers is a melting-point curve. The determination was crude, and we do not claim high accuracy for the values obtained. Mr. Bucknall's criticism is based on the fact that there seems to be a difference of about 20° C. between the melting points of saturated copper–nickel–tungsten alloys and the sintering temperatures at which we maintain that there is a liquid phase present. I think, however, that Mr. Bucknall is wrong in assuming that a liquid phase is neither present nor necessary. It may not be necessary for the whole of the nickel to be dissolved in the copper before any structural change can take place. The remarkable feature is that there is a critical range which coincides with the melting range of the copper–nickel phase, and as soon as the liquid phase is capable of dissolving tungsten we have this sudden change in density and structure. I think that we have proved that the presence of this liquid phase is essential for the development of this structure.

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* C. J. Smithells, *Nature*, 1937, 139, 490. J. C. McLennan and C. J. Smithells, *J. Sci. Instruments*, 1935, 12, 159. *Engineering*, 1937, 144, (3751), 622.

Dr. Chaston is very doubtful about the fact of the greater solubility of small particles than large ones. It is possible to doubt other people's experiments indefinitely, but when a great many people have established something over and over again, ultimately it is accepted. Ostwald and others, about the year 1900, made very careful measurements of the actual solubility and equilibrium between certain particle sizes and their saturated solutions, and established for a large number of inorganic salts this effect of particle size. I have always believed it, and I see no reason to doubt it. I am prepared to take it a little further and apply it to metals; I do not see why we should confine that fact simply to the salts which happen to have been investigated. There are theoretical reasons for it, as well as experimental evidence. Our results show that this critical size of about 1 μ applies as well in our case as in the case of salts of other materials. We do not mean to imply that we think that a liquid phase is always necessary for sintering. In an earlier paper * on the sintering of tungsten there was no question of a liquid phase, and we were actually criticized for stating that we obtained grain growth at low temperatures; now we are accused of saying that we do not believe that we can obtain grain growth in the absence of a liquid phase. The structure obtained in these alloys is the result of having a liquid phase present, and it is not obtained without a liquid phase.

It was suggested that we should get exactly this type of structure even if we did not have a liquid phase, but I have not yet seen a photomicrograph which shows this structure, except in the one case quoted in the paper, in which there was a liquid phase present.

In reply to Dr. Voce, there is at present no application where oxidation-resistance is important. The alloys have good resistance to atmospheric, sea-water, and other forms of corrosion because the copper–nickel–tungsten matrix and tungsten itself are particularly non-corrodible materials, but we know of no potential application of this material at elevated temperatures, Its resistance to oxidation is no better than that of tungsten, which is very poor. If it is heated to 200° C., it becomes tarnished, and at red heat it oxidizes more rapidly because no protective oxide is formed.

CORRESPONDENCE.

Dr. Mike A. Miller † (Member): Several of the wetting problems encountered by the authors are very interesting. It is stated that: " . . . in an atmosphere of hydrogen, molten copper 'wets' tungsten, and when tungsten contacts are brazed on to steel screws in this way a strong joint is obtained. This is, perhaps, a little surprising if copper is completely insoluble in tungsten." The authors further state that: " . . . an essential factor in the elimination of voids during sintering is that the liquid phase should not only wet the tungsten, but actually dissolve it." The proof for these statements is shown in Fig. 19 (Plate XXVIII), and it is noted that though the molten copper wets the tungsten particles and cements them together, there is no change in the size of the tungsten particles and no reduction in porosity, *i.e.* no solubility of tungsten and no growth of tungsten particles.

What do the authors mean when they use the term "wet"? "Wetting" is ordinarily defined as the phenomenon which occurs when a solid phase and a liquid phase come into contact in any manner, so as to form a solid–liquid interface.‡ It is apparent, however, that the most logical expression for the

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* C. J. Smithells, W. R. Pitkin, and J. W. Avery, *J. Inst. Metals*, 1927, 38, 85.

† Research Laboratories, Aluminum Company of America, New Kensington, Pa.

‡ F. E. Bartell, "Colloid Chemistry," Alexander, Vol. III, 1931, p. 41.

degree of wetting will involve the amount of change in surface free energy which occurs when the solid and liquid are brought together; the manner in which the two phases are brought together will, therefore, be of importance also.

From this point of view, spreading wetting may involve any value of the angle of contact from zero to 180°, as given by the Young formula:*

$$S_1 - S_{12} = S_2 \cos \theta_{12},$$

where S_1 and S_2 are the surface tensions of the solid and liquid, respectively, S_{12} is the interfacial tension between the solid and the liquid, and θ_{12} is the angle of contact. Accordingly, if copper *completely* wets tungsten, we would expect zero porosity when copper exists as a liquid phase. It is probable that incomplete wetting, with a finite (greater than zero) contact angle, actually takes place, so that, as in the wetting of pigment powders by their vehicles, all of the gas may or may not be displaced.†

It is common knowledge that it is not necessary for a fluid to dissolve a solid in order to wet it completely.

It may be of interest to make some approximate thermodynamic calculations involving the interfacial free energy relationships which exist in the system copper–nickel–tungsten. Unfortunately, we do not know exactly the liquid solubility–temperature function for this system. The authors have given a value of 16·8 per cent. tungsten for the 27·6 : 55·4 binary copper–nickel alloy. This value is of no use in the following calculations. If, however, the values given in Fig. 3 are plotted on the same diagram as Fig. 1, it will be noted that the melting point–per cent. tungsten curve follows the liquid–alpha phase boundary, though about 100° C. lower. This will be taken to mean a certain inter-relation between melting point and solubility.

The van 't Hoff isochore as applied to the change in melting point of a solution is:

$$\frac{d \ln L}{dT} = \frac{-Q}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or,

$$2{\cdot}3 \log L = \frac{Q}{RT} + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where L is the concentration at temperature T, and $-Q$ is the molal heat of solution or precipitation. It can easily be shown that from equation (1) we obtain:

$$\ln \frac{L_2}{L_1} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We can now solve for $-Q$ in one of two ways. We can plot $\log L$ *vs.* $1/T$ from the values given in Table A. Then, $-Q$ = slope × 2·303 R, where R is now 1·987 cal. Alternatively, we can solve equation (3) for $-Q$, by using values of L at two different temperatures. A glance at equation (3) indicates that only relative values of L are required, since L exists as a ratio.

The Ostwald–Thomson equation, given by the authors is written:

$$\frac{RT}{M} \ln \frac{L_2}{L_1} = 2\frac{S_{12}}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which RT has the usual meaning, M is the molecular weight of the solute, L_2 and L_1 are the molal concentrations of the solutions in equilibrium with particles of radii r_2 and r_1, respectively, ρ is the density of the solid, and S_{12}

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* Young, *Phil. Trans. Roy. Soc.*, 1805, **95**, 65.

† Bartell and Van Loo, *Indust. and Eng. Chem.*, 1925, **17**, 1051; and related papers.

TABLE A.

Per Cent. L.	Mols. L.	log L.	T° K.	$1/T$.	Slope.	$-Q$ calc., cal.	C calc.
0	—	—	1653	$6{\cdot}050 \times 10^{-4}$	$-48{,}000$	219,650	28·25
5	0·27	$-0{\cdot}5686$	1663	6·013			
10	0·54	$-0{\cdot}2676$	1683	5·942			
14	0·77	$-0{\cdot}1135$	1691	5·914			
17	0·92	$-0{\cdot}0362$	1695	5·900			

is the interfacial free energy. In cases where r_1 is large (*i.e.* approaches a plane surface), equation (4) reduces to :

$$ln\frac{L_2}{L_1} = \frac{2MS_{12}}{RT\rho r_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where now L_1 is the normal solubility.

Substituting the value L from the van 't Hoff isochore, equation (1), in equation (5), we obtain :

$$lnL_{(T)} = \frac{2MS_{12}}{RT\rho r} + lnL = \frac{2MS_{12}}{RT\rho r} + \frac{Q}{RT} + k \quad . \quad . \quad . \quad (6)$$

Equation (6) can be transformed in several ways *† into the equation :

$$T' = T\left(1 - \frac{2MS_{12}}{Q\rho r}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which T' is the temperature to which the solution can be under-cooled without precipitation. It is noted that as the particle size increases, $\left(\frac{2MS_{12}}{Q\rho r}\right)$ approaches zero, so that T' becomes equal to T, *i.e.* no under-cooling takes place.

Equation (4) shows that in a supersaturated solution of a given concentration at the temperature T, there is a definite radius, r, which will be in equilibrium with the solution. In short, there is an equilibrium particle size; the solution will be supersaturated towards particles larger than this equilibrium size, and unsaturated towards particles smaller than the equilibrium size.

Equation (7) shows that if the heat of solution is negative, that is, the solute dissolves with an absorption of heat, the function $\left(\frac{2MS_{12}}{Q\rho r}\right)$ will be less than one, so that under-cooling can take place. Now if the radius of the nuclei is less than the above-defined equilibrium radius, r, the temperature of under-cooling, T', will decrease without causing precipitation. The solution will eventually become supersaturated. One would expect the crystallization tendency to be very minute in such a solution if the degree of supersaturation were small. Particles with a radius less than the equilibrium value, r, which undoubtedly form very easily as a result of atomic or molecular collisions, are apparently unstable and immediately redissolve. On the other hand, particles having a radius larger than r, which are ordinarily stable, will not readily form because of their large size in proportion to atomic dimensions. It follows from equation (7), then, that as the temperature of undercooling decreases, the equilibrium radius also decreases, so that conditions are in-

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* Jones and Partington, *Phil. Mag.*, 1915, [vi], 29, 35.

† Chu-Phay Yap, "Colloid Chemistry," III, Alexander, 1931, p. 463.

creasingly favourable to the formation of a large number of particles. Thus, when crystallization actually does take place, its velocity is very large. Such a condition may be more nearly related to age-hardening of alloys than to the present case.

From equation (7), which may be written :

$$S_{12} = \frac{Q\rho r \Delta T}{2MT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\Delta T = T - T'$, and from equation (5), which may be written :

$$S_{12} = \frac{RT\rho r_2}{2M} \, ln \frac{L_2}{L_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

we obtain :

$$\Delta T = \frac{RT^2}{Q} \, ln \frac{L_2}{L_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The results summarized in Table B, and in the authors' Table IV, indicate that for given time periods, a temperature difference of 100° C. exists between fine and medium-sized particles. That is, there is the same amount of tungsten in solution at 1400° C. for fine particles as there is at 1500° C. for medium-sized particles. If it be assumed this temperature difference is equivalent to the amount of under-cooling, we can calculate S_{12} at 1400° C. for the small particles from equation (8), thus obtaining :

$$S_{12} = 73 \times 10^4 \text{ ergs/cm.}^2,$$

and from equation (10), we calculate the solubility of the small particles under the same conditions to be :

$$L_2 = 68 \text{ per cent.}$$

TABLE B.

Tungsten Powder.	Percentage.				Effective diam., μ.*	Effective r, μ.	Effective r, cm.
	0–1 μ	1–2 μ	2–5 μ	> 5 μ.			
	Average.						
	0·5 μ	1·5 μ	3·5 μ	—			
Fine . .	98	2	0	0	0·52	0·26	$2·6 \times 10^{-5}$
Medium . .	13	54	33	0	2·03	1·02	$10·2 \times 10^{-5}$
Coarse . .	1	11	27	61	>33·14	>16·57	$>165·7 \times 10^{-5}$

* Effective diam. = Per cent. × average diam.

It is apparent that the above-calculated values are in error to the extent that: (1) the Ostwald–Thomson equation is inapplicable;* (2) the under-cooling varies from the value used; and (3) a non-proportionality exists between the true solubility and the melting-point values employed. The thermodynamic calculations are presented mainly to indicate the possibilities of calculating equilibrium particle sizes from solubility data, and vice versa, as well as the evaluation of related functions. The data obtained would permit the prediction of the most favourable particle size for a given desired effect. For example, if it were desired to produce a structure having large grains, particles smaller than a certain size would be used; for the production of structures with fine grains, particles greater than a certain size must be employed—the calculations would tell us "how much smaller," and "how much greater."

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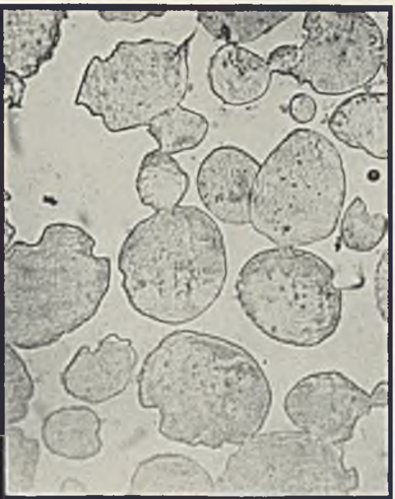
* Bigelow and Trimble, *J. Physical Chem.*, 1927, 31, 1798.

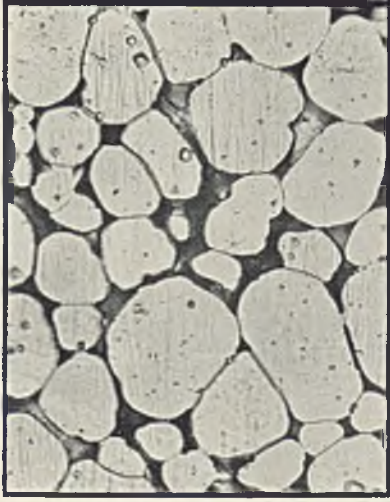
PLATE XXX.

B

C



D



E

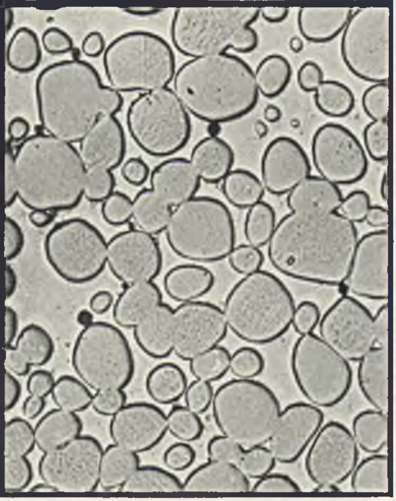


FIG. B.—Iron 10, Tungsten 90%. Sintered 1600° C., 5 hrs. Heated to 1650° C. for 5 minutes. Cooled to Room Temperature in 2 minutes. Etched in alk. $K_3Fe(CN)_6$. × 500.

FIG. C.—Cobalt 15, Tungsten 85%. Treated as Alloy in Fig. B. × 500.

FIG. D.—Nickel 4, Molybdenum 96%. Sintered 5 hrs., 1350° C. Heated to 1420° C. for 5 minutes. Cooled to Room Temperature in 2 minutes. Etched $H_2SO_4 + HNO_3$. × 500.

FIG. E.—Nickel 10, Tungsten 90%. Sintered 1500° C., 1 hr. Unetched. × 200.

[To face p. 262.

Mr. W. P. Sykes,* B.S., Met.E. (Member): Such structures as the authors show in Figs. 13, 14, *et seq.*, have been observed in several binary systems containing tungsten or molybdenum as one component. Among these are the systems tungsten–iron, tungsten–cobalt, tungsten–nickel, molybdenum–cobalt, molybdenum–iron, and molybdenum–nickel. In each of these, with the exception of the tungsten–nickel system, one or more intermediate phases occurs, formed by a peritectic reaction between tungsten or molybdenum and the liquid phase.

In each of these systems, moreover, with the exception of tungsten–nickel, the solid solubility of the second component in tungsten or molybdenum at the peritectic temperature is of measurable magnitude. It ranges from about 12 per cent. in the molybdenum–iron system to about 0·20 per cent. in the tungsten–cobalt system.

In explaining the origin of this type of structure, it seems scarcely proper, therefore, to specify as one of the requisites the complete or nearly complete absence of solid solubility in the tungsten component as the authors have stated on p. 252. In fact, the copper–iron system, an example cited by the authors, refutes this statement, since the solubility of copper in solid iron is given as 9 per cent. at 1400° C. This is obviously not a "very small solubility."

Figs. B, C, D, and E (Plate XXX) are offered as examples of this type of structure which occur in some of the binary systems mentioned. Except in the case of the tungsten–nickel system, an intermediate phase is formed by a peritectic reaction as previously stated.

The Authors (*in reply*): The wetting of a solid by a liquid occurs when the attraction of the solid for the liquid is greater than the attraction of the liquid for itself. This may be expressed in the form:

$$W_{SL} \geq 2Y_L$$

where W_{SL} is the work of adhesion between the solid and the liquid, and Y_L is the surface tension of the liquid.

Now, the work of adhesion is made up of three components:

$$W_{SL} = Y_S + Y_L - Y_{SL} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$Y_S = Y_{SL} + Y_L \cos\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where θ is the angle of contact;
combining (1) and (2) we have:

$$W_{SL} = Y_L(1 + \cos\theta)$$

Then because $W_{SL} \geq 2Y_L$, in the limiting case $\cos\theta = 1$ or $\theta = 0°$, *i.e.*, for perfect wetting, the angle of contact is zero. Now the angle of contact for molten copper and tungsten has been measured in the authors' laboratories by Mr. C. E. Ransley, and is found to have a positive value of the order of 50°. Thus, although there is appreciable wetting of the tungsten grains, it is evident that this is incomplete. There is adhesion, but not complete spreading. Dr. Miller states that "if copper *completely* wets tungsten we would expect zero porosity when copper exists as a liquid phase." It is evident that, even if copper did completely wet the tungsten, there must be a minimum percentage for the copper above which this ideal case would be obtained, and this minimum figure most certainly exceeds the value of 7 per cent., which is the highest that we have considered. Thus, a sintered alloy of 93 per cent. tungsten and 7 per cent. copper would be expected to have a porous structure, partly because the tungsten is

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* General Electric Company, Cleveland, O., U.S.A.

imperfectly wetted by the molten copper, and partly because there is insufficient copper to fill the interstices between the tungsten grains. We would, however, again emphasize the difference between mere wetting of the tungsten grains (even though this might be complete) and solubility of the tungsten grains in the copper. The latter is essential for the production of the typical alloy structure referred to in the paper.

Dr. Miller's thermodynamic calculations are interesting as suggesting other ways in which this subject might be approached. It would appear, however, that he has made a number of entirely unwarranted assumptions, which rather discount the value of his conclusions. In the first case, the van 't Hoff isochore has been applied to the change in melting point of a solution, although there is no relation between the melting point and the heat of solution. In the present case, the heat of solution has, consequently, been given the enormous value of 219,650 cal. This value is high, even for a heat of combination, and seems absurdly so for a heat of solution.

With reference to Dr. Miller's interpretation of our Table IV, it would appear that he has either confused the particle sizes or the time factor. His statement that "for given time periods a temperature difference of 100° C. exists between fine and medium-sized particles" is inconsistent with the figures given. Furthermore, there is no evidence whatever for the assumption that, because two alloys of the same composition have the same density, they must have the same amount of tungsten in solution.

Dr. Miller also appears to have made an error in his Table B, where he gives the effective diameter of the particles of coarse powder as $> 33{\cdot}14\ \mu$. Since there were, in fact, no particles greater than $20\ \mu$. this is absurd. Moreover, we do not agree that the "effective" diameter can be assessed in the way that he suggests, since the distribution of particle sizes is the important factor.

The photomicrographs which Mr. Sykes has secured are very interesting. The alloys shown have all been obtained by sintering at temperatures sufficiently high to ensure the presence of a liquid phase. They thus serve to confirm the suggestion that this peculiar type of structure is only obtained when one of the phases present during sintering is in the liquid state.

Our statement that complete, or nearly complete, absence of solid solubility in the tungsten component is necessary if this type of structure is to be obtained, is perhaps too general. The original object was to discover any other systems in which a *small* addition of a metal of lower melting point would produce this duplex structure. If we are thus limiting ourselves to small additions, it is evident that there must be a limiting maximum value for the solid solubility of the major constituent. If this solid solubility exceeds the percentage of low melting point metal present, there will be no second phase between the grains.

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A STUDY OF SOME OF THE FACTORS CONTROLLING THE POROSITY OF HOT-TINNED COATINGS ON COPPER.*

By W. D. JONES,† M.Eng., Ph.D., MEMBER.

SYNOPSIS.

A distinction is drawn between the surface conditions of a tin bath (in which copper is being tinned) at the entry of the copper and at the exit. Molten salts and other materials maintained on the bath at entry are termed *fluxes*, and control the wetting of the copper surface by the tin; at the exit from the bath such materials are included in the term *cover*, and they control the stability of the molten tin film on the copper surface after it has left the bath.

A major source of porosity in tin coatings on copper is the "running off" or "globularizing" of the molten tin film. This phenomenon is termed *dewetting*, and is indicative of an instability in the molten tin film caused mainly by a high surface tension of the tin. Certain covers such as palm oil, stannic bromide, oxide films, etc., by reducing surface tension, decrease the tendency to dewet. Other covers, such as ammonium chloride, or resin, permitting of a high surface tension, increase the tendency to dewet. Dewetting is favoured by the presence of suitable nuclei, of which the most important are scratches and other discontinuities in the copper surface, imperfectly wetted areas, inclusions, and local variations in surface tension caused by temperature and concentration variations. The extent of dewetting is reduced by increasing the viscosity of the tin film (by presence of intermetallic compounds and by low temperatures) or by rapid solidification.

The experiments upon tin films on copper concerning dewetting have been repeated, employing water films on a gold plate.

INTRODUCTION.

IF a chemically clean surface of copper is inserted in molten tin, reactions occur which lead to the formation of a duplex enveloping film of intermetallic compound, an inner layer of Cu_3Sn, and an outer, much thicker, layer of Cu_6Sn_5.[1] Whilst in the tin bath, these compounds break up by dissolution, and therefore are to be considered as an intermediate product in the dissolution of the copper in the tin.

On withdrawal of the copper surface, two things may happen: (1) The compound film may remain coated with a thick smooth layer of molten tin (or tin containing small amounts of copper), which, remain-

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ing in place until solidification, forms a continuous tin coating of the type usually regarded as normal, satisfactory, and more or less non-porous; such a coating may either be smooth or bright or may exhibit typical crystal boundaries or striations as described elsewhere.[2]

(2) The major portion of the tin may immediately run off the copper, leaving behind a compound film almost uncoated with tin.

In most cases the withdrawal of the tin is not complete, and some of the molten tin may remain behind in the form of globules or ripples having an appearance similar to drops of water on a greasy surface. The solidified coating has a dull finish and exhibits no typical macro-structure. The general appearance gives the impression that the tin has failed to wet the copper surface. This is incorrect, however, since the presence of the compound film indicates that wetting took place on immersion. The phenomenon can accurately be described as dewetting, and is due directly to the inability of the molten tin to continue wetting the previously formed compound film. Fig. 1 A and B (Plate XXXI) shows normal and dewetted coatings.

In previous work, the author [3] has shown that the porosity of these dewetted coatings is high, mainly owing to the fact that inclusions in the copper base are allowed to exert their maximum effect as pore sites. It is not possible to stress too much the importance of preventing dewetting if non-porous coatings are to be attained. The work described in this paper is a study of the conditions which give rise to dewetting.

INFLUENCE OF FLUXES.

Superficial consideration makes it immediately apparent that the tendency of the coatings to dewet is intimately connected with the type of flux in use. The efficiency of a flux can probably be measured to some extent by the amount of copper which it introduces into the tin bath. Analyses of tin baths after the tinning of a number of copper specimens employing a range of fluxes under standard conditions have indicated, however, that the order of efficiency of fluxes obtained in this manner is quite different from that obtained when the fluxes are arranged in their order of dewetting tendency. For example, palm oil and resin both introduce approximately equal amounts of copper into the tin bath, and whilst dewetting is not particularly marked when palm oil is used, it is pronounced when resin is employed. It is probable, therefore (and is here shown to be the case), that those qualities which condition the effectiveness of a material as a flux do not necessarily control the ability of a material to prevent dewetting. This can be made clear by the use of tin baths so partitioned that copper specimens can be introduced through one flux and withdrawn through another. It is then apparent that the tendency to dewet is controlled only by the exit conditions and is independent of those at entry (provided always, of course, that actual initial wetting took place). It is preferred, therefore, to use the word flux here only for that material employed to surround the copper specimens at their entry into the tin bath; for the exit material the word cover will be used. The flux controls the wetting conditions; the cover, the dewetting conditions. When no cover has been added, it is assumed that the oxide film on the surface of the tin bath constitutes the cover.

Using annealed and degreased, remelted electrolytic copper, in the form of foil containing traces of cuprous oxide and with a highly polished surface, and dipping in Chempur tin, a series of tinning tests was made employing the following range of covers: solid ammonium chloride, three varieties of resin, zinc chloride, a mixture of 135 parts of zinc chloride and 53 of ammonium chloride, palm oil, tallow, mixtures of palm oil and tallow, stannic bromide, and oxide films of various thicknesses, as explained above. These experiments have shown that the effectiveness of various covers in preventing dewetting increases approximately in the above order (with very little difference between palm oil and tallow).

When solid ammonium chloride is used, it is practically impossible to prevent dewetting with any type of copper; with stannic bromide no dewetting occurs except under the most unfavourable conditions (copper with high oxygen content);* and with a thick oxide film, dewetting seldom occurs. It is very noticeable that the tendency to dewet increases with temperature. With ammonium chloride, dewetting took place at the lowest temperatures; zinc ammonium chloride permitted moderately satisfactory coatings below 240°–250° C.; palm oil or tallow, alone or together, below approximately 280°–300° C.; and stannic bromide gave good coatings below approximately 340° C. At higher temperatures than this the results appear to become confused, because of the rapid rate of compound formation.

SURFACE TENSIONAL FACTORS.

These results indicate a theory which ascribes to surface tensional forces the major factors in controlling dewetting. To provide approximate data on the influence of the surface tension of tin at various temperatures of the above cover materials, surface tension measurements were made by the sessile drop method. Globules of molten tin were maintained at various temperatures under the various covers, and an image of the shape of the globule was projected, by means of a source of light and an optical system, on to a screen several feet away, thus

* 0·5 per cent. oxygen, for example.

permitting very simple and moderately accurate measurement of the globule. The influence of covers was determined by measuring the height of the top surface of the globule above the point of contact of the vertical tangent at the greatest diameter. Accurate computation of surface tension figures was not attempted, and the figures recorded here serve only to establish the order of the cover effects. Assuming the height of a globule having a clean unoxidized surface to be 100 per cent., the following figures were obtained for various covers: ammonium chloride or resin 100, zinc ammonium chloride 98, tallow 95, palm oil 91, stannic bromide 90, and oxide film from 90 to 75 per cent., depending on the thickness. These results show, therefore, that the use of ammonium chloride or resin results in the maximum figure of surface tension for tin, whilst with stannic bromide or oxide films considerably lower figures can be obtained. It will be noted that the order of these covers in causing a reduction of surface tension is identical with their order of tendency to prevent dewetting.

It can be concluded, therefore, that dewetting can only be prevented by the artificial reduction of the surface tension of the tin film. Such a conclusion is too simple, however, to account for all of the observed facts. It is found, for example, that if tinning experiments are conducted in a hydrogen atmosphere, there is generally no tendency to dewet, although, presumably, owing to the absence of oxide films, the surface tension should be fairly high (assuming that hydrogen itself does not cause substantial reductions). An even more remarkable fact, for which the above theory does not account, is that it is easily possible to tin copper specimens in ammonium chloride vapour without any marked dewetting tendency, although instantaneous dewetting occurs once a particle of the solid touches the tin surface.

EFFECT OF NUCLEI.

These facts have led to the conclusion that before dewetting can occur a nucleus or starting point is necessary, and that in the absence of such a nucleus it is possible to prevent dewetting even although the surface tension of the tin film may be high. Strong support for this theory is afforded by the fact that under normal tinning conditions, using, for example, zinc ammonium chloride as a cover, dewetting invariably initiates at the edges of the specimens and at areas of scratches. This effect of scratches has been proved not to be due to the difficulty of degreasing and fluxing such areas, since scratches produced after fluxing and whilst the copper is in the tin bath lead to the same result. Moreover, it is also noticeable that under normal tinning conditions dewetting mainly occurs whilst the specimen is actually being withdrawn, that is, as if the tin-cover–air interfaces are acting as nuclei. Probably local temperature and composition variations in the cover on the specimen after withdrawal can also be regarded as acting as nuclei. Evidence for this theory has been provided in the following manner. Specimens of oxygen-free copper,* 2 in. × 1 in., were prepared with a microscopic polish and with smooth rounded edges, and, after degreasing, were tinned as satisfactorily as possible, using Chempur tin, and with stannic bromide as a flux and a cover. As soon as the coating had solidified, but before any appreciable further cooling took place, the specimens were quenched in dilute hydrochloric acid, a procedure which has the advantage of removing and dissolving the cover of stannic bromide from them. They were then washed in distilled water and dried in a steam oven, care being taken not to touch them with the fingers. These specimens were then completely immersed to a depth of 2 in. in baths of resin, zinc ammonium chloride, palm oil, tallow, and stannic bromide at 200° C., the temperature of the baths being quickly increased to 245° C. Precautions were taken to avoid vibration and local variations either in temperature or composition. To this end the baths were heated as uniformly as possible, and stirred continuously. In none of the above cases did any appreciable dewetting occur within 10 minutes, except at the edges of the specimens, although withdrawal of the specimen effected dewetting in most cases.

Further evidence has been obtained by deliberately causing local temperature or composition variations. For example, copper specimens tinned as described above, if heated in air to a few degrees above their melting point, will not dewet if the heating is uniform and a visible oxide film has been established. Dewetting immediately occurs, however, if the tin film is touched with a minute jet of burning hydrogen, or with molten drops of any of the above-mentioned covers, or with a crystal of ammonium chloride.

Similarly, specimens after withdrawal from a tin bath, and whilst still molten and covered with a film of cover, can be made to dewet by local touching with a globule of a different cover, or by the same cover of a different composition or temperature. These experiments make it clear that the reason why solid ammonium chloride is so detrimental (although satisfactory coatings can be obtained under suitable circumstances in the vapour) is due to the local variations caused by the separate crystals of the solid.

The local dewetting that occurs in these experiments can be divided approximately into two types: when the local addition causes a local

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* High-conductivity copper, free both from microscopically visible cuprous oxide and residual deoxidant.

reduction of surface tension (as, for example, when a specimen with a bright, practically unoxidized surface is touched with molten stannic bromide) then dewetting occurs away from the point of contact, Fig. 2 A (Plate XXXI). When the local addition increases the surface tension (as, for example, when an oxidized surface is touched with ammonium chloride or molten resin), then dewetting also occurs away from the point of contact, but a globule of tin is drawn to the contact point and remains there (Fig. 2 B). This second result is presumably occasioned by the local increase in surface tension withdrawing tin into the point of contact, and leaving a dewetted ring which then provides the nucleus for the surrounding tin to dewet.

DEWETTING WITH GOLD AS A BASE.

Considerable support for the theory of dewetting described above has been obtained by a series of analogous experiments, using a polished gold plate as a support (analogous to the copper) and various water solutions as a liquid film (analogous to the tin). Two aqueous solutions were employed, one containing potassium carbonate, having a surface tension measured by the bubble method of approximately 98 (assuming water to be 72), and a saturated solution of octyl alcohol, having a surface tension of approximately 40. The gold plate was first degreased by coating it with Necol varnish, which was then stripped off by making the plate the cathode in a dilute solution of sodium carbonate. Even after this treatment, there was some difficulty in maintaining the plate completely wet with water for periods longer than 5 minutes. This difficulty was much more pronounced with the potassium carbonate solution and much less pronounced with the octyl alcohol solution. In all cases dewetting initiated at the edges of the plate and at scratches. On wetting the plate with potassium carbonate solution and touching it locally with a drop of the octyl alcohol solution, dewetting of the type shown in Fig. 2 A occurred instantly. On reversing this procedure, dewetting of the type shown in Fig. 2 B took place. These experiments leave very little doubt as to the validity of the principal conclusions concerning the conditions under which copper can be tinned. (For further elaboration of this theory, however, see the Appendix.)

INFLUENCE OF GRIT.

A phenomenon of importance equal to the tendency of a coating to dewet is the rate at which it dewets. Obviously it is possible to prevent serious dewetting in a coating which has a marked tendency to do so if the rate of dewetting is sufficiently slow to permit solidification to proceed before any appreciable dewetting takes place. The resistance to movement of the coating is conditioned by its viscosity, which is reduced by temperature and increased by copper content. These two factors are opposed, since the rate of solution of copper increases markedly as the temperature is increased. The apparent viscosity of the tin coating is greatly increased in the act of solidification by its copper content, since the copper is deposited throughout the tin layer either as a eutectic or as primary dendrites of Cu_6Sn_5. This " grit," as it has been termed by Daniels,[4] assists greatly in reducing the extent of dewetting before solidification. It is effective only to an important extent in hyper-eutectic coatings. " Grit," whether a reaction product between the two metals concerned, or whether due to an added metallic content (*i.e.* in the case of tin baths, nickel, or cobalt, see Daniels [4]), is most beneficial in slowing down dewetting before solidification, in circumstances where the molten film is naturally unstable.

Where there is no dewetting tendency, it becomes unnecessary. For example, in the tinning of highly polished oxygen-free copper * at low temperatures with palm oil or stannic bromide, it is unnecessary to maintain any appreciable copper content in the tin bath. If circumstances are such that dewetting is likely to occur rapidly, then the more rapid the rate of cooling the less chance dewetting has to proceed to a serious extent; in such cases, quenching may be beneficial, a fact which has been noted by Daniels.[1]

INFLUENCE OF DEGREASING.

All of the foregoing conclusions have been based on the supposition that satisfactory fluxing and wetting of the copper take place at its entry into the tin bath. Whilst oil or grease in obvious amounts will naturally hinder the reaction between the copper surface and the molten bath, nevertheless grease in lesser amounts can be almost as detrimental. Some experiments with copper sheets of various types showed that improvement in tinning can generally be obtained by degreasing the " as-received " surface with trichlorethylene. Still further improvement is possible by the use of sodium silicate.[5] In some special cases (and in one example the copper was oxygen-free) no amount of treatment with these degreasing reagents would permit of satisfactory tinning. It has to be realized that a surface after degreasing may not be grease-free even although it passes the water-break test. It is assumed that in these cases the grease resides at the bottom of scratches, or has been rolled in. In most cases the trouble is experienced with

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* High-conductivity copper, free both from microscopically visible cuprous oxide and residual deoxidant.

scratched or slightly rough surfaces. Pickling in strong nitric acid generally suffices to overcome the trouble.

CONCLUSIONS.

The preceding theoretical discussion permits some conclusions of an important practical nature. In order to obtain coatings of a minimum porosity, the following points should receive attention :

(i) The copper base should be thoroughly degreased and adequately fluxed.

(ii) A cover which reduces the surface tension of the tin bath is desirable, although satisfactory coatings using only an oxide film can be procured (with some deterioration in the appearance). The use of ammonium chloride alone should be avoided.

(iii) Precautions should be taken to prevent the formation of dewetting nuclei, of which general roughness and scratches are the most important types. It is not possible to stress too much the necessity of a highly polished surface if all dewetting is to be avoided. Inclusions in the copper base also act as nuclei, a fact which affords an explanation of the difficulty in tinning copper containing high percentages of oxygen. Oxygen-free copper is to be preferred.

(iv) The viscosity of the tin bath should be maintained as high as possible. Low temperatures and additions of copper are favourable in this respect.

(v) The object should not be removed from the tin bath so slowly that dewetting can easily occur during the operation.

APPENDIX.

Caution must be exercised in applying the above principles to other hot-dipped coatings. For example, there is little or no tendency for tin coatings on steel to dewet unless they are treated with ammonium chloride or resin. Generally, most hot-dipped coatings appear to be more stable and have less tendency to dewet than those of tin on copper.

The previously outlined theories supply no explanation for such differences, and the probable reason for this is that one important factor, namely, interfacial tension, has not received consideration. In view of the lower degree of reactivity of tin and iron compared with that of tin and copper, there is every reason to assume that the interfacial tension in the first case is less than in the second. Such a fact would adequately explain the varying behaviours of the two coatings, but until satisfactory measurements of interfacial tensions in this connection have been made explanations of this type must remain speculative.

A. B.

FIG. 1.

A. B.

FIG. 2.

[To face p. 272.

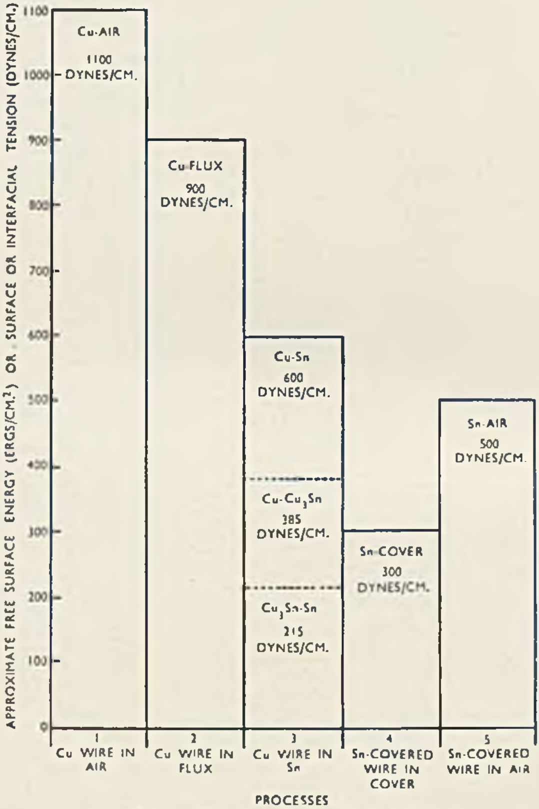

Fig. A.—Free Surface and Interfacial Energy Levels Occupied During Hot-Tinning of Copper.

Acknowledgments.

The author wishes to record his appreciation of the constant collaboration of Dr. B. Chalmers which he has enjoyed during the prosecution of this work.

This investigation forms part of a programme of research carried out for the International Tin Research and Development Council, to whom the author is indebted for permission for publication. The author wishes to thank the Director of Research, Mr. D. J. Macnaughtan, for valuable advice. Grateful acknowledgment is also made to the Principal and Governors of the Sir John Cass Technical Institute for the necessary facilities.

References.

[1] P. D. Merica, *Tech. Paper (U.S.) Bur. Stand.*, 1917, (90), 18 pp.
E. J. Daniels, *J. Inst. Metals*, 1936, 58. 199–205.
[2] B. Chalmers and W. D. Jones, *Trans. Faraday Soc.*, 1935, 31, 1299–1303.
[3] W. D. Jones, *J. Inst. Metals*, 1936, 58, 193–198.
[4] E. J. Daniels, *Trans. Faraday Soc.*, 1935, 31, 1277–1285.
[5] D. J. Macnaughtan, S. G. Clarke, and J. C. Prytherch, *Tech. Publ. Internat. Tin Res. Develop. Council, Series A*, 1935, (7).

DISCUSSION.

(*Condensed.*)

Mr. A. W. Hothersall,* M.Sc. (Tech.) (Member): I have confirmed that the dewetting phenomenon is independent of impurities in the copper surface, or between the copper and the tin, in an experiment in which a specimen prepared by electrodepositing tin on a continuous electrodeposited copper surface was plunged into molten tin covered with palm oil. A smooth, continuous tin film was obtained which, however, gathered into characteristic irregular mounds a few seconds after a crystal of ammonium chloride had been placed on the surface.

An interesting result, on which the author's comments would be useful (particularly as regards the probable nature of the nuclei which he regards as essential to the phenomenon), was that when a piece of this tin-plated electrodeposited copper was immersed in a horizontal position in paraffin at 250° C., the tin melted, giving initially a continuous film, but, after a lapse of 5–10 seconds, small spots appeared on the surface and the tin then quickly gathered into the characteristic irregular mounds.

The author directs attention to the importance of thoroughly degreasing the copper before tinning, but the methods which he gives, and the method which he used, for degreasing his gold specimen are not of the highest order of efficiency—they are, in fact, methods specially developed for degreasing tinplate surfaces prior to porosity testing, where it is necessary to adopt a compromise, to avoid attack of the tin. Much more effective degreasing would be obtained if the specimen were made the cathode in a warm alkaline solution at a moderately high current density (*e.g.* 50 amp./ft.^{2}) for 5–10 minutes, preferably supplemented by abrasive treatment with fine powder (*e.g.* scrubbing with a wet brush dipped into powdered pumice, chalk, or magnesia).

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* Research Department, Woolwich.

Using such a method, I have not found difficulty in maintaining a stable film of water or of potassium carbonate solution on a polished gold surface.

Dr. JONES (*in reply*): I thank Mr. Hothersall for his information on degreasing; I shall know better next time. I am also glad to have his confirmation concerning the effect of ammonium chloride on dewetting. There may possibly be an explanation of his experiment. I know that the theory seems a little improbable, but I have found it very difficult indeed to prevent films of tin dewetting under conditions like this, and have had to go to some trouble in stirring the oil bath and maintaining uniform temperature conditions, and in keeping the oil bath clean and free from dirt. In time, of course, the intermetallic compound film will grow, and the film itself will provide its own nucleus for dewetting, as the intermetallic compounds grow to a large size.

CORRESPONDENCE.

DR. MIKE A. MILLER * (Member): The author has made a valuable contribution to the knowledge of "dewetting" phenomena, particularly as experienced in the hot-tinning of copper. I wish, however, to take exception to some of the terminology of surface tension used by Dr. Jones; or rather, to elucidate some of the free surface energy functions applicable to the problem. I have been tempted to use the same words regarding Dr. Jones' paper as Chalmers and Jones † applied to C. C. Miller's ‡ paper on soldering fluxes, despite the fact that skeletons in cupboards were best left to lie undisturbed.

In the synopsis to the paper Dr. Jones states (my italics) that: "This phenomenon is termed dewetting, and is indicative of an instability in the molten tin film caused mainly by a *high surface tension*. Certain covers, such as palm oil, stannic bromide, oxide films, etc., by *reducing surface tension, decrease the tendency to dewet*. Other covers, such as ammonium chloride, or resin, *permitting of a high surface tension, increase the tendency* to dewet."

So far as I can ascertain, Dr. Jones really means *interfacial tension* rather than surface tension. Interfacial tension is mentioned in the appendix, where it is admitted that this important factor has not been considered. *Surface tension* is generally considered to represent the tension at a fluid–air interface; § the tension at a fluid–fluid or solid–fluid interface is generally referred to as an *interfacial tension*. This may be said to be only a matter of definition. If one considers, however, the free surface energy equations developed by Young,‖ Freundlich,¶ and Bartell and Osterhof,** it becomes apparent that more than a definitive distinction exists. In fact, Antanoff's †† rule, which is important in the present work, is based on such a distinction.

It is not at all apparent how palm oil, stannic bromide, etc., insoluble in molten tin, act "by reducing surface tension." In order to alter a surface tension, other than by thermal means, a *solute* must be positively or negatively adsorbed *in the solvent–air interface*. It follows that the surface tension of the molten tin remains sensibly constant, except as modified by the amount

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* Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pa., U.S.A.

† B. Chalmers and W. D. Jones, *Met. Ind.* (*Lond.*), 1937, **50**, 537, 560.

‡ C. C. Miller, *Met. Ind.* (*Lond.*), 1937, **50**, 503.

§ This may, of course, also be termed an interfacial tension with air considered as the second phase.

‖ T. Young, *Phil. Trans. Roy. Soc.*, 1805, **95**, 65.

¶ H. Freundlich, "Colloid Chemistry," London: **1926**, p. 157.

** F. E. Bartell and H. J. Osterhof, *Indust. and Eng. Chem.*, 1927, **19**, 1277.

†† Antanoff, *J. Chim. phys.*, 1907, **5**, 372.

of copper in solution,[*] and that only its interfacial tension against the second fluid, *i.e.* the molten flux, changes with the character of that second fluid and the adsorption of a third component *at the fluid–fluid interface.*

Chalmers and Jones (*loc. cit.*) have stated that their "investigations show the effect of a flux is, indeed, to lower the surface tension of the clean metal, but generally to a figure which is still considerably above that of the oxidized surface." I have been concerned with the theoretical and practical aspects of free surface energy for some years, but have yet to find a case where the apparent surface tension of an oxidized molten metal has been lower than the true surface tension. The interfacial tension, against a second fluid, may, however, be lowered by oxidation, especially if the oxide is soluble in the second fluid phase.[†][‡][§]

Removal of an oxide film, as by the use of fluxes, merely allows the true surface tension to exhibit itself. A molten metal covered with a coherent oxide film exhibits at its surface, *i.e.* to an air phase, a free surface energy equivalent to the value of the interfacial tension of the molten metal against its solid oxide; this value depends on the free surface energy of the oxide. Complications in sessile drop measurements, as pointed out below, commonly occur when oxide films are present.

In short, it appears that C. C. Miller[¶] was correct in saying that "the surface tension of the solder would be *apparently* reduced, although the actual reduction would be the difference in surface tension between unoxidized solder and oxidized solder." By the same token, Douglas,[**] in his discussion of Miller's paper, is incorrect in stating that "the removal of an oxide film raises the surface tension." Daniels and Macnaughton, in a recent discussion of the wetting of metals by metals, stated that fluxes lower the surface tension (interfacial tension) of the metal drop. Barber[††] is of the opinion that "the flux exerts some action which serves to keep the metal surface clean in order that the normal surface tension inherently present may completely assert itself."

Referring again to the paper under discussion, I would ask Dr. Jones on what base did the globules of molten tin, under the various "covers," rest? Very superficial considerations make it apparent that sessile drop measurements are without meaning unless the drop does not wet the base, *i.e.* the contact angle must be 180° (or zero degrees, depending through which phase the measurement is made). When the molten metal drop is covered with a second fluid, *e.g.* a flux, the contact angle may vary with the character of this second fluid.[‡‡]

In the Appendix, it was briefly stated that: "In view of the lower degree of reactivity of tin and iron compared with that of tin and copper there is every reason to assume that the interfacial tension in the first case is less than in the second." A more complete explanation of this important point is as follows. When molten tin comes in contact with a copper (or iron) surface, there exists a definite tendency for the tin to decrease the free surface energy of the solid;

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[*] G. Drath and F. Sauerwald, *Z. anorg. Chem.*, 1927, **162**, 301. At approximately 900° C., and probably in the same ratio at lower temperatures: 25Cu–75Sn, 540; 50Cu–50Sn, 623; Cu_3Sn, 713; 71Cu–29Sn, 777; and 82Cu–18Sn, 911 dynes/cm., respectively.

[†] Quincke, *Wied. Ann.*, 1888, **35**, 580.

[‡] Christiansen, *Ann. Physik*, 1903, [iv], **12**, 1070.

[§] M. A. Miller, "Notes on the Motion of Fluid Metallic Drops"; unpublished.

[¶] C. C. Miller, *Met. Ind.* (*Lond.*), 1937, **50**, 560.

[**] V. B. Douglas, *Met. Ind.* (*Lond.*), 1937, **50**, 577.

[††] C. L. Barber, *Indust. and Eng. Chem.*, 1937, **29**, 1114–1117.

[‡‡] F. E. Bartell and M. A. Miller, *J. Physical Chem.*, 1936, **40**, 881–888, 889–894, 895–904.

the extent of the decrease depends on the nature of the solid (copper or iron) as well as on that of the fluid (tin). A great degree of decrease indicates a high attraction between fluid and solid; this in turn is indicative of the solid going into solution in the fluid (or at least reacting with it).* The decrease in free surface energy which occurs when a fluid replaces air or other fluid from a solid–air or solid–fluid interface is, in the absence of a finite contact angle, simply the difference between the surface tension of the solid against air and the interfacial tension of the solid against the fluid. Accordingly, assuming the surface tensions of solid copper and solid iron to be approximately the same in the solid as in the fluid states (at least in the same ratio), the respective interfacial tensions can be calculated by taking the difference between the surface tension of the solid and the surface tension of the tin. Drath and Sauerwald (*loc. cit.*) give the surface tensions of tin, iron, and copper as approximately 500, 940, and 1100 dynes/cm., respectively. The interfacial tension of tin against iron would then be 440, and of tin against copper 600 dynes/cm. After a layer of a copper–tin compound had formed on the copper, the interfacial tension would be less. These reasonings also apply to Chalmers' † work on tin plate.

Whilst not entering into a detailed theoretical discourse on the matter ‡ at the moment, one other important point should be mentioned. Consider now the various free surface and interfacial energy levels which the copper occupies during its journey through the bath. The process may be pictured schematically as in Fig. A (Plate XXXII), in which it is assumed that the surface tensions of the flux and cover are 200 dynes/cm. each, and the surface tensions of the solid phases are identical with those of the fluid phases of the same substances. Though it is not claimed that the numerical values have more than a relative meaning, it is suggested that such a schematic diagram represents the relative energy levels of the various steps in the process.

I would like to reiterate the fallacy of arguing that the removal of an oxide film or the covering of a molten metal with a flux increases the surface tension; only in special circumstances is this true. The use of the term surface tension should not be used in the absence of an air-phase.

The AUTHOR (*in reply*): The sessile drop measurements consisted in the estimation of the vertical height between the horizontal tangent and the point of contact of the vertical tangent to the surface of the drop. These measurements are not influenced by the surface upon which the drop rests. As Dr. Miller suggests, his remarks are in fact only based on a matter of definition. Using Dr. Miller's exact, but pedantic, terminology, what I have in fact shown is that measurements by the sessile drop method indicate numerical values of interfacial tension between metallic tin and tin oxide, and between molten tin and stannic bromide, palm oil, tallow, etc., which are less than the numerical value of the surface tension of tin, and I have demonstrated, in addition, beyond all reasonable doubt, that the tendency of these various covers to prevent dewetting is closely related to these numerical values. The theory which I have offered as an explanation is a normal deduction from such measurements, and is satisfactorily supported by the gold–water experiments.

Using the term "surface tension" in the customary sense, as I have done, and bearing in mind the influence of the tensile strength of an oxide film, Dr. Miller's criticism of my point of view with respect to oxide films becomes a quibble.

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* F. E. Bartell, "Colloid Chemistry," Alexander Vol. III, 1931, pp. 41–60.

† B. Chalmers, *Trans. Faraday Soc.*, 1937, 33, 1167–1176.

‡ M. A. Miller, "The Free Surface and Interfacial Energy Relationships Active in Metal–Metal Bonding," unpublished.

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THE INFLUENCE OF SURFACE ALLOYING ON THE STRENGTH OF SOFT SOLDERED JOINTS.*

By R. CHADWICK,† M.A., Member.

Synopsis.

Thin copper strips were joined by soft soldering, using various lead–tin alloys and also pure tin and pure lead. A rapid method of joint-making was developed, so that large numbers of joints could be made under reproducible conditions, the influence of variables such as time and temperature of joining, surface preparation, fluxing, &c., being first studied.

It was found that for pure tin and alloys containing tin, brittle copper–tin alloys were formed at the copper surfaces during joining. These copper–tin alloy films were found to increase in thickness by holding joints at elevated temperatures either above or below the melting point of the solder. Fracture on testing occurred near one of the copper surfaces and in the copper–tin alloy film. Three copper–tin alloys were identified, and the part played by each of these distinct and separate layers in joint failure was ascertained.

Using H.C. copper, the joint strength did not decrease below the characteristic strength of the copper–tin alloy layer in which failure occurred. Using a lower grade of copper, failure occurred after prolonged ageing at elevated temperatures by the complete stripping of the solder layer, leaving bright untinned copper, the strength ultimately decreasing to zero. This second type of failure occurred only with copper containing both arsenic and oxygen.

Joints made with pure lead formed no alloy film, and fracture occurred in an irregular manner through the lead, but the formation of a brittle copper–tin alloy film, and also the stripping phenomenon with arsenical copper after prolonged ageing, were observed in a lead-base solder containing only 2 per cent. of tin.

Introduction.

The experimental work dealt with in this paper was undertaken with the object of improving the strength of soldered structures made from thin copper strip. The suitability, as solders, of a number of low melting alloys was studied, both at normal and at elevated temperatures.

For alloys containing tin, the changes taking place were found to be of special interest. The development of a rapid method of making and testing joints under accurately reproducible conditions, made it possible to cover the wide field necessary to determine the conditions, and to show the causes of the weaknesses and failures obtained in such joints.

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† Research Metallurgist, I.C.I. Metals, Ltd., Birmingham.

Previous Work.

There are two aspects which have been dealt with by previous workers in the investigation of soldered joints. The first of these is the physical aspect, dealing with the strength of the joint, and the second is the chemical aspect, dealing with the nature of the bond between the solder and the material joined. The effect of surface alloying on joint strength has caused a good deal of controversy, and no complete agreement has been obtained on this question.

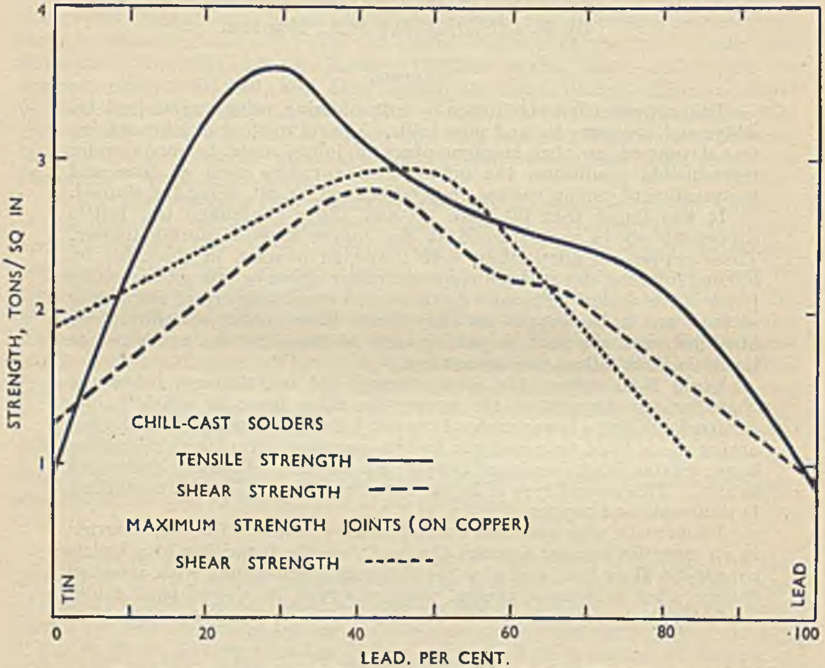


Fig. 1.—Strength of Solders and Soldered Joints (Nightingale).

Previous workers dealt almost entirely with joints between quite thick specimens, and determined joint strength by shearing tests. In most cases a simple lap or butt joint [1,2] was employed, but Nightingale [3] used a plug and ring test, which gave more accurate results, with better control of the solder film thickness. Nightingale's investigation showed clearly that for joints made under the optimum conditions, the shear strength measured was that of the solder alloy used. Curves reproduced from Nightingale's work illustrating this point are shown in Fig. 1.*

* See also footnotes, p. 292.

Lower shear strengths were shown to be due either to less sound joints or to weakening of the solder alloy by dissolving of the material being joined.

All previous investigators agreed that interstitial alloys formed between copper and lead–tin solders were copper–tin alloys, lead forming no separate phase with copper. Three possible phases might be anticipated in the alloy film between the copper and tin, namely the δ phase containing about 67 per cent. copper, the η phase (Cu_3Sn) containing about 62 per cent. copper, and the ε phase (CuSn) containing about 39 per cent. copper. Weiss[4] recognized all three phases in the alloy film formed by the reaction between copper and tin at temperatures of 400° and 550° C. Crow[5] and Nightingale,[3] however, did not observe the δ-bronze. More recent investigations on the copper–tin system[6,7] suggest that the δ phase would only be formed by reaction at temperatures in excess of 330° C.

From his observations, Nightingale concluded that the strength of the solder itself, and not that of the film between solder and specimen, determined the joint strength. Crow, on the other hand, stated that when a thick alloy film was formed by prolonged attack, joint failure occurred in this film, the fracture being stated to occur through the Cu_3Sn, rather than CuSn, when both phases were present. He also found that when all surplus solder was squeezed out, so that the first formed copper–tin alloy films were in contact, a weak joint resulted.

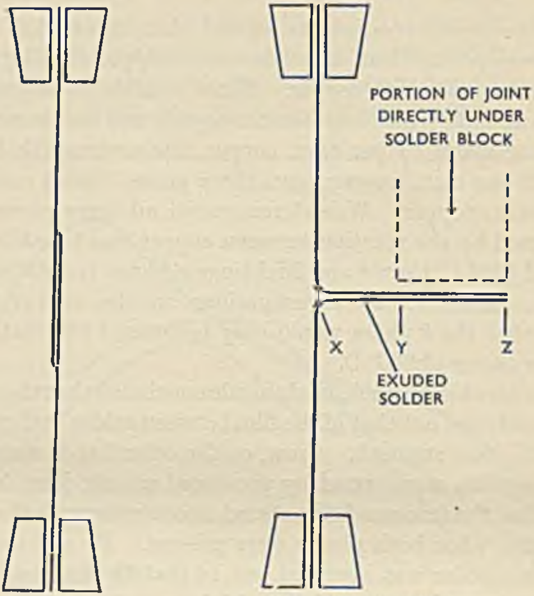
EXPERIMENTAL INVESTIGATION.

The mechanism of failure in a structure of thin strips joined by solder would not appear to involve shear of the solder as illustrated by the test (*a*)—Fig. 2—but rather by stripping or tearing apart at the joint, as illustrated by the test (*b*). Test (*b*) was adopted, and appeared to be novel, in that it tested adhesion between solder and strip, whilst previous workers had tested the shear of the solder itself, as illustrated by (*a*).

Materials.

Copper was prepared in the form of strip 0·005 in. thick and sheared to 1 in. width. Four samples of different commercial grades of copper were used, and four other coppers were specially prepared in the laboratory. In each case analytical determinations were made of arsenic, oxygen, and phosphorus, whilst minor impurities were estimated spectrographically.

Lead and tin for the preparation of solders were the purest commercially available. The double refined lead contained 0·0036 per cent., and the "Chempur" tin 0·015 per cent. total impurities. The lead–tin alloys were prepared by twice melting in a silica crucible, and casting in a narrow mild steel open mould, beads being melted off the strip just before use. No absorption of impurities was detected spectrographically.



(*a*) Shear Test. (*b*) Adhesion Test.

Fig. 2.—Methods of Testing Joints in Tensile Machine.

Preparation of Copper Strip for Joint-Making.

The method of surface preparation of copper strip for making joints received much attention in the early stages of the investigation. Briefly, the most important variables examined were:

Temper of Strip.

A. Hard-rolled.
B. Bright-annealed.
C. Air-annealed, pickled, and cleaned.

Surface Preparation.

a. Brief dip in 50 per cent. nitric acid.
b. As rolled condition.
c. Abraded with Hubert "0" emery.
d. Polished by hand with metal polish.

Fluxes.

1. Eutectic zinc ammonium chloride (10 per cent. in water).[3]
2. Zinc chloride (10 per cent. in water).
3. Tin ammonium bromide (in water).
4. Oleic acid.
5. No flux.

Except in the case of the nitric acid, the surface preparation required a subsequent degreasing operation. This was done by dipping first in ether, transferring to alcohol, and finally to the aqueous flux solution. The aqueous flux solution was in all cases applied, and immediately dried off in a Bunsen flame, just before making the joint.

Briefly, the results obtained under carefully controlled conditions showed that none of the factors enumerated above had any marked effect on the joint strengths obtained. Generally, roughening of the strip surface slightly increased joint strength, but differences were small as compared with those due to other effects to be described.

The fluxes were found to be the most satisfactory in the order enumerated, *i.e.* zinc ammonium chloride was the best, for as a result of its low melting point (below the tin–lead eutectic), sound joints could be made at lower temperatures than with the other fluxes, and also joining commenced in all cases with the first formation of liquid solder. The other fluxes made joints equally strong, but greater difficulty was experienced in getting the joints sound, and soldering conditions were more restricted. The use of a zinc salt in the flux was found to have no effect on the behaviour of joints under any of the conditions investigated.

The procedure finally adopted was to use soft bright-annealed strip, pickle in 50 per cent. nitric acid, wash and dry; finally, just before use, the strips were coated with zinc ammonium chloride flux and dried. All the results described in the subsequent portions of the paper were obtained on joints made with strip so prepared.

Preparation of the Joints.

The development of a technique for making sound joints under reproducible conditions required considerable preliminary investigation, and many hundreds of joints were made before this was achieved. A movable rectangular block, with 2 in. × 1 in. base and 2 in. deep, was mounted in a hand press, and fitted into a shallow slot in the fixed anvil on the bed of the press. The block was of aluminium, to prevent alloying by contact with the squeezed out solder, and also to give good heat transfer to the joint. The anvil was of cast iron, and was insulated from the joint by three strips of asbestos paper placed in the slot;

these strips of paper also served to soak up excess flux, and were frequently changed. The block and anvil were heated together with a large Bunsen burner, the temperature of the block being determined by a thermocouple in a lead-filled hole reaching to near the lower face; the anvil was always at a lower temperature than the block, and, as a result of the asbestos paper insulation, took no part in the melting of the solder. The joints were rapidly frozen by lifting out and placing on a cold steel plate, and the tools thus prepared very quickly for the next joint.

To make the joint, the strips were placed in position with one or two beads of soldering alloy (weight about 2 grm.) in between; the beads were melted from a stick of alloy just before use. In closing the tools, the alloy spread outwards and filled the entire space between the strips.

Joints made by melting together pre-tinned strips were unsound, owing to flux and air inclusions. Sound joints could only be obtained by a method in which a meniscus of liquid solder swept forward, pushing before it the flux from the metal surfaces. The soldering face of the aluminium block was slightly domed, in order to give this uniform outward flow of solder. A total absence of oily matter was found to be necessary in order to obtain sound joints in the lower temperature ranges.

A thin solder film produced under pressure was found to give a very weak joint. About 0·005 in. was found to be the most suitable solder film thickness. Uniformity was maintained by having two parallel ridges near the edges of the lower strip, whilst a clearance of a few thousandths of an inch in excess of the total joint thickness was maintained between the press tools. The slight variation obtained in solder film thickness did not affect, to any measurable extent, the results subsequently obtained.

The slide of the press was kept much tighter than is customary on a hand press, so that the soldering tools did not drop in operation. The tools were closed quite slowly, the speed being such that the upper strip was pushed down into position as the separating solder beads melted. With the standard soldering temperatures finally selected, the speed required for closing the tools was approximately the same for all soldering alloys.

Testing of the Joints.

The joints were tested by tearing apart in a tensile machine as shown in Fig. 2(*b*). The speed of testing employed was about one inch per minute. The load required was found to vary along the length of the joint, the first pull (X, Fig. 2(*b*)) being quite large, and then decreasing slowly until a steady value was achieved over the last 1½ in. to 2 in. of joint (Y to Z, Fig. 2(*b*)). A variable pull was also required if any unsoundness appeared, the strength decreasing across the unsound portion, and increasing above the normal value at the final meniscus of the inclusion. Only steady pull values in sound material were accepted. The tensile values obtained were expressed in pounds per inch width of joint. From a number of experiments in which joints were cut up before testing, it was shown that such values were true values for all widths of strip, and that the solder meniscus at the edge did not affect the strength produced; the grooving of one of the strips was found also to produce no effect on the joint strength.

Joining Conditions.

The relationship between the block temperature and the temperature of the joining alloy was explored in a preliminary series of experiments, by means of a very fine thermocouple inserted in the joints during the soldering operation described above. The heating was found to be very rapid, as will be seen from Fig. 3, the maximum solder temperature being attained in less than 5 seconds.

It was found that the effects of the solder block temperature, and the time for which the joint was kept in the soldering press, were profound. Joints made rapidly at the lowest possible temperature were strong, whilst joints made at higher temperatures, or after a prolonged period in the press were weak.

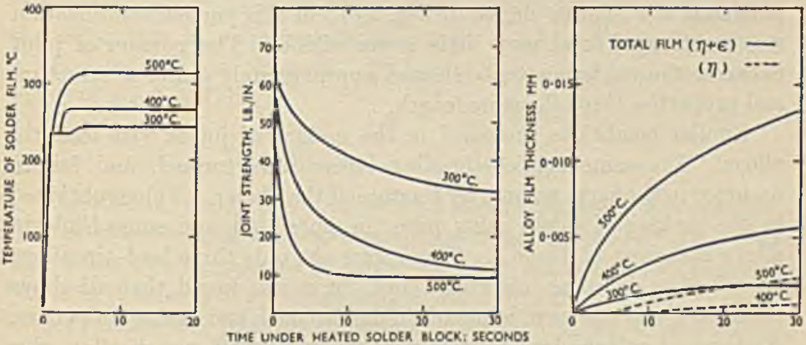


Fig. 3.—Making of Joints on HC. Copper with Pure Tin.

The strength of pure tin joints using different solder block temperatures for increasing periods of application is shown in Fig. 3. It will be seen that the strengths decreased rapidly in the first 10 or 20 seconds, and then remained fairly constant.

Microexamination of joint sections showed that a thin film of surface alloy was immediately formed at the copper–tin interface, and rapidly increased in thickness with increase in time and temperature of joining. This first formed alloy was identified as CuSn, or ε.

Fracture always occurred at the junction between copper and tin, and this appeared to be due to the low strength of the ε phase. This failure is shown in Fig. 9 (Plate XXXIV) for a joint made in 1 second, the particles of ε being only just visible at a magnification of 500 diam. With a 30-second joining period, a much thicker ε film was present, and a weaker joint resulted, the failure of such a joint being shown in Figs. 7 (Plate XXXIII) and 10 (Plate XXXIV). The photomicrographs do not show much of the ε layer remaining attached to the copper after testing, but this was seen to be continuous, by the white "tinned" appearance of the copper surface. Chemical analysis showed this film to be equivalent to a layer of tin 0·001/0·002 mm. thick. The decrease in joint strength, and the concurrent growth of the film during joining operations at various temperatures, are shown in Fig. 3. It will be seen that after a thick layer had been built up, another phase, η or Cu_3Sn, made its appearance between the copper and ε. Failure, however, continued to occur in the ε phase when both ε and η were present. The minimum value of about 10 lb./in. appeared to represent the strength for a continuous fracture in the ε layer.

The maximum joint strength was that encountered in the exuded portion of the joint as shown in Fig. 2(*b*); in this portion solidification was most rapid, and very little ε was visible. The portion of joint between the soldering tools showed approximately uniform structure and properties throughout its length.

Similar conditions prevailed in the making of joints with lead–tin alloys. The same copper–tin alloy layers were formed, and failure occurred in the same manner by fracture of the ε layer. Values obtained in the making of joints using pure tin, pure lead, and some lead–tin alloys are given in Table I. These were the only three lead–tin alloys examined in detail as soldering alloys, for it was found that all alloys containing eutectic gave joints of similar strength and ageing properties. A standard solder block temperature was selected for each alloy, this being about the minimum temperature possible for making a sound 1-second joint; it also ensured an approximately standard speed of operating the soldering tools. Values are given for joints produced with 1 second and 30-second periods of joining, the maximum strength on the exuded portions of 1-second joints also being given.

It will be seen from Table I that the behaviour of the tin-rich alloy and eutectic joints was similar to that of pure tin. The same alloy layers were formed, but, as would be anticipated, they were thinner, owing partly to the lower soldering temperatures, and partly to the decreased rate of attack in the presence of lead. Failure, as for pure tin, occurred in the ε layer, and the lowest strengths obtained when failure was taking place in this phase were little different from those for pure tin.

TABLE I.—*Making of Joints on HC. Copper with Lead-Tin Alloys.*

Alloy.	Block Temperature, ° C.	Maximum Joint Strength (Exuded Portion), Lb./in.	Joining Time—1 Second.				Joining Time—30 Seconds.			
			Maximum Solder Temperature, ° C.	Joint Strength, Lb./in.	Alloy Film Thickness.		Maximum Solder Temperature, ° C.	Joint Strength, Lb./in.	Alloy Film Thickness.	
					η mm.	ε mm.			η mm.	ε mm.
Tin . .	420	55	232	40	N.V.	0·001	285	11	0·001	0·006
98 Tin : 2 Lead	400	44	—	36	—	—	270	10	—	—
63 Tin : 37 Lead	360	32	185	26	N.V.	0·0005	230	9	N.V.	0·002
2 Tin : 98 Lead	550	53	—	45	N.V.	N.V.	370	27	N.V.	N.V.
Lead . .	600	57	327	50	N.V.	N.V.	410	45	N.V.	N.V.

(N.V. = None Visible.)

The lead-rich alloys and pure lead behaved rather differently, the joints obtained being much stronger; for pure lead there was little loss in strength with the more prolonged period of joining, but for the 2 per cent. tin alloy the loss in strength was appreciable. The nature of the separation in pulling apart was more rough and jagged, and no brittle alloy film was observed. Failure of a pure lead joint is shown in Fig. 8 (Plate XXXIII).

REPRODUCIBILITY OF JOINTS.

The time of joining was obtained by a stop watch, and it was not easy to reproduce joining time accurately on 1-second joints. All joints were made by one operator (the author), which eliminated any personal factor in the mode of operating and timing. For short joining periods, 75 per cent. of the individual joints made gave strength values within 15 per cent. of the values shown, whilst for long joining periods better reproducibility was obtained. It should not be supposed, therefore, that values given represent absolute values independent of conditions; they do show, however, the effect of joining conditions, materials employed, and the subsequent ageing of joints, and it is claimed that the results obtained are comparable. It will be observed that, where possible, diagrams are given rather than absolute values, for the above reasons. Absolute values, where given, are based on a large number of joints, and are probably true to within 1 or 2 lb.

AGEING OF JOINTS.

The real importance of the investigations described lay in the study of the behaviour of the joints on prolonged exposure to elevated temperatures. Joints prepared under controlled conditions, as described above, were the basic material for the investigation, all joints being made at standard temperatures for the alloy concerned, and either with 1- or 30-second joining period. The nature and strength of the starting material was therefore known—a matter of great importance, for the surface reactions to be studied had already commenced in the making of the joint.

The growth and thickening of the copper–tin alloy film was found to take place at a measurable rate at temperatures from 100° C. upwards, and was examined under both solid and liquid conditions. The most important results to be recorded in detail are divided as follows: (1) The behaviour of pure tin joints at temperatures from 100° to 500° C., the higher temperature investigations giving valuable data on the relative importance in joint failure of the three possible intermetallic alloy phases; (2) The behaviour of joints of the five selected standard lead–tin alloys on prolonged ageing at 150° C., *i.e.* entirely solid ageing. These results are given for two grades of copper, high-conductivity oxygen-bearing copper (HC., Table II), and a lower grade of oxygen-bearing copper (LAR., Table II) containing a little arsenic together with other impurities. It was found that copper–tin alloy growth did not differ

TABLE II.—*Composition of Coppers Used in Making Joints.*

	OF. Oxygen-Free Copper.	HC. High-Conductivity Copper. O.R.C.	Commercial Coppers.			Synthetic Coppers.			
			LAR. Low-Arsenical Tough-Pitch.	AR. Arsenical Tough-Pitch.	DOA. Deoxidized Arsenical.	As 1.	As 6.	As 33.	As 8.
				Chemical Analysis.					
Arsenic	nil	nil	0·04	0·43	0·45	0·002	0·012	(0·4)	0·96
Oxygen	nil	0·04	0·07	0·065	nil	0·075	0·08	0·10	0·07
Phosphorus	nil	nil	nil	nil	0·08	nil	nil	nil	nil
				Spectrographic Examination.					
Tin .	nil	nil	<0·01	<0·01	<0·01	nil	nil	nil	nil
Lead .	<0·001	<0·001	<0·005	abt. 0·02	abt. 0·01	<0·001	<0·001	<0·001	<0·001
Iron .	<0·005	<0·005	<0·005	<0·005	<0·005	<0·01	<0·01	<0·01	<0·01
Nickel .	<0·001	nil	abt. 0·02	abt. 0·08	abt. 0·03	abt. 0·001	abt. 0·01	abt. 0·001	abt. 0·001
Silver .	abt. 0·001	abt. 0·002	abt. 0·005	abt. 0·006	abt. 0·006	abt. 0·002	abt. 0·002	abt. 0·002	abt. 0·002
Antimony	nil	nil	abt. 0·005	abt. 0·01	<0·005	nil	nil	abt. 0·005	abt. 0·01
Bismuth .	nil	nil	<0·0005	<0·0005	<0·0005	nil	nil	abt. 0·002	abt. 0·01

for these two grades of copper, but with the less pure grade a new type of joint failure was observed; (3) The ageing of joints made from a larger number of copper samples. These observations were made

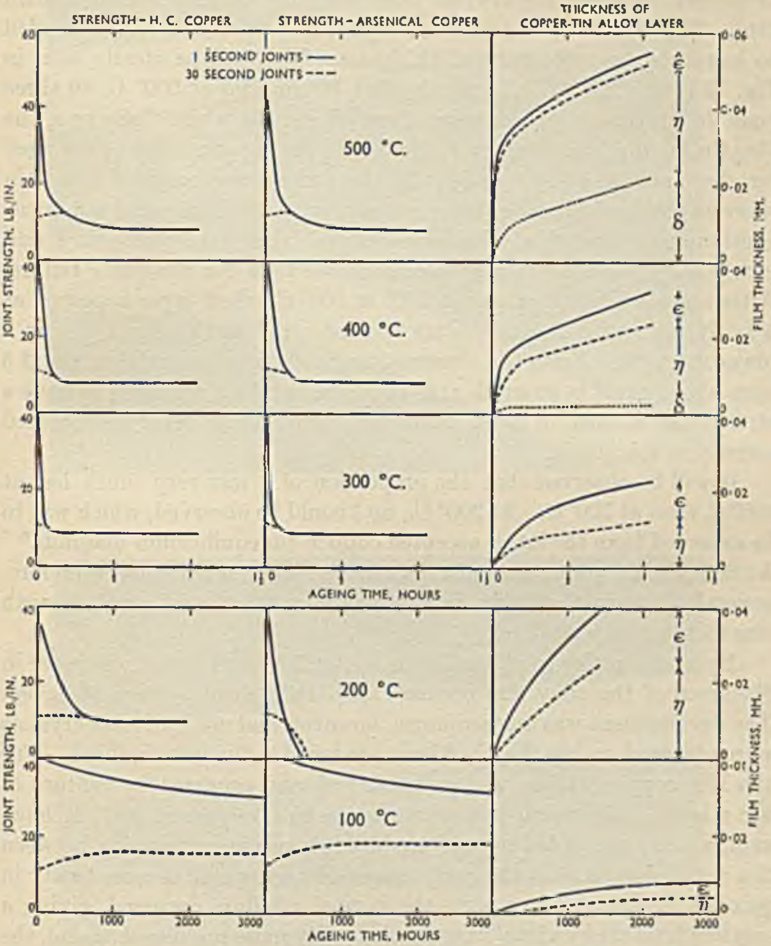


Fig. 4.—Ageing of Pure Tin Joints at Elevated Temperatures.

with the object of discovering the cause of this new type of failure, for in this case no brittle phase could be observed micrographically; (4) The effect of alloying additions to tin and solders on the ageing of joints.

(1) *Pure Tin.* Details of the formation of alloy films and the resulting joint strengths for pure tin on the two grades of copper,

temperatures of ageing being from 500° down to 100° C., are shown in Fig. 4. The reaction with liquid tin at the copper surface invariably resulted in an irregular denticulated alloy film, whilst individual crystals of copper–tin alloy might cross from one side to the other of the tin film. The later-formed and more copper-rich phases, however, tended to have greater uniformity of thickness. This will be clearly seen in Fig. 13 (Plate XXXVI), in which after 15 minutes at 500° C. all three possible copper–tin phases were observed, *i.e.* the white CuSn or ε, the blue Cu_3Sn or η, and the grey δ adjacent to the copper. For joints aged for short periods at 400° or 500° C., the ε phase was confined to a thin layer on the outside of the jagged η layer, so that failure could not occur continuously through ε. Failure occurred, therefore, partly in ε and partly in η, resulting in a greater strength than for straight ε failure. After more prolonged attack at 400° or 500° C., the δ layer appeared as a fairly uniform film, and failure now occurred in this layer, giving a lower strength. From the observations made, it appeared that ε and δ were about equal in strength at 8–10 lb./in., whilst η appeared to have a strength of at least 18 lb./in., although failure could never be obtained entirely in this phase.

It will be observed that the proportion of δ was very much less at 400° C. than at 500° C. At 300° C., no δ could be observed, which was to be expected from the latest accepted copper–tin equilibrium diagram.[6, 7] At 300° C., the proportion of ε was much higher, and failure, therefore, generally occurred entirely in this phase, so that minimum strength was more rapidly attained.

By ageing under solid conditions, *i.e.* at 200° and 100° C., increase in thickness of the alloy film occurred, and both ε and η were observed. The development was more uniform, however, and no denticular crystals were obtained, unless they had been produced in the joint making. For the HC. copper, failure was quite normal, and occurred by rupture of the ε layer. By ageing joints on low-arsenical copper at 200° C., however, a new type of failure was produced, involving separation between the η and copper. In the early stages of ageing this occurred only in patches, whilst at other parts the normal ε failure occurred, giving a mottled fracture by visual examination. By more prolonged ageing, the area showing interphase separation increased, until finally the whole of the joints stripped, leaving a bare and bright copper surface, the strengths of joints being then too small to measure. Sections showing the failure of an HC. copper joint and an arsenical copper joint after 3 weeks at 200° C. are shown in Figs. 11 and 12 (Plate XXXV); the difference between the failures occurring in the two cases is clearly seen.

At 150° C., the interphase failure involved only slight patches even

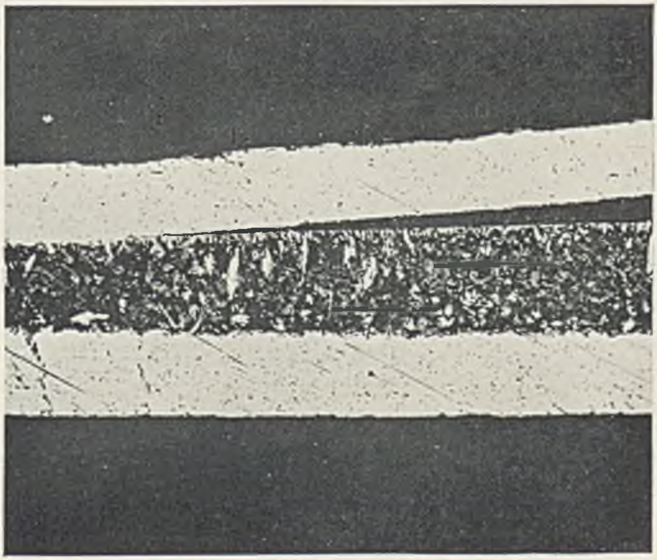


FIG. 7.—Pure Tin and HC. Copper. 30-Second Joint, Showing Fracture. Strength 111 lb./in. × 75.

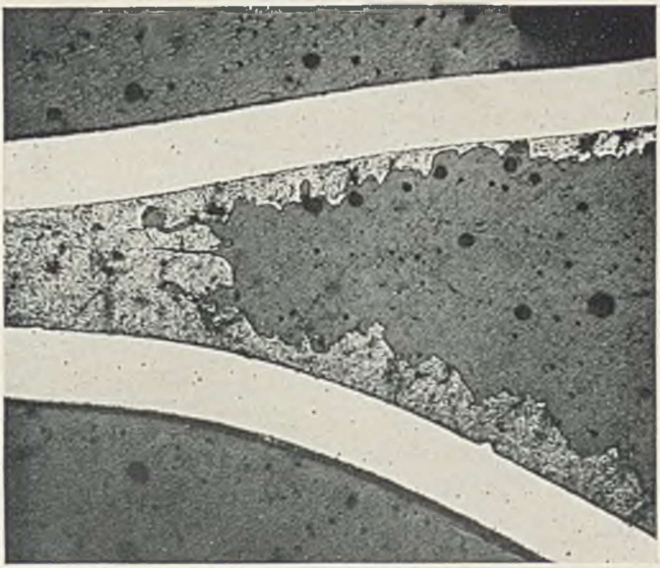


FIG. 8.—Pure Lead and HC. Copper. 30-Second Joint, Showing Fracture. Strength 45 lb./in. × 75.

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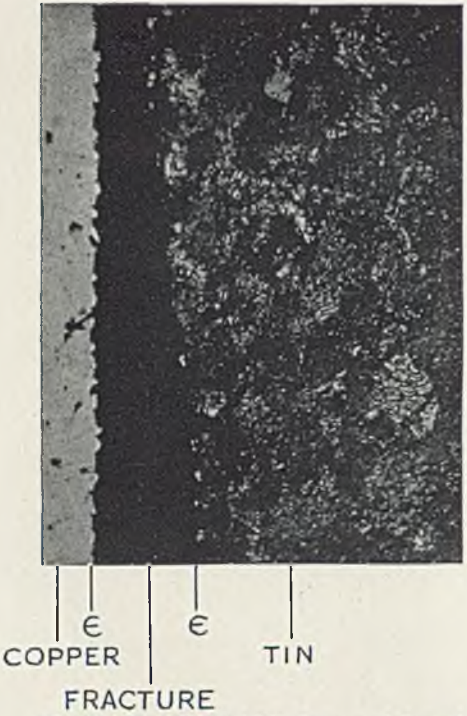

FIG. 9.—Pure Tin and HC. Copper. 1-Second Joint Fractured. Strength 40 lb./in. × 500.

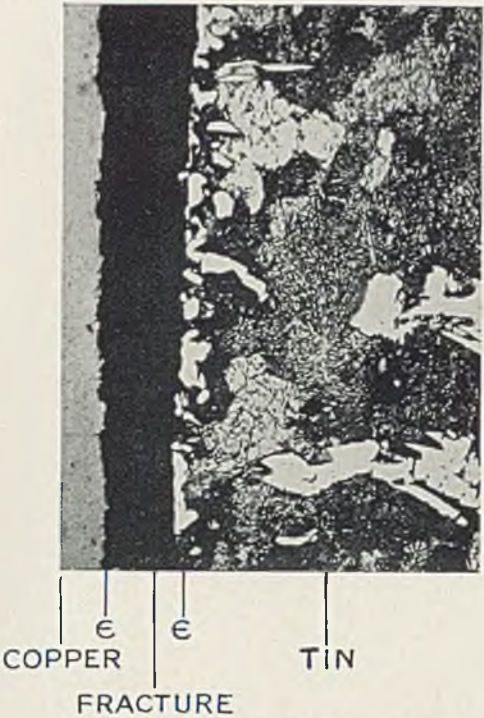

FIG. 10.—Pure Tin and HC. Copper. 30-Second Joint Fractured. Strength 11 lb./in. × 500.

PLATE XXXV.

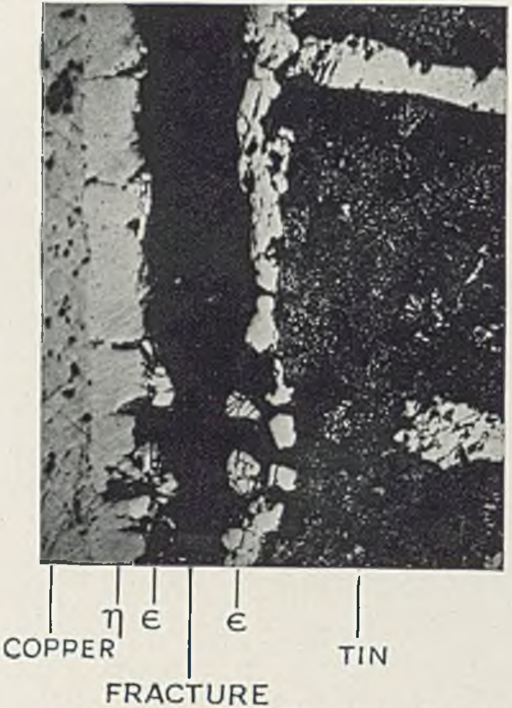

Fig. 11.—Pure Tin and HC. Copper. 30-Second Joint Aged 3 Weeks at 200° C. and Fractured. Strength 12 lb./in. × 500.

Fig. 12.—Pure Tin and Arsenical Copper. 30-Second Joint Aged 3 Weeks at 200° C. and Fractured. Strength nil. × 500.

Plate XXXVI.

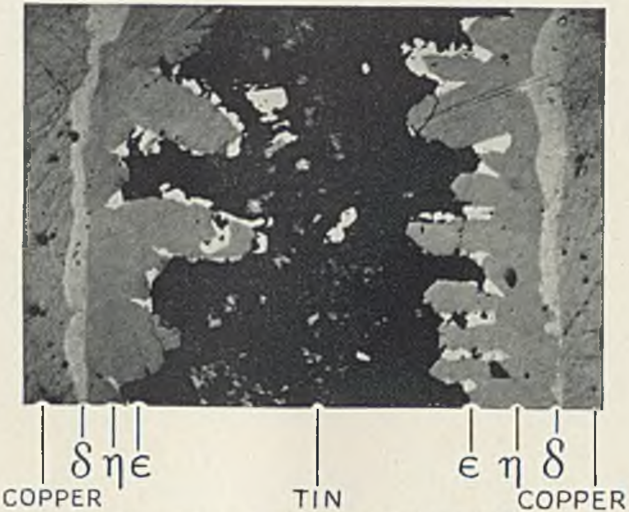

Fig. 13.—Pure Tin and HC. Copper. Aged 15 Minutes at 500° C. × 500.

δ—grey-yellow.
η—blue-grey.
ε—white.

after ageing for 3000 hrs., and it was obvious that very prolonged ageing would be required for complete failure. No signs of interphase failure occurred on the most prolonged ageing at 100° C.

(2) *Lead–Tin Alloys*. The liquid ageing of joints made with lead–tin alloys did not show any special features, the alloy layers being formed much in the same way as for pure tin. As might be expected, the alloy film growth under equivalent conditions was slower than that for tin, and, generally, there were larger proportions of the higher copper alloy phases; these differences were probably due to local lead enrichment as a result of the tin being removed as copper–tin alloy. Joints made with pure lead showed no change on prolonged ageing.

The solid ageing of joints made with lead–tin alloys showed many points of interest, and a detailed description is given for ageing at 150° C. The results of this examination for pure tin and lead–tin alloys are shown

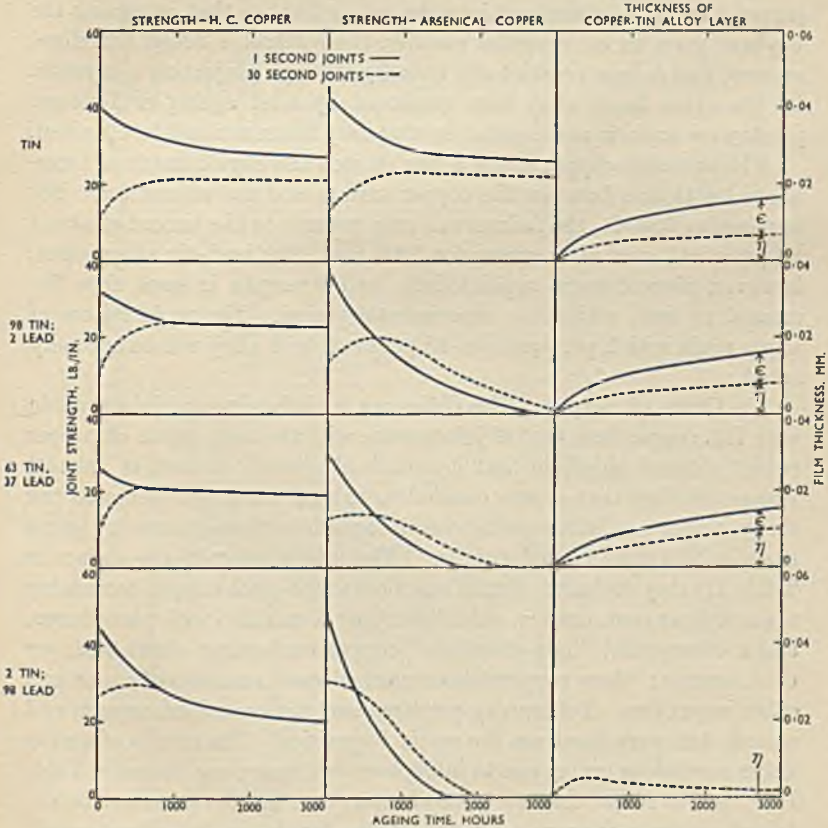

Fig. 5.—Ageing of Lead–Tin Alloy Joints at 150° C.

in Fig. 5, no changes being observed for pure lead joints. It will be seen that the η and ε alloy layers increased in thickness with ageing for all lead–tin alloys, but that with increasing amounts of lead the proportion of η tended to increase, until with the 2 per cent. tin–98 per cent. lead alloy only η was formed. Microexamination clearly showed the reason for this change, for in the eutectic alloy the formation of the copper–tin alloy film resulted in an adjacent layer of pure lead, from which the tin had been removed by alloying.

The loss in strength of HC. copper joints on ageing at 150° C. was, for all the alloys examined, quite small, although the high strength of the 2 per cent. tin–98 per cent. lead alloy was not maintained, and the strength of this alloy tended to decrease to that of the higher tin alloys. The weak 30-second joints all showed an initial tendency to increase in strength; this appeared to be due to the fact that 30-second joints had jagged ε crystals jutting out into the solder film, so that on ageing the η phase grew in an irregular manner, the residual ε being, therefore, uneven, and failure occasionally crossing through projecting η crystals. On the other hand, alloy films produced by solid ageing of 1-second joints were uniform and regular, so that easy fracture could be obtained.

The arsenical-copper joints again showed the development of interphase brittleness between the copper surface and the adjacent η. For pure tin at 150° C., the failure was only present to the extent of about 20 per cent., even after ageing for 3000 hrs. The lead–tin alloy joints, however, showed more rapid failure, and strengths in each case decreased to zero, within the experimental period. The rapid failure of joints made with 2 per cent. tin–98 per cent. lead alloy will be specially noted.

(3) *Grade of Copper.* The difference in behaviour of joints made with HC. copper from that of joints made with the lower grade of copper (which differed chiefly in that it contained a small amount of arsenic) was so striking that it was decided to extend the experiments to the study, under conditions giving rise to rapid interphase failure, of joints made with other alloyed coppers. The alloys selected are shown in Table II, they included normal arsenical tough-pitch copper containing about 0·4 per cent. arsenic, a similar copper deoxidized with phosphorus, and a commercial "non-arsenical" copper containing about 0·04 per cent. arsenic; these coppers also contained small amounts of nickel and other impurities. Laboratory-prepared samples contained oxygen and arsenic, but were free from the minor impurities. The results of ageing under conditions giving rise to interphase brittleness are shown in Table III. It was found that no trace of interphase brittleness could be obtained on coppers prepared from pure materials, except when arsenic

TABLE III.—*Ageing of Joints from Various Grades of Copper.*

Soldering Alloy.	Temperature of Ageing, ° C.	Period of Ageing.	OF. Oxygen-Free Copper.		HC. High-Conductivity Copper O.R.C.		Commercial Coppers.						Synthetic Coppers.							
							LAR. Low-Arsenical Tough-Pitch.		AR. Arsenical Tough-Pitch.		DOA. Deoxidized Arsenical.		As 1.		As 6.		As 33.		As S.	
			Strength, Lb./in.	Failure.	Strength, Lb./in.	Failure.	Strength, Lb./in.	Failure.	Strength, Lb./in.	Failure.	Strength, Lb./in.	Failure.	Strength, Lb./in.	Failure.	Strength, Lb./in.	Failure.	Strength, Lb./in.	Failure.	Strength, Lb./in.	Failure.
Tin	200	As made	46	ε	40	ε	42	ε	38	ε	48	ε	40	ε	40	ε	41	ε	44	ε
		8 days = 200 hrs.	23	ε	24	ε	11	ε/interphase=60/40	24	ε	26	ε	22	ε	18	ε/interphase=85/15	8	ε/interphase=70/30	20	ε
		3 weeks = 500 hrs.	12	ε	11	ε	0	Interphase	14	ε	13	ε	9	ε/interphase=95/5	4	ε/interphase=20/80	6	ε/interphase=50/50	9	ε
Eutectic Lead-Tin	150	As made	28	ε	26	ε	30	ε	30	ε	30	ε	26	ε	26	ε	27	ε	26	ε
		3 weeks=500 hrs.	22	ε	22	ε	17	ε/interphase=50/50	22	ε/interphase=95/5	24	ε	20	ε	22	ε	10	ε/interphase=50/50	22	ε
		6 weeks=1000 hrs.	23	ε	21	ε	10	ε/interphase=30/70	18	ε/interphase=90/10	25	ε	23	ε	19	ε/interphase=95/5	6	ε/interphase=20/80	20	ε
		18 weeks=3000 hrs.	18	ε	19	ε	0	Interphase	17	ε/interphase=90/10	20	ε	20	ε	12	ε/interphase=70/30	0	Interphase	19	ε

was added. The addition of a small amount of arsenic to a pure oxygen-bearing copper (As 6), gave rise to failure occurring as rapidly as in the commercial arsenical-coppers, whilst even joints containing only 0·002 per cent. of arsenic (As 1) gave signs of the interphase failure after prolonged ageing. The deoxidized arsenical-copper again gave no signs of the interphase failure. It seemed fairly definite, therefore, that both oxygen and arsenic were necessary for failure, the failure being apparently most severe with low arsenic contents, whilst on extending the arsenic outside the normal commercial range, *i.e.* to an amount of 1 per cent., complete freedom from interphase failure was obtained.

(4) *Alloying of Solder.* Alloying additions to tin and lead–tin alloys were made with the object of obtaining, if possible, some inhibition of both copper–tin alloy formation, and of the development of interphase brittleness. Nightingale had claimed some diminution of copper–tin alloy formation in the presence of antimony. Alloys of tin and lead–tin eutectic were prepared with antimony up to the maximum amount obtainable in solid solution, *i.e.* 5 per cent. of the tin content. Other alloys prepared contained, respectively, 0·1 per cent. of antimony, arsenic, and bismuth. No differences were found in the behaviour of joints as a result of any of these alloying additions, either as regards the rate of formation of the copper–tin alloy film, or the occurrence of interphase brittleness. The initial strengths of 1-second joints using the maximum antimony content were, however, about 10 per cent. greater.

HIGH-TEMPERATURE TESTS.

The testing of joints at slightly elevated temperatures showed, in an interesting way, the results of the normal mechanism of failure by rupture of the ϵ layer; for, whereas at 100° C. the lead–tin alloys all showed very much diminished strength, on the other hand joints made from these alloys showed only slightly decreased strength. This is shown in Fig. 6,* where scales for the tensile strength of die-cast solders †

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* It will be noticed that, in addition to the higher tensile strengths obtained in die-cast alloys, as compared with the gravity castings of Nightingale, the curve obtained is of considerably different shape where it approaches the composition of pure tin or of pure lead. Nightingale did not examine these terminal alloys, and in his original paper showed these portions of the strength curves as broken lines. The following are the alloys, on which curves for cast strength are based in the two cases:—

Fig. 1. (Nightingale) Tin, 66/34, 56/44, 45/55, 34/66, Lead.
Fig. 6. Tin, 98/2, 85/15, 63/37, 50/50, 30/70, 15/85, 2/98, Lead.

† The alloys were pressure die-cast in an Ekert machine designed for brass casting. On this machine the piston injection was operated by compressed air at 1000 lb./in.^{2}, giving an actual pressure on the piston of about 4 tons/in.^{2}. The dies were used cold, and test-pieces were cast in pairs. The test-pieces were of standard shape used for die-casting, being 6 in. long × $\frac{1}{8}$ in. thick; they were 1 in. wide at the ends with a central parallel portion $2\frac{1}{2}$ in. long and $\frac{1}{2}$ in. wide. The speed of

(tons/in.^{2}) and for the strength of corresponding joints (lb./in.), have been so chosen that for pure lead the die-cast strength and the joint strength approximately coincide, for in such a joint it appeared that the true strength of the joining alloy was most nearly attained in testing the joint. It will be seen that for the lead–tin alloys the strengths obtained in joints did not in any way approach the strength attained by the solder film itself at normal temperature; at 100° C., however, the solder strength had decreased so much that joint strengths were now little less than solder strengths.

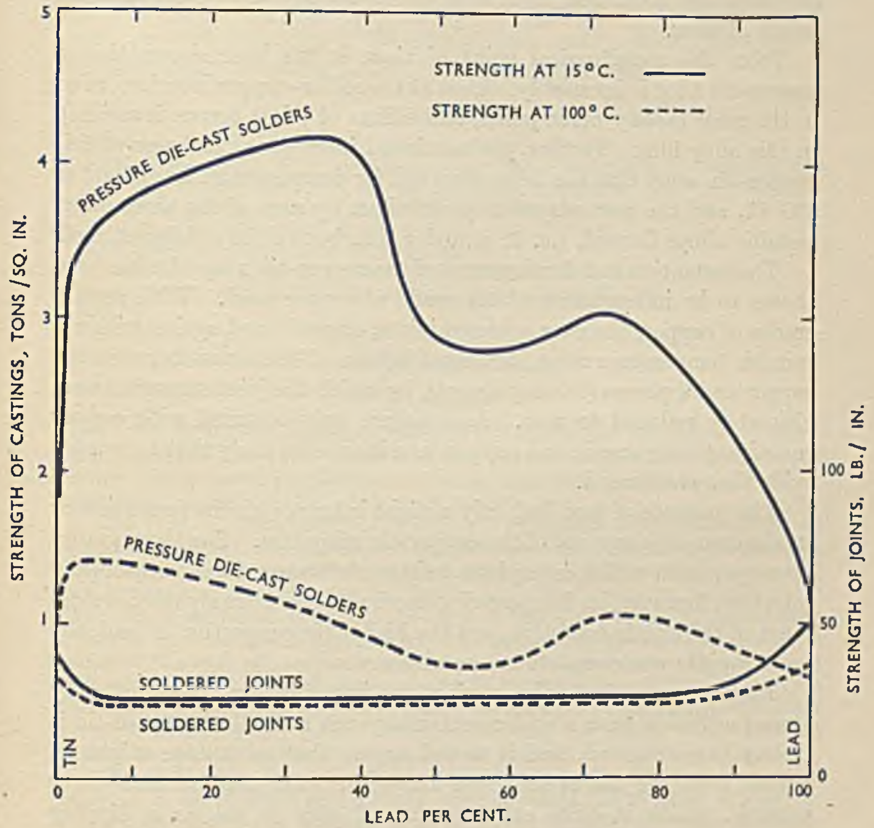

FIG. 6.—Strength of Solders and Soldered Joints.

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testing was the same as for joints, namely one inch per minute. These test-pieces were of very fine structure, and in this respect resembled the solder film of a joint more closely than did gravity castings.

SUMMARY AND CONCLUSIONS.

The observations made in the course of the experimental work described are of interest from both the metallurgical and the practical points of view.

From the metallurgical point of view, it has been shown that a copper–tin alloy is invariably formed at the solder–copper interface, even in the most rapidly made joints, and failure of joints occurs invariably in this alloy film. Further, the continued increase in thickness of this copper–tin alloy film has been observed for temperatures from 100° to 500° C., and the part played in joint failure by each of the three intermetallic alloys formed, *i.e.* δ, η, and ϵ, has been clearly differentiated.

The formation and development of the copper–tin alloy film has been shown to be independent of the grade of copper used. With certain grades of copper, however, soldered joints, on prolonged ageing within a suitable temperature range, developed a form of brittleness between the copper and η phases (δ being absent), by which the joint strengths were ultimately reduced to zero. Such failure only occurred with copper containing both arsenic and oxygen, and it appears likely that a complex oxide film was formed.

The presence of lead had only a slight influence on the formation or subsequent development of the copper–tin alloy film. For those grades of copper with which interphase brittleness occurred at the η–copper interface, however, lead appeared to accelerate considerably the development of the brittle condition, and the higher the proportion of lead, the more rapidly was complete failure obtained.

From the practical point of view, the impossibility of getting really strong adhesion from a solder containing even a small amount of tin is clearly demonstrated, and it would appear that advantage might be gained from the use of lead-base alloys, for example, the lead–silver eutectic, which is quite satisfactory and easy to use as a dipping solder.

Where soft soldered joints are to be made on articles for use at elevated temperatures, the avoidance of arsenical copper is clearly desirable, but the choice of available material includes all phosphorus deoxidized coppers, as well as high conductivity coppers, either oxygen bearing or oxygen free.

The possibility of interphase brittleness causing complete failure on soldered structures should not however cause undue anxiety. Soft soldered structures are rarely designed to operate at temperatures exceeding 100° C., and by exposure at this temperature no signs of interphase failure have been observed on any grade of copper.

ACKNOWLEDGMENTS.

The author's thanks are due to the Management Board of Messrs. I.C.I. Metals, Ltd., for permission to publish the observations contained in this paper. He also wishes to acknowledge the valuable encouragement received from Dr. H. W. Brownsdon, and to thank Members of the Laboratory Staff for analysis of the materials used.

REFERENCES.

[1] H. Hanemann, *Z. Metallkunde*, 1936, **28**, 68.
[2] B. W. Gonser and C. M. Heath, *Trans. Amer. Inst. Min. Met. Eng.*, 1936, **122**, 349.
[3] S. J. Nightingale, *Brit. N.F. Metals Res. Assoc.* **C 234/214**; also "Tin Solders." London: **1932**. (*Brit. N.F. Metals Res. Assoc.*)
[4] H. Weiss, *Rev. Mét.*, 1924, **21**, 18.
[5] T. B. Crow, *J. Inst. Metals*, 1926, **35**, 55.
[6] E. A. Owen and J. Iball, *J. Inst. Metals*, 1935, **57**, 267.
[7] E. A. Owen and E. C. Williams, *J. Inst. Metals*, 1936, **58**, 283.

DISCUSSION.

(*Condensed.*)

DR. J. MCKEOWN,* M.Sc. (Member): The author has provided useful information on the quick strength of this type of joint. The mechanism of failure under such conditions of testing has been clearly demonstrated, especially by the beautiful photomicrographs.

The type of joint shown in (*b*), Fig. 2, is inherently weak when compared with the type (*a*), and should not be used where use of (*a*) is at all possible. The author's method of test of the joint of type (*b*), Fig. 2, is novel, but should not be taken as a suitable test for the comparison of solders to be used where the joint is subjected to shear. In view of this, the title of the paper may give rise to some misunderstanding. The author has shown clearly that, in joints of the type (*b*), surface alloying has an influence on the strength of the soft solder joint, but it was shown clearly by Nightingale, and verified by more recent work, that if the joint is in shear, the strength of the joint is the shear strength of the solder used. I suggest altering the words "soft soldered joints" in the title to read "soft solder butt joints."

The author has shown by the rapid tensile tests the influence of surface alloying on the strength of the joints, but one would like to know whether, if creep properties are of importance in this type of joint, the same influence would be indicated by the results of creep tests on the joints. We know only too well that results obtained from rapid tests are no criteria of the behaviour, nor even of the relative behaviour, of materials under conditions of loading producing creep. In view of the hard, brittle nature of the compounds, is it not possible, or even probable, that under prolonged load, much less than the quick breaking load of the joint, the soft ductile solder would fail rather than the hard layer of compound? If this were so, the general conclusion that solders producing such alloy layers are undesirable would be invalid. It is to be hoped, therefore, that the author will extend this work to the consideration of the creep strength of such joints and of the method of failure in creep.

MR. R. G. HARPER,† M.Sc. (Member): The author is to be congratulated on

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† Research Metallurgist, Fry's Metal Foundries, Ltd., London.

his adaptation of the "sardine tin" test, which has for years been the standard workshop test for soldered joints. Although the shear test is important, the tearing test utilizes a type of failure which is very common in practice. For example, vibration, which is a frequent cause of joint failure, will almost always involve a repetition of this tearing action. It is possible, therefore, that the use of solders such as the silver–lead alloys mentioned in the paper will effect an increase in the life of soldered joints which at present fail by vibration at normal temperatures. It is at temperatures above 100° C., however, that such solders have a definite field of application. The paper shows that it is undesirable to use tin-containing solders at such temperatures, owing to the initial formation of the brittle and weak copper–tin alloy layers and the subsequent continued growth of those layers. The silver–lead alloys do not suffer this type of weakening; moreover, they have the further advantage that the shear strength of the joint does not decrease so rapidly with increase of temperature. We have found that, while such alloys are weaker than the soft solders at normal temperatures, they are stronger at elevated temperatures, owing to their higher melting point, which is approximately 305° C. It should be pointed out that these solders can be applied almost as easily as the tin-containing alloys.

The observation that the addition of antimony to the solder had little effect on the growth of the alloy layers is interesting. The author refers to Nightingale's results, which were obtained by immersing solid copper cubes in molten tin and tin alloys for comparatively long periods of time. The antimony–tin and antimony–lead–tin alloys produced less attack than pure tin, but the conditions were much more severe than those in the author's test.

The question of the attack of solid metal by molten metal merits more attention. Scheil and Wurst,* in a study of the attack on solid iron by molten zinc, found that there was a critical relation between rate of attack and temperature, and that the attack proceeds in two ways, the first involving diffusion of iron through the alloy layer to react with the molten zinc, and the second involving flow of molten zinc to the junction between the alloy layer and iron. In connection with the influence of alloying elements, they found that the addition of silicon to the iron or of aluminium to the zinc accelerated the rate of reaction; if, however, both additions were made together, the reaction was almost suppressed. These points have some bearing on the author's results and show that the action is not by any means simple.

Mr. E. J. DANIELS,† M.Sc. (Member): In considering a paper which gives the results of tests on materials in common use, it is natural to ask: How do the results compare with those of tests previously carried out? If there are any remarkable divergencies, the further question arises as to why this should be so.

Since the results of other tests are available, a comparison can be made. Fig. A shows results obtained by (1) ‡ investigators in this country and (2) § and (3) || in the U.S.A., using three methods of testing, while Fig. B shows the author's results.

There is an extraordinary difference. Quite contrary to Mr. Chadwick's findings, lead and lead-rich alloys give joints of low strength as compared with medium-tin and high-tin alloys. If the author's test is of practical value, and is accurate, then the results obtained by other investigators have no

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* *Z. Metallkunde*, 1937, 29, 224.

† International Tin Research and Development Council, London.

‡ S. J. Nightingale, "Tin Solders," London, 1932.

§ B. W. Gonser and C. M. Heath, *Trans. Amer. Inst. Min. Met. Eng.*, 1936, 122, 349.

|| *Amer. Soc. Metals*, Progress Report, Feb. 15, 1937.

relationship to actual joints. This, however, is not so—the lap joint, for example, is one of the commonest types of solder joint in use. Results with this joint (Fig. A) are quite consistent with the others.

Mr. Chadwick seems, therefore, to have adopted a type of test which does not relate so directly to practical conditions. In fact, were it not so, it is difficult to see why tin solders should be used as extensively as they are. I know of no joint that is subjected to stress applied in the manner adopted by Mr. Chadwick.

What, therefore, is the significance of the present work? Has this test any special features which merit its use? Looking at the methods of testing,

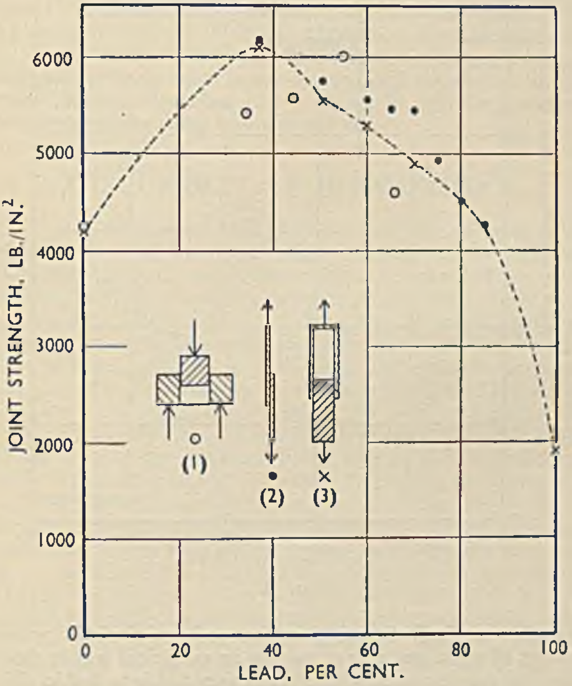

Fig. A.

I fail to understand how any real knowledge of the stress causing joint failure can be obtained. On application of the load at the outside of the joint, what is the stress concentration? Presumably, it is a maximum at the edge of the joint and decreases inwards, but in an unknown manner.

Take, for instance, the alloy containing 37 per cent. lead. A joint made with this alloy is expected to break at 6000 lb./in.^{2}. If the stress distribution is such that this figure is reached at the edge of the joint, we know that it will part. This stress will then be transferred inwards, and the process will be repeated, opening up the joint.

In this test joints made with pure lead withstood a higher *load* than joints made with tin–lead alloys, and containing tin–copper compounds. Mr. Chadwick deduces from that that the presence of tin–copper compounds is therefore deleterious. We already have figures, however, showing that lead joints have a strength of only 2000 lb./in.^{2}. It seems more reasonable to deduce that the stress distribution in Mr. Chadwick's test varies with the nature of the joining material, and that the load applied is carried by a much greater area of join when lead is used than when a solder containing tin is employed.

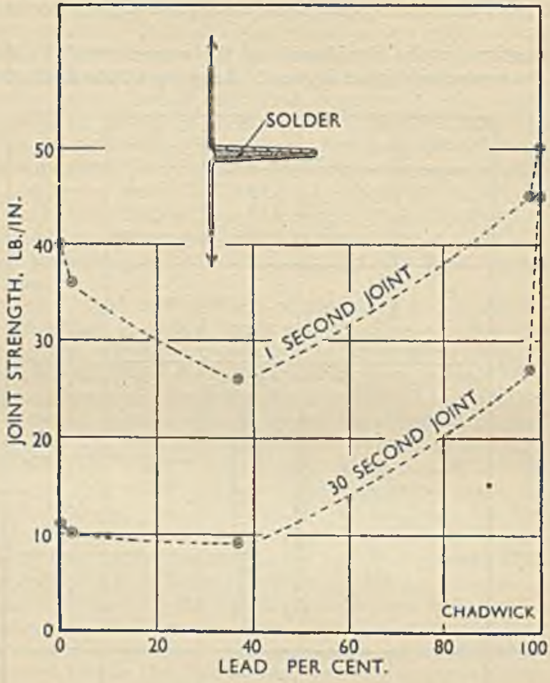

Fig. B.

To me such a method of testing appears to be of doubtful value from the scientific point of view, and if it is used as an empirical test it should imitate certain practical conditions in which joints were liable to fail in this way, and give results in terms of generally accepted dimensions, such as pounds per square inch.

Dr. R. Genders,* M.B.E. (Member of Council): As Mr. Daniels has pointed out, the results given in this paper are entirely governed by the character of the test which the author has employed. This was, in principle, a slow notch-bar test, and that explains completely why the results do not agree with the properties of the solders in the massive form. The notched-bar test reveals mainly the resistance of the material to the propagation of a crack. One can thus understand why lead has given good results under such conditions, and why hard and brittle intermetallic compounds, such as ε and η, show little resistance. It is questionable whether soldered joints are ever subjected in service to the conditions represented by the test.

* Research Department, Woolwich.

The **Author** (*in reply*): For the most part the discussion has turned on the great difference between the results obtained with this tearing type of test and shear types of test employed by previous workers. It might be well in the first place to point out that in order to test a lap joint between 0·005-in. thick copper strips by means of a shear test, there must not be more than about 1 mm. overlap, otherwise the copper strip itself would be broken. The new technique developed, however, has enabled tests to be made on typical lap joints between thin strips, and has shown a whole new range of phenomena associated with the making of joints and their exposure to elevated temperatures. The shear type of test has been so completely investigated by Nightingale that little further work is necessary. The present series of experiments supplements those results, but does not in any way invalidate them.

I was pleased to hear Mr. Harper's remarks on the use of lead-base alloys as solders. I can confirm his observations that, as dipping solders, the lead–silver alloys are quite as easy to use as the lead–tin alloys; in making test joints by the methods described in the paper, no difficulty was encountered in obtaining good joints using lead-rich alloys.

DISCUSSION AT BIRMINGHAM.

Dr. H. W. Brownsdon,* M.Sc. (Vice-President): The serviceability of any constructional work in which soldered joints are used depends on the strength and reliability of such joints, and this is especially the case when the strength of the structure as a whole depends practically entirely on that of the soldered joints, as is the case with radiators used for motor-cars and aircraft, where a number of very thin metal members are assembled to form a block by means of soldered joints. In such cases temperatures fluctuate between normal and that of boiling water or above, and the effect of temperature on the strength of the joint, both when making the joint and during service, are important factors clearly brought out in this paper. The results given in the paper indicate some of the weaknesses that may arise in soldered joints unless careful choice of materials and temperatures for making the joints are observed.

The lead–tin alloys have properties which make them eminently suitable for use as solders, and they are not likely to be displaced by other alloys except under special conditions, where their relatively low melting point may render them unsuitable. I would suggest that the lesson to be learned from Mr. Chadwick's paper is that if the best results are to be obtained from these lead–tin solders then they must be applied under carefully controlled conditions, otherwise the strength of the joint may be seriously reduced. Another point is that the strength of the joint is also dependent on the composition of the metal being soldered, and, whilst this paper deals more especially with copper, the problems associated with the soldering of other materials, such as brass, cupro-nickel, or iron, require equally careful study, and the author is now engaged on such further investigation.

Mr. W. F. Brazener † (Member of Council): The author has performed a very useful service in showing that the ε and η phases are of importance to the practical application of soldering, and also that theoretical considerations of an industry's practical problems can be solved in the laboratory.

I am interested in the manufacture of the ordinary copper water ball, which is made by joining two copper hemispheres, principally by soft soldering. On seeing the times given by Mr. Chadwick for the processes of soldering, I wondered whether there might be any marked difference in the results if

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* Research Manager, I.C.I. Metals Ltd., Birmingham.

† General Manager, The Mint (B'ham) Ltd., Birmingham.

one took the times actually employed by a soldering operator in effecting the joints. When watching solderers at work, it can be seen that in 1 second they cover several inches of surface of the metal, so that any particular spot on the metal is probably not affected by the temperature of the soldering iron for more than a fraction of a second. In that time is there any alloying at all, and are those peculiar effects of the formation of the ε phase in the copper–tin series obtained?

Has the author carried out any depth measurements, and can measurements be made by any means of the depth of the alloying for any particular time and for any particular type of solder? It occurred to me that for the very short time taken to effect a joint in some soldering operations, metal spraying might, under certain conditions, be as effective.

There seems to be one alloy missing from the list mentioned by Mr. Chadwick; namely, non-arsenical, deoxidized copper. Has the author any results on the making of joints with that particular alloy? I was astonished to see the photomicrograph of the lead joint. It had not occurred to me that one would get, with lead alone, such strong adhesion to the surface of copper. As it is known that copper and lead do not alloy easily, has the author any explanation for what appears to be an extraordinary effect in attempting to make a soldered joint with pure lead?

Mr. E. C. ROLLASON,* M.Sc. (Member): Can Mr. Chadwick give any information on the effect of such soldered joints as he has described on other types of bases, and what would be the influence of the flux used in connection with such joints? Several different types of flux are used in practice, and the particular type of flux used might have profound influence on the joint.

In one of the samples shown by the author (the one which seemed to tear away very readily at the joint) there appears to be some cavities in the soldered layer. What is the explanation? Are the cavities due to the small globules of solder which have been put on during the manufacture of the joint?

Dr. N. P. ALLEN,† M.Met. (Member): I am interested in the fact that the strongest joints were obtained when the minimum time was allowed for diffusion or chemical action, and when pure lead was used—a metal with no very pronounced chemical action on copper. Certain investigators, in studying the production of metallic coatings by hot-dipping processes, have thought that the first condition for good adhesion is that the molten metal shall wet the surface of the metal to be coated, and that a certain degree of chemical combination is necessary for wetting. The evidence put forward by Mr. Chadwick seems completely to refute that point of view. Apparently, chemical combination between the metals to be joined is undesirable, and if a strong joint is required, two metals should be chosen which have no chemical action on each other, and in which the cohesive forces are as nearly as possible of a physical nature.

The makers of fusion welds usually like to obtain a uniform diffusion of the weld metal into the base metal, but it is possible to doubt whether this diffusion is really necessary. Nickel-clad steel sheets, consisting of nickel welded to mild steel, show a clean line of demarcation, with no evidence of the martensitic structures which might be expected if the nickel and iron diffused into each other: yet the union is perfectly strong, and bending and twisting tests appear to show that the full strength of the constituent metals is realized in the joint.

Mr. J. W. JONES,‡ M.Sc. (Member): At first sight, this paper appears to

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‡ Lecturer in Metallurgy, Birmingham University.

condemn the soft soldering process. However, the method of testing chosen is such as to bring out the possible weaknesses rather than the possible strength of the soldered joint. The author has shown how from the copper-to-copper one obtains the formation of strata of brittle compounds, and it appears that the stress distributed under this method of test is such that (as for any failure by tensile stress) the strength of the chain is its weakest link, and the stress *directly imposed on the outcrop of* ε *or* η initiates a fracture which rapidly propagates more or less in the same strata, right down the test-piece.

It has been suggested that the shear test is not quite satisfactory and does not provide the same data as does the new form of test. It seems to me that the whole interpretation of the microstructure is that a hard, brittle constituent can play two parts. If the hard, brittle constituent itself be stressed, failure results, or is at least initiated and afterwards progresses. Alternatively, where the hard, brittle constituent is reinforcing a more ductile and tougher constituent, it strengthens rather than weakens the structure, and that appears to be more or less the state of affairs in the ordinary shear test, since there is a tendency for the shear stress to be distributed over the section as a whole and less concentrated on the particular outcrop of the brittle strata. Nevertheless, the test, as such, is a logical and sound indication as to where brittleness may result, and it is a function of the Institute to anticipate trouble of that kind as well as to cure it after it has arrived.

Was the same flux used for the arsenical, oxygen-containing coppers as was used for the pure coppers? The complete parting of the solder from the surface in the sample would, at first sight, appear to be due to fluxing trouble. There is no visual physical or chemical union of these surfaces, except possibly in patches.

I am intrigued by the method of preparation of the specimens initially selected. I understand that all were treated alike, and that they were subjected to a preliminary cleaning by dipping in 50 per cent. nitric acid. Has there been any standardization of that procedure? It would seem that the roughening of the surface and the exposure of crystal facets which appear on etching, would be a definite factor in determining the strength of a layer of solder some 0·005 in. thick.

Dr. F. Johnson * (Member): Does the author think that arsenic in the *tin* would have the same kind of effect as in the copper? It seems possible that a brittle layer composed of an infinitesimally thin film of arsenide of tin might be formed. I am not quite clear as to the author's remarks regarding the arsenic : oxygen ratio in the copper, and as to whether oxygen-free arsenical copper is worse or better than copper containing oxygen.

Mr. J. S. G. Primrose,† A.R.T.C. (Member): Regarding the question of flux for solders mentioned by Dr. Allen and Mr. Jones, there is another aspect of the subject to be considered; that is, the effect of corrosion in destroying the joints after the use of flux. This problem arises in connection with petrol filters, etc., which have to be soldered. Even though there should not be anything in the petrol to cause corrosion, some fluxes leave a residue which causes corrosion, whilst others give no trouble in this respect.

Dr. E. G. West,‡ B.Sc. (Member): The type of adhesion obtained by the methods described appears to be analogous in its physical characteristics to that obtained in electrodeposits. Alloying is not obtained with electro-

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† Chief Metallurgist, Rover Motor Company, Ltd., Birmingham.

‡ Metallurgist, English Needle and Fishing Tackle Company, Ltd., Redditch.

deposited coatings, and the work of Hothersall[*] and others has shown that the atoms of the deposited crystals often continue the lattice of the crystals of the base metal. This continuation is possible when basis metal and deposit belong to different crystal systems, and also when the lattice of the basis metal is distorted. A study of the nature of the stress between atoms might throw some light on the adhesion which is obtained without alloying, as exemplified by the lead and copper joint.

Dr. H. T. ANGUS,[†] M.Sc. (Member): An interesting point arising from the paper is that the strength of the soldered joint does not deteriorate to the same extent as that of the pure solder when exposed to a temperature of 100° C. In many sections of industry, two points have to be considered in connection with soldered joints: (*a*) strength, and (*b*) corrosion-resistance, though soldered joints are usually not expected to stand any great strain. Has the use of a high temperature or a long jointing time during soldering any effect on the ultimate corrosion-resistance, and would a joint of the lead–copper type be more likely to resist corrosion than a joint of the tin–copper type, where one is likely to get a metal compound? Where the strength of a joint is important, and may be affected by corrosion in service, it seems possible that more serious corrosion might be obtained with a joint containing an intermetallic compound.

Dr. C. H. DESCH,[‡] F.R.S. (President): I am surprised at the excellent quality of the joint made with pure lead. Without much experience of soldering, I should not care to make soldered joints with pure lead, but I wonder, if the joints behave as described in the case of the test-piece, why it should be impracticable to make such joints for ordinary purposes.

I agree with Dr. Allen in preferring to see a complete absence of intermetallic phases. I should have thought that a material which adheres (after proper wetting of the surfaces) without forming any alloy, would behave better than one which forms brittle phases. The joints made with pure lead realized the full strength of the lead. In work carried out years ago with non-metallic substances, the late Sir William Hardy showed that a thin layer of a material which wetted the surfaces perfectly gave remarkable strength, without any chemical relationship existing between the two substances.

What Dr. Allen has said about the absence of alloying would not apply to fusion welds. A fusion weld in steel with an abrupt transition of one structure to the other would be bad. There should be as perfect continuity as possible—in other words, the structure should be the same all through.

The AUTHOR (*in reply*): This method of making and testing joints has become almost a routine laboratory test, and it is possible to make joints very quickly. It is unfortunately not possible to carry out ageing tests quickly; it takes several weeks to obtain observations of value.

Regarding the time employed in making commercial joints, in many cases, such as that mentioned by Mr. Brazener, where the operator uses a soldering iron, the time for which the solder is molten is short, and therefore little alloying is obtained. In dipping a structure such as a radiator, the alloying corresponds more nearly to a 30-second joint than to a 1-second joint, because the whole thing is brought to a considerable temperature. Mr. Brazener has also raised a question regarding non-arsenical, deoxidized copper. In Table II, I described such copper as "low-arsenical tough-pitch" copper, because I thought it possible that the paper might be read by

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[*] A. W. Hothersall, *J. Electrodepositors' Tech. Soc.*, 1935, 10, 143.

[†] Chief Chemist, Parkinson Stove Company, Ltd., Stechford, Birmingham.

[‡] Superintendent, Department of Metallurgy, National Physical Laboratory, Teddington.

those not familiar with this material, who might not realize that the usual "non-arsenical" copper of commerce is characterized by the presence of traces of arsenic up to 0·05 per cent. along with other minor impurities. Quite a number of samples of non-arsenical coppers were tested; the one given in Table II is a typical example.

Mr. Rollason asked about the joining of other materials. A certain amount of experimental work has been carried out. Brass has been fairly thoroughly examined, and steel to a lesser extent; nickel and cupro-nickel are now being examined. The characteristics of all those materials which form intermetallic compounds are very much the same, in that a compound layer is built up more or less rapidly, according to the rapidity of the attack on the basic material. In the case of brass, it is very much slower than in the case of copper. Similar alloy layers have been observed with other basic materials, and it is only a question of plotting standard curves, similar to those in Fig. 3, for the different materials.

The influence of flux was dealt with fairly thoroughly in the paper. In order to make sure that the zinc content was not having some sort of effect (because when using brass instead of copper entirely different results are obtained), a tin ammonium bromide solution was used as one alternative, whilst oleic acid was also used as a flux; no difference was found in any of the phenomena, and the same types of failure were obtained. The only reason for choosing a zinc ammonium chloride flux was that it gave the soundest joints at the lowest possible temperature, and therefore one could reduce surface compound formation to a minimum. Excess of flux was always removed so far as possible after making the joint, in order that no corrosion should take place during the ageing of the joint.

The cavities in the sample joint to which Mr. Rollason referred are due to the original beads of solder. There was a certain amount of oxide film on the beads, and as the solder flowed away this oxide was left behind. That did not matter very much, because in testing it was possible to ignore strengths obtained in portions of joint which were unsound or porous. Many of the joints were tested more than once; that is to say, a joint was made, partly pulled as made, and then aged and pulled a little further. There is considerable advantage in carrying out a series of tests on one single joint.

Mr. Jones raised the question of the shear test; there is really very little to add to what has already been said. The effect of fluxing and etching on adherence has been fairly thoroughly investigated, and one of the methods of making joints was to polish the copper and then to flux it by means of a series of dips; the first dip was ether, to remove grease, then the strip was transferred to alcohol, and finally, without intermediate drying, an aqueous solution of zinc ammonium chloride was brushed on, and the strip finally dried. Parallel results were obtained whether that method or the nitric acid dip was used, and the slight etching effect in the nitric acid method did not have any effect on the joint strength. The interphase failure was not in any way connected with the flux, for such joints when tested prior to ageing showed a white tin film on the copper, with the normal strength of 10lb./in. or more according to the time employed in making the joint.

In reply to Dr. Johnson, for interphase failure the presence of both arsenic and oxygen in the copper is a necessity. Such failure does not take place in the case of deoxidized arsenical copper or in tough-pitch copper free from arsenic, but it takes place in all tough-pitch arsenical coppers, except those with high arsenic and low oxygen, and more rapidly with low arsenic and high oxygen; so that a high oxygen : arsenic ratio appears to be the cause of failure.

Mr. Primrose and Dr. Angus raised the question of corrosion in regard to flux. I am unable to say much about that, though it is common knowledge that chlorides are about the worst things possible for corrosion. Experimental joints were cleaned by boiling in water to remove the flux, but there is a strong objection to the use of chloride fluxes where corrosion is likely to occur; in such cases it is advisable to use oleic acid or some of the more recently discovered fluxes,* which are, however, not quite so easy to use. The eutectic chloride flux was selected because it enabled a very wide range of conditions to be explored, and it does not follow that it is recommended for commercial soldering operations.

I cannot say anything about the effect of intermetallic compounds on corrosion. The corrosion of a tin-to-copper joint and of a tin-to-lead joint presumably depends entirely on the corrosive conditions; and as the one always contains intermetallic compounds whilst the other does not, it is difficult to say whether any corrosion is due to the metal itself or to the intermetallic compounds.

Finally, there is the question of surface alloying, raised by a number of speakers, and in particular by Dr. Allen and Dr. Desch. This is a question of very great interest, and it appears from the present work that it is not necessary to have an intermetallic compound in order to obtain a high-strength joint; in fact, it appears to be definitely preferable to have no intermetallic layer at all. In this connection, however, it is useful to realize that those metals which seem to have a high affinity for each other appear at the same time to form intermetallic compounds. There is a greater affinity between tin and copper than between lead and copper. If two strips of copper be taken, fluxed and pressed into contact and dipped into liquid tin, it will be found that the tin rapidly penetrates to form a good joint, and that is the basis of ordinary soldering operations. Lead does not penetrate a copper joint so readily. In the method of making joints that has been employed, the beads of solder were put between the strips and the tools pressed down, so that the lead was mechanically forced to fill the joint. Pure lead, however, is extremely difficult to use with a soldering iron. In that connection, the use of a lead-silver alloy definitely appears to be advantageous, for it flows more readily over the surface of the copper, and it is therefore much easier to make joints on a commercial basis. My own opinion is that, provided that there is a wetting of the surface of one metal by another in such a way that there is no interfering layer (that is to say, all the air or flux is pushed out, and there is absolutely atom to atom contact between the two materials), then a good joint is obtained; in the same way two perfectly clean pieces of copper can be welded together below the melting point; there appears to be no necessity for any intermediate compound. To illustrate this point, I would remind you that if one takes two pieces of clean glass or metal (copper or cast iron), wets them with water, and puts them together, and then decreases the temperature below 0° C., a strong joint is obtained; but if one increases the temperature above 0° C., the water can be dried off, and there will be no alloying or change in the structure of the material.

Dr. Desch: Has Mr. Chadwick tried to effect the making of exceedingly thin layers of solder, for which it would presumably be necessary to have very flat surfaces and copper at a high temperature? With flat surfaces and a uniform layer of solder, the strength of the joint should become greater as the solder became thinner.

A point brought out by the paper, which ought to be borne in mind, is the importance of the wetting properties. Under ideal conditions, with no gas film present on the surface, lead should make the strongest joint, because it does not alloy at all.

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* J. W. Willstrop, A. J. Sidery, and H. Sutton, *J. Inst. Metals*, 1936, 59, 53.

Mr. Chadwick: The tools were so arranged as to leave a gap between the strips to be joined, because if pressure was applied so as to bring these into intimate contact a very weak joint resulted, owing to the fact that all the solder was pressed out, leaving only a layer of brittle compound.

CORRESPONDENCE.

The Author: After reading the detailed criticism, I should like to correct the impression, which appears to have been received by more than one speaker, that any condemnation of previous work on shear testing of joints was intended in the paper. The intention was rather to emphasize the difference in the two methods of testing, and this has also been done by a number of speakers in the discussion.

The view that intermetallic compounds are more favourable to the propagation of cracks than the soft solder alloys appears to have been generally expressed, and such brittle layers would tend to accelerate failure by vibration or other forms of alternate stressing. Examples of service failures in soft solder joints which I have examined have invariably fractured at the solder–copper interface. The argument of Mr. Daniels with regard to the area of joining material carrying the load during testing, would appear to be invalid, for in the case of the tin–lead alloy joint it was shown, by micrographic observation, that failure took place in the ε layer, whereas in the lead joint it took place in the lead itself; comparison of joint strengths with the strength of the soldering materials must therefore be without meaning.

In reply to a question by Mr. Harper on the attack of copper by tin, there appeared to be no appreciable inhibition by alloying additions to the tin, except in so far as attack was slowed down by dilution with lead. Attack was generally limited, however, by the small amount of tin present.

MAY LECTURE, 1938.

PLASTIC STRAIN IN METALS.

800

By Professor G. I. TAYLOR,* M.A., F.R.S.

TWENTY-EIGHTH MAY LECTURE TO THE INSTITUTE OF METALS, DELIVERED MAY 4, 1938.

SYNOPSIS.

The work of the author with Dr. Elam on the straining of metallic single crystals is described. The application of experimental results with single crystals to polycrystalline aggregates is discussed.

IN the May Lecture last year Professor Andrade [1] gave a very clear account of some of the main lines along which researches on metallic crystals have developed. I hope now to discuss some of the questions treated by Professor Andrade, but in greater detail than he was able to do in the time at his disposal. I propose also to put forward some thoughts about how our knowledge of metallic single crystals can help us to understand the mechanical properties of crystal aggregates.

I must begin by making the confession that I am not a metallurgist; I may say, however, that I have had the advantage of help from, and collaboration with, members of your Institute, whose names are a sure guarantee that the metals I have used were all right, even if my theories about them are all wrong. Perhaps I may be excused if I give an account of how I first came to have anything to do with metals. I was present at the Royal Society on the occasion when Sir Harold Carpenter described the fascinating series of researches which enabled him and Dr. Elam to prepare very large single crystals of aluminium. He showed test-pieces which had been pulled in a testing machine with the result that lines originally scratched on them at right angles to their longitudinal axes had become oblique during the plastic straining. These lines, it seemed, must provide the clue to the relationship between the crystallographic axes and the plastic strain. At that time the existence of slip lines on the surface of strained metals was well known, and it was known also that they are the traces of crystallographic planes. It was freely stated that they became visible, owing to slipping

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* Yarrow Research Professor of the Royal Society.

of the metal, just as the edges of cards in a pack become visible when the top of the pack is pushed sideways. This, however, is a very different matter from stating that the total strain is identical with that which is produced in a pack when cards slide over one another. The surface markings may, for instance, develop quite independently of what goes on inside the crystal, because the surface is known to be in a different physical state from the interior.

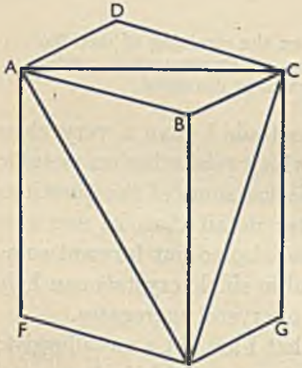


Fig. 1.—Measurement of Six Lengths to Determine Strain.

When the phenomena shown by Sir Harold Carpenter's strained crystals were regarded from the geometrical point of view, it was clear that one could completely determine the strain in the crystal: (*a*) if the strain was uniform, so that lines in the specimen which were originally parallel remained parallel when it was strained, and (*b*) if the extensions or contractions in six independent directions could be measured. We may, for instance, imagine that a square-sectioned bar is cut from a single crystal. In Fig. 1, *ABCD* is the square section which we may suppose marked with scratches on the surface, and *AF*, *BE*, *CG* are edges of the bar. If now we measure the proportional extension during strain of the six lines, *BA*, *BC*, *BE*, *AC*, *AE*, *EC*, then the strained position of every particle is determined. If we measure only five, then the strain is not completely determined, unless some further assumption is made. We may find, for instance, that the density is unchanged by the strain; then five, and only five, independent extensions or components have to be measured to determine the strain. The six components of strain need not, of course, be those shown in Fig. 1. One may, for instance, measure the extensions *BE*, *BA*, *BC*, and the angles *ABE*, *CBE*, and the angle between the faces of the specimen. Sir Harold Carpenter and Dr. Elam's original specimens were not suitable for making accurate measurements of the six components of strain. Accordingly, encouraged by Sir Harold, Dr. Elam and I collaborated in preparing and marking single crystals of such proportions that accurate strain measurements could be made. Fig. 2 (Plate XXXVII) shows one of our specimens after 70 per cent. extension. The strain was very uniform, even after such great extension.

The usual method by which strains are analyzed is to find the positions and elongations of the axes of the strain ellipsoid, *i.e.* the strained

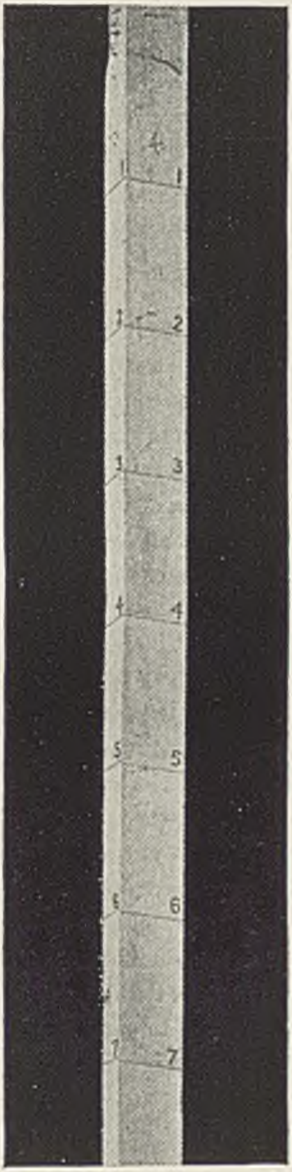


FIG. 2.—Marked Specimen Cut from Aluminium Single Crystal, after 70 Per Cent. Extension.

PLATE XXXVIII.

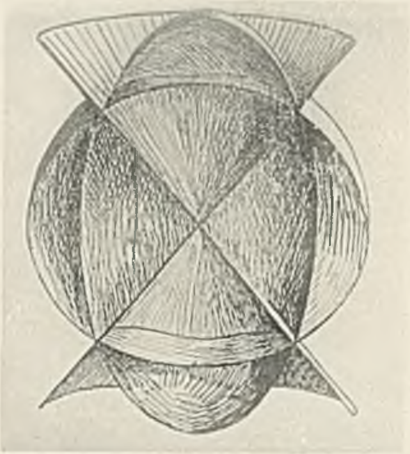


FIG. 3.—Unextended Cone and Strain Ellipsoid.

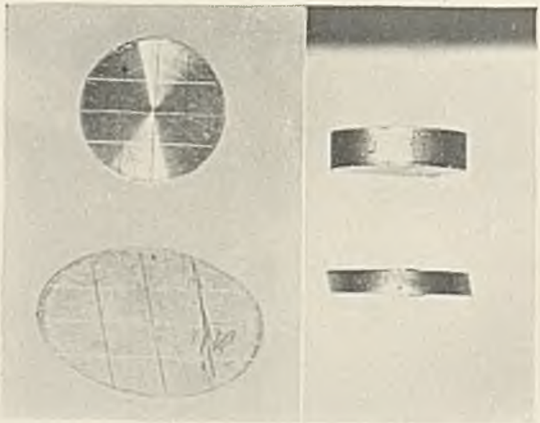


FIG. 5.—Front and Side Views of Compressed Disc Cut from Single Crystal.

shape and position of an originally spherical piece of material. In our case, however, we found instead the cone which passes through the intersection of the strain ellipsoid and the original sphere. This cone, which is shown in Fig. 3 (Plate XXXVIII) with the strain ellipsoid, evidently contains the strained positions of all directions which remain unstretched, and is therefore termed the unstretched cone. Our reason for adopting this procedure was that if the whole strain is, in fact, due to slipping parallel to one crystal plane, that crystal plane must form part of this cone, because slipping parallel to a plane gives rise to strain which leaves all directions in the plane of slipping unchanged in length. If part of the unstretched cone consists of a plane, it is a mathematical necessity that the whole cone must consist of two planes.

I will not trouble you with the method by which we calculated the position of the unstretched cone[2] in the strained specimen, but it is necessary for the argument that one should understand how this cone and the directions of the crystal axes were represented on plane diagrams. For this purpose we used the stereographic projection. Each direction in space can be regarded as marking a point on a sphere. The surface of this sphere is then projected on to a plane from a point on its circumference.

In the projection, great circles on the sphere, which contain all directions in space which lie in a plane, are projected into circles. Of these, the great circle which represents the plane parallel to the plane of projection is the smallest. I will call it the " bounding circle." The part of the projection which lies inside the bounding circle corresponds with a complete hemisphere, and if we are thinking about orientations in space, and are not concerned with the sense of directions on a straight line—*i.e.* if we do not consider whether a vertical line is pointing upwards or downwards, but only concern ourselves with the fact that it is vertical—then all orientations can be represented on a hemisphere, and so by the part of the stereographic projection which lies inside the bounding circle.

One property of the stereographic projection is that small circles on the sphere, which represent circular cones in space, also project into circles. Small circles can be distinguished from great circles, however, by the fact that projected great circles always cut the bounding circle in the projection at opposite ends of a diameter. Small circles never do so.

When we came to set out on a stereographic projection the points representing directions in our unstretched cone, calculated from the measurements made on our stretched single crystal specimen, we found that they did in fact lie on a circle which cut the bounding circle at opposite ends of a diameter.

Fig. 4 shows the stereographic projection of points on the unextended cone calculated from measurements made before and after a strain which extended a specimen cut from an aluminium crystal from 10 per cent. to 30 per cent. elongation. The circles drawn most nearly through the calculated points are shown in the diagram. It will be seen that they do in fact cut the bounding circle at opposite ends of diameters. This is a proof that, in the case to which this diagram refers, the unstretched cone really does degenerate into two planes, so that the total distortion can in fact be produced by slipping on either of these planes. It is impossible from two sets of external measurements made before and after straining to say which of these two planes is the plane on which slipping takes place, but we always found with aluminium that one of the two coincides with an octahedral crystal plane. This plane we took as the slip plane, and we found that the direction of slip is the diagonal of a cube face or edge of the octahedron.

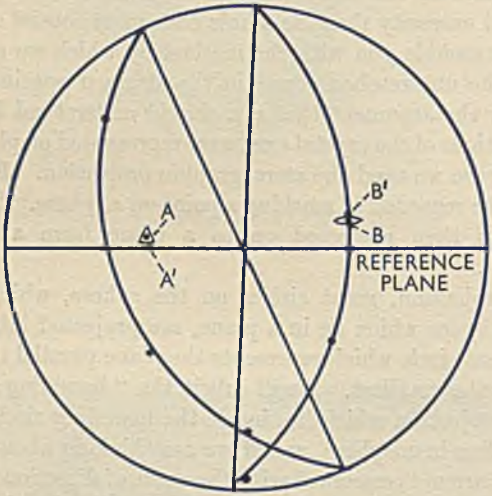


Fig. 4.—Stereographic Projection of Unextended Cone, with Diameters Marked to Prove that Cone is Two Planes.

In Fig. 4, *B'* is the direction of slip calculated from the external measurements of lines on the specimen, and *B* marks the orientation of a crystal axis represented by (101), *i.e.* it is in the direction of one of the diagonals of a cube face, or an edge of the octahedron corresponding with the cubic symmetry of the crystal. The point *A'* represents the direction of the normal to the plane which is represented in Fig. 4 by the circular arc containing *B'*. The point *A* represents the crystal axis, determined by X-rays, which is the diagonal of the cube in cubic symmetry. The crystal axes A and B are evidently associated with one of the planes of the unextended cone, but not with the other. The plane has accordingly been taken as the plane of slip. It will be seen that the plane of slip is parallel to a face of the octahedron associated with the cubic symmetry of the crystal and the direction of slip is parallel to an edge of the octahedron.

This method is more complicated than that used by Professor Andrade and by practically all other workers in the field. They strain the crystal and observe marks on the surface, which they prove are the traces of a crystallographic plane. They then *assume without further proof* that the strain is of a simple type consisting of a shear parallel to the plane marked out by the surface markings, and then make the two angle or extension measurements which are necessary to determine the direction of slip if their initial assumption is true.

Professor Andrade offers the opinion, in one of his papers, that this simplified method is in some cases more accurate than the complete analysis that I have described. I do not agree with this contention, provided that *proper precautions are taken* to ensure that the specimen is strained uniformly. In some cases the simplified method is inapplicable, because the assumed strain by shearing parallel to a crystal plane does not in fact take place; in others the slip lines on which the method relies do not make their appearance.

Fig. 8 shows the stereographic diagram of one of the cases analyzed. The unextended cone is nothing like two planes; in fact this diagram was proved to correspond with compound slipping on two octahedral planes. For cases to which it is applicable, the simple method provides a quick means of identifying slip planes provided that one has made certain, by complete strain measurements, that the strain is due to shear parallel to a plane.

The accuracy of the complete analysis depends on the uniformity of the strain. If a tensile specimen slips unequally in different parts of its length, strain measurements on its surface will vary from place to place. For this reason, I developed a method of straining in which flat discs cut from a crystal were compressed between parallel steel faces. This method ensured that the compression at all points of the disc was the same, and thus secured uniformity in one, at any rate, of the components of strain.

Fig. 5 (Plate XXXVIII) is a photograph of a circular disc cut from an aluminium crystal, before and after compression. In spite of reduction to half the original thickness, the scribed lines are still quite straight, and with this technique there is no " barrelling " of the section perpendicular to the parallel faces.

The great uniformity of our compression specimens was obtained by a special technique. If one compresses a short cylinder of solid metal between parallel planes the friction at the top and bottom normally holds the ends from expanding laterally and the specimen assumes a shape like a barrel. If the compressing faces are ground and polished and then greased, the first thing that happens when a compressive load is applied is that the grease is squeezed out. This causes an outward tangential force due to viscous drag to act over the top and bottom of the specimen, that is, a force in the opposite direction to the friction which would act in the absence of grease. By compressing the specimen in very small stages one can in this way get far greater uniformity of strain than can be obtained in a tensile specimen.

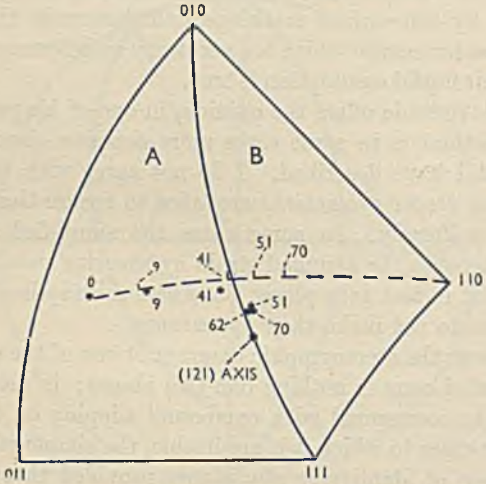


Fig. 6.—Change in Orientation of Axis of Specimen (see Fig. 2) Relative to Crystal Axes, During Extension of 70 Per Cent.

• Observed by X-Rays. ı Calculated.

When a single crystal is extended, the orientation of the crystal axes relative to the axis of extension varies as the straining proceeds. If the strain simply consists of sliding parallel to a crystal plane in a crystal direction, the cause and nature of this change in orientation becomes clear if we imagine the slip plane as fixed, and the orientation of the axis of the specimen as changing. The specimen axis must rotate in a great circle towards the direction of slip. In Fig. 6, 0 represents the initial position of a specimen axis in one of the triangles of cubic symmetry. The point (110) represents the crystal axis towards which slipping has occurred. The dotted line represents the great circle along which the specimen axis would move if the slipping were of the type contemplated, and the calculated positions of the specimen axes for extensions of 9, 41, 51, and 70 per cent. are marked off on the dotted line. The positions of the specimen axis measured by X-rays are also shown. It will be seen that at 9 and 41 per cent. extension there is good agreement, but that as soon as the representative point reaches the boundary between the two symmetry triangles it does not continue along the calculated path, but remains close to the boundary of the two triangles. This is because symmetry requires that when the representative point gets into the right-hand triangle slipping shall start in the direction of the axis represented in Fig. 6 by (011). Slipping towards the direction (011) would move the representative point back to the boundary between the triangles. Thus slipping continues on two planes, and the representative point remains on the plane midway between the two directions of slip. Finally, it reaches a crystal axis shown by (121) in Fig. 6, which is the point midway between the two directions of slip (110) and (011).

This, and the similar case of a single crystal under compression, are the only two cases in which a preferred orientation of crystal axes due to straining has been explained, though the phenomenon of preferred orientation has been found experimentally by means of X-rays in a large number of drawn, rolled, and otherwise worked metals.

I have mentioned that with aluminium the slipping is on an octahedral plane in the direction of its edges. An octahedron has eight faces, but pairs of them are parallel to one another so that there are four possible slip planes, and on each of these there are three possible directions of slip, making twelve possible types of slipping in all. We have seen that, when a single crystal of aluminium is pulled, the strain is due to one only of these twelve. As Professor Andrade told you last year, we found that if the shear stress is resolved parallel to all the four possible slip planes in each of the three possible directions of slip, the operative slip is that one of the twelve possibles for which the shear stress is greatest. We found, further, that this law of maximum shear stress determines the same slip plane and direction for all possible positions of the specimen axis within one of the triangles into which the diagram of cubic symmetry is divided. When a single crystal of aluminium, or an aggregate of such crystals, is strained, the resistance to further straining increases as the plastic strain increases. When the slipping is on one crystal plane, the resistance to shear depends only on the amount of shear strain that has occurred since the crystal was in its original fully annealed state. Professor Andrade showed some curves giving the relationship between the plastic shear strain *s* and the shear stress *S*. Fig. 7 shows the relationship between *S* and *s*, derived from experiments on the crystals of identical material in tension and in compression. It will be seen that the fact that though in one case there was compression perpendicular to the slip plane, while in the other there was tension, no difference is observed in the *S*–*s* relationship.

On the other hand, the resistance seems to increase rather more rapidly when double slipping occurs than when the whole strain is due to single slipping. One of our specimens had its crystal axes in the symmetrical position where double slipping might be expected to take place. The complete analysis of double slipping was carried out for various stages of compression. The unstretched cone was worked out from the measurements of the specimen, and also calculated on the assumption of equal slipping on each of the two possible slip planes. The two cones are shown in Fig. 8, and it will be seen that they are only very slightly different. Thus, the strain is in fact very nearly due to the type of double slipping which the symmetry and maximum shear stress rule prescribes. Fig. 9 shows the *S*–*s* curve derived from the analysis of double slipping; it is of the same type as that for single slipping, but is rather higher.

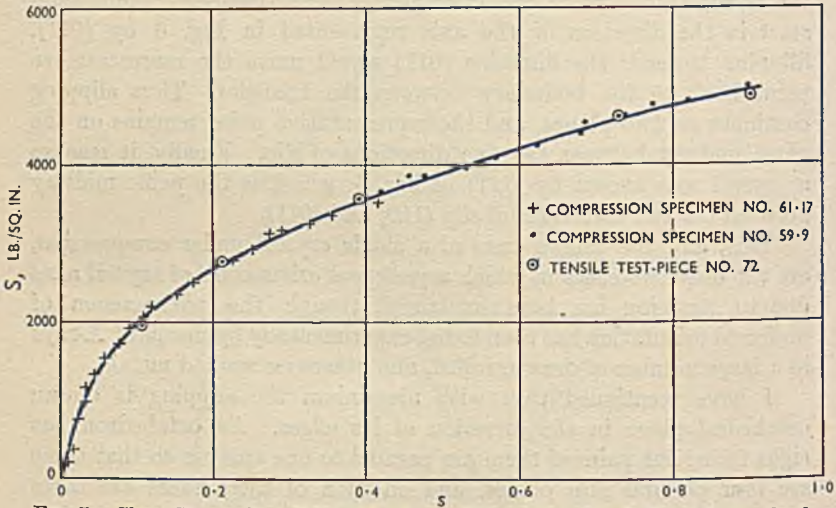


Fig. 7.—Shear Stress, *S*, and Shear Strain, *s*, of Aluminium Single Crystals Resolved on to Slip Plane and Direction.

$\left.\begin{array}{c}\bullet\\+\end{array}\right\}$ In Compression. ⊙ In Tension.

Now we approach a complicated and difficult problem, namely the analysis of stress and strain in an aggregate of crystals when the whole aggregate is strained plastically.

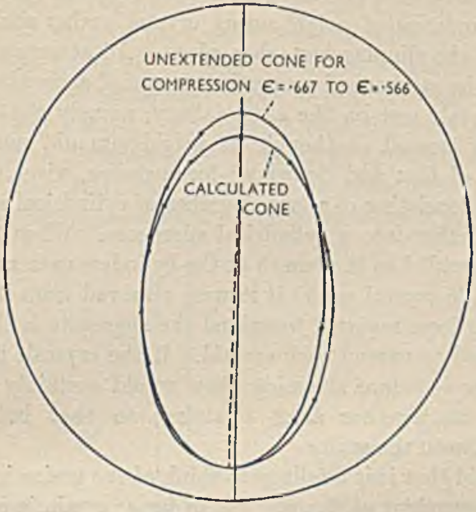


FIG. 8.—Stereographic Projections of Calculated and Observed Cones for Double Slipping.

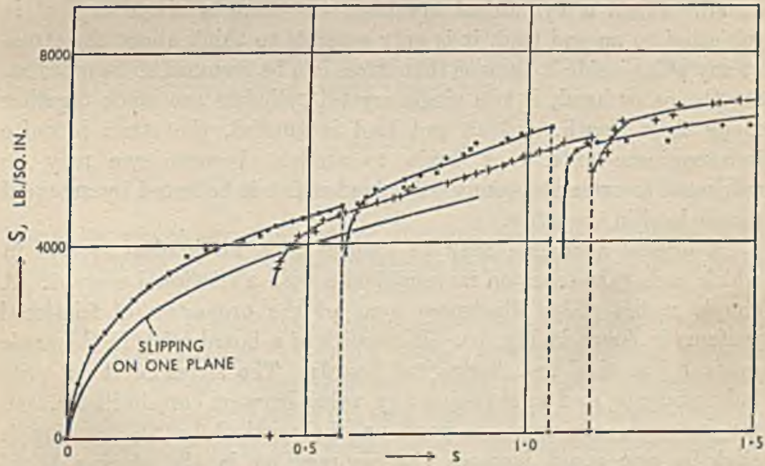


FIG. 9.—Shear Stress, S, and Shear Strain, s, for Double Slipping.

I think that I can say, without fear of contradiction, that no self-consistent or valid theory of plastic crystal aggregates has yet been put forward, though a number of invalid attempts have been made in this direction. The essential difficulty in connecting experimental results obtained with single crystals with those obtained in aggregates is to imagine how it is possible for slipping to go on inside crystals so that the boundaries of neighbouring crystal grains shall still be in contact after the slipping has taken place. All attempts made so far to correlate the mechanical properties of crystal aggregates with those of single crystals rest on the same fallacy, namely that each crystal grain can be treated as though its neighbours did not exist. The recent work of Cox and Sopwith,[3] for instance, visualizes a crystal aggregate as consisting of a large number of cylindrical single crystals combined together into a cylindrical aggregate. When the aggregate is extended parallel to the length of the cylinders each crystal extends just as a single crystal would if it were removed from its neighbours, and the total force required to extend the aggregate is the sum of the forces required to extend each crystal. If the crystals fitted together as a solid mass before straining they would certainly not, in this conception, fit together after straining, so that holes would be produced between the grains.

I have said that it is a fallacy to think of the grains in an aggregate as being independent of one another so far as strain is concerned, but it seems to me that a still more fundamental fallacy is involved in the existing way of thinking of stresses in the grains of plastic aggregate at all. When a cylindrical specimen cut from a single crystal is subjected to an end load, it is only possible to think about the stress at any point inside it because that stress can be assumed to be uniform. On the other hand, if two single crystal cylinders are stuck together along their length, and an end load is applied, the stress is quite indeterminate until they begin to stretch, because one may be subjected to an initial compressive load which is balanced by an equal tensile load in the other.

A crystal aggregate may be likened to a mechanical system in which each part bears on its neighbours with a frictional contact. A simple model which illustrates some of the properties of frictional systems is shown in Fig. 10. It consists of a board lying in the angle made by vertical and horizontal boards. The stress in it is quite indeterminate, and might have any value between certain limits. If, for instance, one were to push on the vertical board, bending it slightly, one could increase the compression in the sloping board without making it slip. Now suppose we push the sloping board till it slips. Amonton's law of friction, according to which the ratio of the tangential to the normal force at a sliding contact is equal to the coefficient of friction, now makes the forces everywhere determinate.

If, instead of obeying Amonton's law, the friction at both sliding surfaces were independent of normal force, the force system would again be determinate if the tangential force at each contact were known. To find P, the force with which the sloping board must be pushed in order that it may slide, we can solve the equations of equilibrium, calculating normal reactions at the points of contact. On the other hand, we can proceed more simply by what is called the principle of virtual work. We imagine that the force P pushes the system through a distance x at its point of application. The work done is then Px. If s_1 and s_2 are the distances through which the ends of the sloping board slide, and the friction forces are f_1 and f_2 the energy wasted at the points of sliding contact is $s_1 f_1 + s_2 f_2$. The principle of conservation of energy then gives

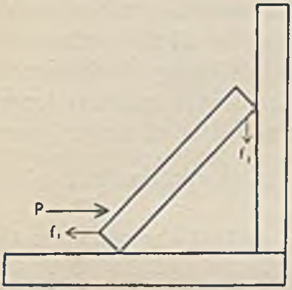


Fig. 10.—Model Illustrating Simple System with Friction.

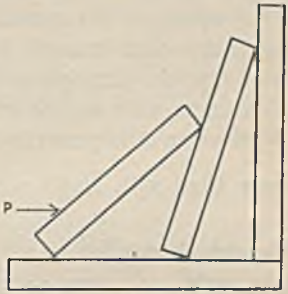


Fig. 11.—Friction System with Two Possible Modes of Slip.

$$P = f_1 \frac{s_1}{x} + f_2 \frac{s_2}{x}$$

The ratios $\frac{s_1}{x}$ and $\frac{s_2}{x}$ are determined by purely geometrical considerations. It will be seen that by this principle of virtual work we have determined the force P without bringing in the conception of stress at all.

Now consider the more complicated system consisting of two boards, which is shown in Fig. 11. When the outer sloping board is pushed, one of two things happens: either the inner sloping board remains fixed, the contacts at the two ends of the outer board slipping, or no slipping occurs at the contact of the two sloping boards, but all the remaining three contacts slide. One cannot arrange the boards so that all the possible contacts slide at once when the outer one is pushed. In systems like this the only general rule that can be given for determining the force necessary to cause motion is to assume that there is no slipping at as many of the frictional contacts as is possible in view of the geometrical constraints in the system. We can then calculate the force P which corresponds with each of the motions which satisfy this condition, using the principle of virtual work. The motion which actually occurs will be that for which P is least.

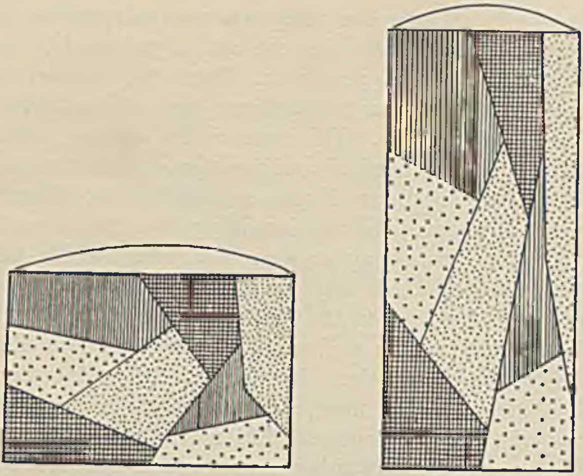
Now let us see how this principle can be used to determine the combination of shears or slips which will arise when any given strain is forced on a crystal by an external agency. Take first the case of a cubic single crystal extended in one direction, and able to expand or contract freely in all perpendicular directions. The single geometrical condition can be satisfied if one only of the twelve possible types of slipping is operative. In this case, the virtual work equation is $Ss = Px$, where s is the amount of slip corresponding with extension, x, so that if the shear strength S is the same for all the twelve possible types of slip, the principle of least possible energy dissipation for a given extension tells us that only that slip plane is operative for which s is least when x is prescribed. It is a matter of simple geometry to show that with single slipping, $\frac{x}{s}$ is identical with the "stress factor," *i.e.* it is equal to the ratio $\frac{S}{P}$, so that the condition that $\frac{s}{x}$ shall be the least possible is identical with the condition, derived from the conception of stress that the operative slip is that for which $\frac{S}{P}$ is the greatest of the twelve possible values.

We are now in a position to see how one can determine the system of complex slipping which will occur when any given strain is produced in a crystal. A strain has, as I stated earlier, six components, but when the strain is composed of shear strains only, without volume expansion, this is reduced to five. If these five components of strain are given, we can combine five out of the twelve possible shears or modes of slipping to produce the required strain. We could, of course, combine six, seven, or more shears to produce the same strain, but our study of the mechanics of frictional systems shows that the least energy is wasted, or virtual work done, with a combination of five only. To choose the five, we can only try every combination of five out of the possible twelve, and see which corresponds with the least virtual work or energy dissipated.

At first sight, this seems a formidable task, because there are 792 ways of choosing five things from a group of twelve. We must remember, however, that the range of choice is much more restricted than that contemplated in this estimate. In the first place, the three directions of slip on any one plane are not independent, since the strain due to slipping in one direction can be produced by combining shears in the two other directions. Thus, the twelve shears are divided into four groups of three shears each and only two can be assigned to any one group. This reduces the number to 648. Next it is found that the geometrical condition for a given strain cannot be satisfied if the five shears are chosen so that two are taken from one group, *i.e.* one slip plane, and the remaining three are chosen one from each of the three remaining groups. This reduces the number of choices to 324, all of which must be chosen so that two shears occur on each of two planes, one on the third and none on the fourth. Next it must be noticed that on a plane where there are two shears there are three ways of choosing the pair. Thus, if we work out any one of the 324 combinations, eight more can immediately be deduced without further analysis. This reduces the 324 in the ratio 9 : 1, *i.e.* to 36. Finally, it turns out that a further geometrical inconsistency rules out one-third of these 36, so that, finally, we are left with an irreducible number of 24 combinations of five shears.

Since the resistance to shear S has been shown, experimentally, to be the same for all the twelve crystallographically similar shears, the energy dissipated in any combination of five shears is simply equal to S multiplied by the sum of the five component shears. Thus, to find which of the 24 combinations is effective, we must take each of the 24 possible combinations of five shears and determine their five values so that they give rise to the given external strain (which is specified, of course, by five components) when combined together. In each case we then form the sum of the five shears, without regard to sign. The smallest of the 24 resulting sums is that which, by the principle of virtual work, or least energy dissipation, corresponds with the operative combination of five shears. All this sounds complicated, but the whole process involves only the simplest mathematical operations, repeated a great many times.

I have now described how the system of complex slipping which will occur on application of any given externally applied strain to a single crystal can be determined. It remains to apply the results to crystal aggregates. If you look at a microphotograph of the cross-section of a drawn wire, you will see that the crystal grains are all elongated in the direction of extension, and contracted in the perpendicular direction. Each grain, in fact, suffers exactly the same strain as the surrounding material in bulk. With this strain, all the grain boundaries necessarily remain in contact, no holes forming between them. I have therefore taken the case of an aggregate in



a *b*

Fig. 12.—Crystal Aggregate: *a*, Unstrained; *b*, After 125 Per Cent. Extension.

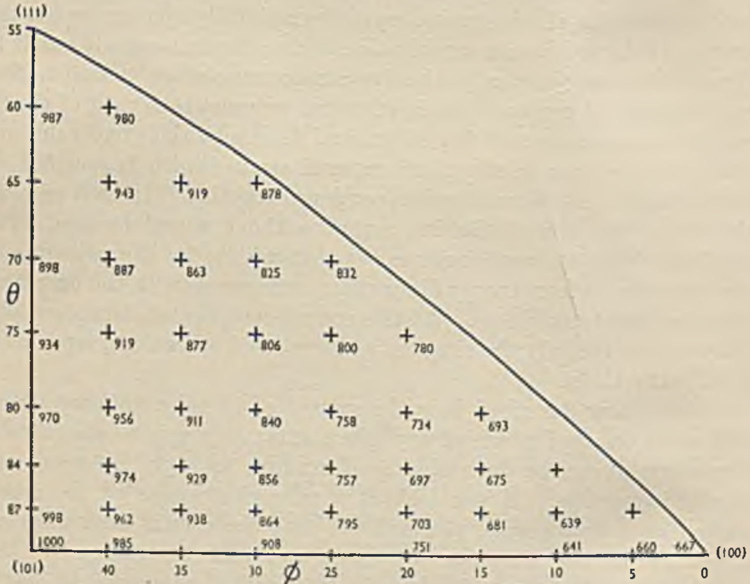


Fig. 13.—Stereographic Projection Showing Orientations for which Complete Calculations were Made.

Figures are Sum of Shears when Extension Per Unit Length of Aggregate is 272.

+ Crosses Show Orientations for which Complete Calculations were Made.

which the grains take up all possible orientations, and have imagined that the aggregate is strained by extending it by a small amount in one direction, while at the same time contracting it by half the amount in all perpendicular directions, thus keeping the volume unchanged. The diagrams shown in Fig. 12, which are drawn to scale, show on the left an imaginary section of a coarse-grained, round bar, on the right the same bar with the same grains when extended to 2¼ times its initial length.

I selected a number of orientations of the axis of extension in relation to the crystal axes, and have worked out by the method described above and with the help of Mallock's equation-solving machine, the particular combination of five shears which is effective at each orientation. The points representing the axis of extension are nearly uniformly distributed over the fundamental spherical triangle of cubic symmetry (see Fig. 13) so as to represent random orientation in the aggregate.

RESULTS.

The sum of the five shears necessary to give rise to an extension of the aggregate equal (in arbitrary units) to 272 is shown in Fig. 13 (in the same units for each orientation). From this, the direct stress P which must be applied to the aggregate in order that plastic strain by complex slipping may proceed, has been calculated. Then assuming, as is warranted by experiments on single crystals, that the increase in shear stress on a crystal plane in complex slipping depends on the sum of the shears in the same way that S depends on s in single slipping, one can deduce the load–extension curve for an aggregate from the S–s curve of a single crystal. The result is shown in Fig. 14. Fortunately, Dr. Elam had measured the load–extension curve with a polycrystalline specimen of the same material from which the single crystals had been grown. Her observed points are marked in Fig. 14.

The rotation of the crystal axes due to the five shears in each grain inside the aggregate was next calculated, in exactly the same way as the rotation due to single slipping. The rotation of the specimen axis relative to the crystal axis for an extension of 2·37 per cent. is shown, in Fig. 15, for each of the calculated orientations. This diagram is not a stereographic one; it shows in rectangular co-ordinates the co-latitude θ and longitude φ of the specimen axis referred to crystal axes placed with a cubic axis at the pole and a cubic plane as the meridian $\varphi = 0$. Comparison with Fig. 13 shows that this diagram is only slightly distorted when compared with a true stereographic projection. The arrows in Fig. 15 show the extent of the rotation;

the orientation at the beginning of the extension is represented by the point from which the arrow springs, and the final position by the point of the arrow. You will see that over a large part of the total area of the triangle there are two arrows radiating from each point. This is because at points within those areas two different combinations of five shears correspond with exactly the same sum of the shears. Any combination of these two sets of five shears taken in varying proportions could equally well occur. I have accordingly filled in the angles between the arrows to show the range of possible movement of the specimen axis relative to the crystal axes. The whole triangle is divided into areas within which one or two combinations of five shears are effective. Each operative combination of five shears is denoted by a letter in Fig. 15. It will be seen that within the area *G* the axes of all grains rotate so that a (111) axis tends to come into line with the axis of extension of the aggregate. Moreover, the representative points of many grains which are in the area *EC* will move until they

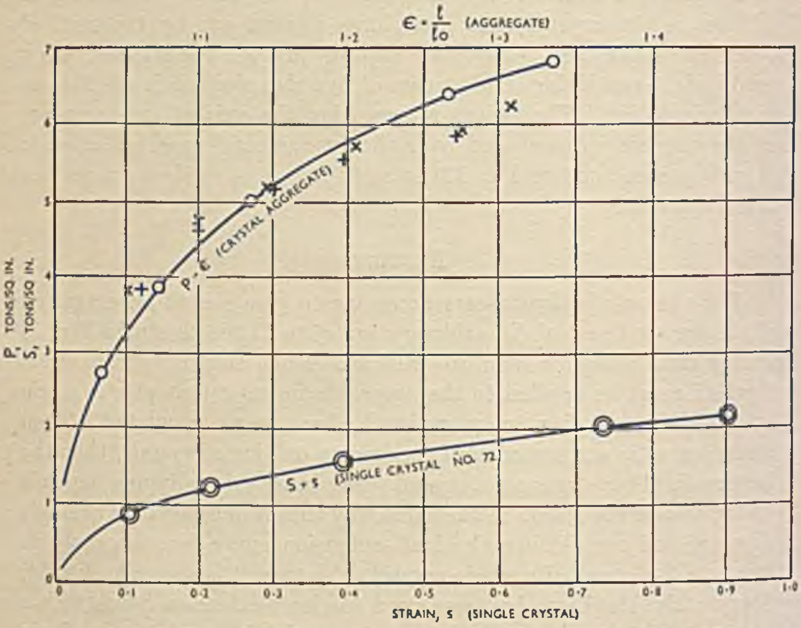


Fig. 14.—Load–Extension Curve ($P-\epsilon$) for Aggregate and Stress–Strain Curve ($S-s$) for Single Crystal.

○ Calculated from Single Crystal Measurements.
× } Aggregate }
\+ } } Measured by Dr. Elam.
◎ Single Crystal }

cross the boundary between *G* and *EC* and will then move along unambiguous paths towards the (111) axis. Grains whose representative points are in the neighbourhood of the (100) corner of the triangle will rotate until a cubic axis is parallel to the specimen axis. The crystal axes of grains which are near the (101) axis will tend to rotate towards either the (111) or the (100) axes. Thus, the aggregate will tend to attain a state in which the crystal axes of grains have either

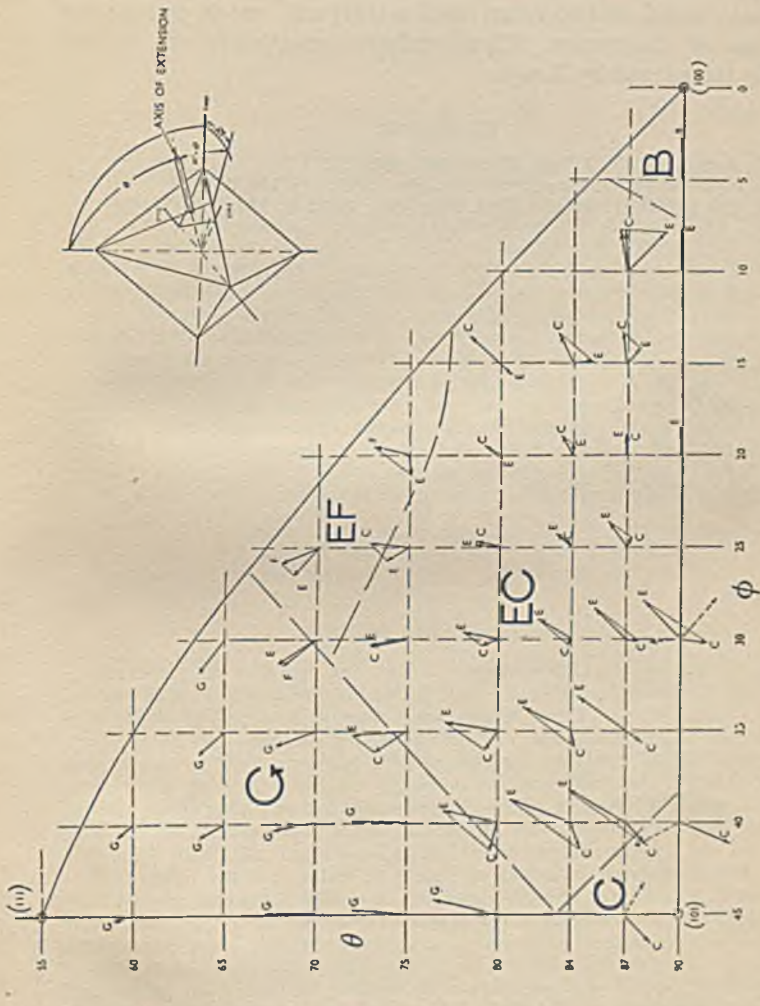


FIG. 15.—Rotation of Crystal Axes in Aggregate During Extension of 2·37 Per Cent.

a (111) or a (100) axis, but no grains with a (101) axis in the direction of extension. For compression of a crystal aggregate, exactly the reverse rotation would occur; no grains would be expected with (111) or (100) axes in the direction of compression, but the crystal axes of all grains would tend to rotate until a (101) axis was in or near the direction of compression. These preferred orientations are in fact exactly those found by X-rays.

REFERENCES.

[1] E. N. da C. Andrade, *J. Inst. Metals*, 1937, **60**, 427.
[2] G. I. Taylor and C. F. Elam, *Proc. Roy. Soc.*, 1923, [A], **102**, 643.
[3] H. L. Cox and D. G. Sopwith, *Proc. Phys. Soc.*, 1937, **49**, 134.

OBITUARY.

AUGUST BOERNER.

August Boerner, a prominent figure in the German metallurgical and mining industries, died suddenly on November 27, 1937.

Born at Emmerich (Rhine) in 1884, Herr Boerner studied economics at the Handelshochschule, Cologne, before becoming secretary to William Merton, the former director of the Metallgesellschaft, Frankfort. Subsequently, he was appointed to the board of the Metallbank and of the Metallurgische Gesellschaft, of which he was the London representative in the years before the war. During the war, he was employed on the erection of new factories for the introduction of special processes, and afterwards was engaged in restoring the foreign interests of his company. In 1929, after 18 years with the Metallgesellschaft, Herr Boerner became director of the Krupp works at Berndorf in Austria, and four years later he was appointed to a similar post with the Ballestrem concern, where he proved himself of great value.

Herr Boerner's success lay in his tact and his natural technical ability; his early death is a great loss to German industry.

He was elected a member of the Institute of Metals on March 8, 1926.

JOHN ALLEN CAPP.

American metallurgy suffered a considerable loss by the death on January 6, 1938, after an operation, of John Allen Capp, Engineer of Materials to the General Electric Company, Schenectady, N.Y.

Mr. Capp was born at Philadelphia in 1870, and graduated in Mechanical Engineering at the University of Pennsylvania in 1892. After being connected for a short time with the Thomson-Houston Company at Lynn, Mass., he went to the main plant of the General Electric Company, where he became chief of the testing department. From its establishment in 1927 to the time of his death, Mr. Capp was head of the works laboratory.

Mr. Capp was a member of numerous technical societies, but he was most closely connected with the American Society for Testing Materials, whose President he became in 1919, and of which he was elected an Honorary Member last year. He was prominent in the establishment of standards in the metallurgical industry, and served on no less than eighteen of the Society's committees, most actively perhaps on Committee B-1—Copper and Copper Alloy Wires for Electrical Conductors—of which he was chairman from 1909 until his death.

Innumerable friends testify to Mr. Capp's integrity, ability, sound judgment, and wide experience; he excelled on both the technical and the administrative sides of his work.

He was elected a member of the Institute of Metals in 1911.

WILLIS EUGENES EVERETTE.

Dr. Willis Eugenes Everette, ethnologist, lawyer, and inventer, died on February 9, 1938. He was a native of Brooklyn, N.Y., and studied natural sciences, medicine, and law, being admitted to the bar of the United States Supreme Court in 1894, where he specialized in mining and technical branches of the law. Dr. Everette was the holder of a number of patents, among them one for producing steel direct from iron ore, and another for the extraction of nitrates and cyanides from the air.

Dr. Everette belonged to numerous learned and scientific societies, and became a member of the Institute of Metals on April 13, 1927.

EDWARD GEISLER HERBERT.

By the death, on February 9, 1938, of Edward Geisler Herbert, the Institute has lost a member of rare originality of mind, and engineering in general a man of great ability and charm. No one could know Herbert without admiring his patient search for truth, his freshness of outlook, and, at last, the man himself. That it has not always been possible for others to repeat the results which he himself obtained was probably due, more than to any other single factor, to his wonderful manipulative ability. In his modesty, the wideness of his interests, his personal experimental skill, his enthusiasm—in the best sense of that word—and his freedom from mental rigidity, he belonged to the very best type of scientific worker.

Born in 1869, he received his early education at the Nottingham High School, and then proceeded to University College, London, where he graduated in science in 1889. His business career commenced in Manchester in 1892 when he joined a small firm of electrical engineers, but it was in 1895, when he started as a maker of machine tools, that he found his real vocation. His researches on the efficiencies of cutting tools, and the ingenious machines which he devised in collaboration with his partner, the late Mr. Charles Fletcher, for their measurement, brought him a wide reputation. To metallurgists, however, he will be remembered chiefly for his " pendulum " hardness test, his " cloudburst " process of superficial hardening, and his work on the magnetic properties of steel. Almost up to the end he was engaged on the development of a method for the continuous measurement of hardness at temperatures above the normal, and it is some satisfaction that there is reason to hope that his last piece of work will not be left uncompleted.

Herbert's outlook was essentially that of a man of science, but that his work should prove of value to the community was ever his constant hope.

Mr. Herbert was elected a member of the Institute on October 30, 1930.

F. C. Thompson.

EUGENE HENRY HUGH HILT.

A motor accident in South Wales resulted in the death on April 5, 1938, of Mr. E. H. H. Hilt, director of Messrs. H. Hilt (Engineers), Ltd., and of Messrs. A. M. Erichsen and Son, Ltd., Slough.

Mr. Hilt, who was born in 1899, was by profession a mechanical engineer, and had studied both in England and in Germany. Prior to holding the positions that he did at his death, Mr. Hilt was successively engineer to Junkers Flugzeugbau, A.G., Dessau, and to Cantieri Orlando, Leghorn, and manager to Messrs. John Rolland and Company, Ltd., London.

He was elected a member of the Institute of Metals on October 26, 1933.

ADRIEN GASTON SAINT-PAUL DE SINCAY.

M. Adrien Gaston Saint-Paul de Sincay died in Brussels on March 19, 1938.

Born in 1854, at Angleur, Belgium, and educated at Paris University, where he graduated as Doctor of Laws, M. Saint-Paul de Sincay was throughout his life connected with the Société Anonyme des Mines et Fonderies de Zinc de la Vieille Montagne. He was appointed inspector in 1879, became secretary of the Board of Directors in 1884, succeeded his father as general manager in 1890, and was elected a member of the Board of Directors in 1891.

In addition, M. Saint-Paul de Sincay played a prominent part in the establishment of the International Cartel of Zinc Producers which existed from 1908 to the outbreak of the war, and was President of another International Cartel which lasted from 1928 to 1934. He was also President of the Federation des Usines à Zinc, Plomb, Cuivre, et autres Métaux non-ferreux, a Belgian organization which was formed shortly after the armistice.

M. Saint-Paul de Sincay was elected a member of the Institute of Metals on April 13, 1927.

NAMES INDEX.

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