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OF THE
INSTITUTE OF METALS

VOLUME XLVIII

EDITED BY

G. SHAW SCOTT, M.Sc.

SECRETARY

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LONDON
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36 VICTORIA STREET, LONDON, S.W.1
1932

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

Form A. (*Membership Application*)

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

The INSTITUTE of METALS

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

Founded 1908. *Incorporated* 1910.

To the Secretary,
The Institute of Metals.

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

Name of applicant in full..

Address...

Business or Profession...

Qualification...

Degree and/or honorific distinctions ....

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

....
....
....

Signatures of three Members.

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

To be filled up by the Council.

....

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

Chairman.

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

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

(*It would be a convenience if the Candidate's Card were sent with this form.*)

48.

SIR HENRY FOWLER, K.B.E., LL.D., D.Sc.
President.

[*Frontispiece.*

EXTRACTS FROM THE RULES

(MEMORANDUM AND ARTICLES OF ASSOCIATION.)

MEMBERS AND MEMBERSHIP

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

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

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

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

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

(*a*) Students of Metallurgy; or

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

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

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

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

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

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

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

SUBSCRIPTIONS

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

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

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

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

DUTIES AND OBLIGATIONS OF MEMBERS

Rule 12.—Every member shall be bound:

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

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

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

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

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

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*).

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Leonard Sumner, O.B.E., M.Sc., F.Inst.Met., 1922–1924.

Professor Thomas Turner, M.Sc., A.R.S.M., F.Inst.Met., 1924–1926.

Sir John Dewrance, G.B.E., F.Inst.Met., 1926–1928.

Walter Rosenhain, D.Sc., F.Inst.Met., F.R.S., 1928–1930.

Richard Seligman, Ph.nat.D., F.Inst.Met., 1930–1932.

LIST OF OFFICERS
OF
THE INSTITUTE OF METALS
1932-1933

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Sir Henry Fowler, K.B.E., LL.D., D.Sc.

Past-Presidents.

Professor Sir Harold Carpenter, Kt., M.A., Ph.D., A.R.S.M., F.R.S.
Sir John Dewrance, G.B.E.
Walter Rosenhain, D.Sc., F.R.S.
Richard Seligman, Ph.nat.D.
Leonard Sumner, O.B.E., M.Sc.
Professor Thomas Turner, M.Sc., A.R.S.M.

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H. Moore, C.B.E., D.Sc., Ph.D.	Woolwich.
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H. B. Weeks	London.

Secretary and Editor.

G. Shaw Scott, M.Sc., F.C.I.S.

Assistant Secretary.

S. C. Guillan.

Telegraphic Address—"Victoria 2320, London." *Telephone*—Victoria 2320.

Institute of Metals,
36 Victoria Street, London, S.W.1.

June 1932.

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Department of Metallurgy, The University, Melbourne, Victoria.

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Canada.
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24 Bruce Street, Fort, Bombay.

Japan.
Professor K. Tawara, Sc.D., 232 Kagomachi, Koishikawa, Tokyo.

South Africa.
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University of the Witwatersrand,
P.O. Box 1176, Johannesburg, Transvaal.

Sweden.
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Switzerland.
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United States of America.
W. M. Corse, S.B.,
810 18th Street N.W., Washington, D.C.

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Hon. Secretary : HERBERT P. GADSBY, Assoc.Met., 193 Sandford Grove Road, Sheffield.

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Hon. Secretary : ROOSEVELT GRIFFITHS, M.Sc., Metallurgical Department, University College, Singleton Park, Swansea.

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THE INSTITUTE OF METALS

SECTION I.

MINUTES OF PROCEEDINGS.

ANNUAL GENERAL MEETING.

The Twenty-Fourth Annual General Meeting of the Institute was held in the House of the Institution of Mechanical Engineers, Storey's Gate, Westminster, London, S.W.1, on Wednesday and Thursday, March 9 and 10, 1932, Dr. Richard Seligman, President, occupying the Chair at the opening of the meeting.

Wednesday, March 9.

The Minutes of the Annual Autumn Meeting held in Zürich from September 13 to 18, 1931, were taken as read.

Welcome to Members from Overseas.

The President welcomed those members who had come from overseas to attend the meeting, and in particular Dr.-phil W. Rohn, Member, who attended the meeting as representative of the Deutsche Gesellschaft für Metallkunde.

Dr.-phil. W. Rohn: It is a special pleasure and a great honour to me to bring you the very heartiest greetings of your German sister Society. We are always happy to take part in these meetings, and we are glad to be able to co-operate with you. We are sorry that the general situation is not of the best, so that not so many of our members as usual are able to be present and to take part in this meeting. We were especially glad that at the last General Meeting of our Society in Germany we had the pleasure of having with us Dr. Seligman and Dr. Hutton, and we hope that this co-operation will continue to the mutual benefit of our institutes and to the development of our science and the industry.

The President thanked Dr. Rohn for his message.

The Secretary (Mr. G. Shaw Scott, M.Sc.) then presented the following Report of Council:

REPORT OF THE COUNCIL

for the Year ended December 31, 1931.

In its last report the Council described the year 1930 as one of "unprecedented disturbance in the economic life of the world."

The fact that the Institute has since passed through twelve months of far greater stress without being compelled to curtail its activities or to diminish in any way its services to its members, to science, or to industry should give it courage to face whatever lies ahead.

But a note of warning must be sounded, for the full effects of the disastrous conditions obtaining in the world have not yet been felt, and there is every reason to think that unless some unexpected turn for the better takes place the Institute may be faced with grave difficulties before the year 1932 is out. There is, therefore, room neither for complacency nor for any slackening of effort.

There are, however, also encouraging and hopeful elements in the situation. Once more an increase of membership can be recorded—this time almost double the increase achieved in 1930—and that in spite of the fact that more members than usual have found it impossible to maintain their connection with the Institute; while death has claimed twice as many victims as in 1930.

One feature of this increased membership, which is particularly gratifying at such a time as the present, is that a number of firms, not directly interested in the work of the Institute, have recognized the indirect benefits accruing to them from its activities, and have encouraged members of their technical and other staffs to apply for membership.

This should stimulate those who are trying to secure fresh strength for the Institute among the large engineering firms and other users of non-ferrous metals. It should, at the same time, furnish the most convincing argument with which to approach the many engineers and even metallurgists who remain outside the ranks of the Institute, although largely depending on the work which it is carrying on so energetically and so successfully. No one who gains advantage from that work should be willing to leave his share of the burden to be borne by others.

In one respect the year 1931 has been definitely less favourable than its predecessors. Last year the Council was able to say that the Institute's financial position had been more than maintained. The accounts presented this year tell the same or an even better tale, if allowance be made for certain non-recurring items of expenditure. Since they were made up, however, it has been necessary to trench upon the small capital of the Institute—the exiguous savings of more than twenty years—to meet the cost of publishing the exceptional number of papers offered during the year, no fewer than forty-two in number. So far the Council has thought it better to draw upon capital than to decline to publish the results of researches held to be of value to one branch or other of non-ferrous metallurgy, but it is obvious that there must be an early limit to what can be done in this direction. It is essential, therefore, if the work of the Institute is not to be curtailed by sheer inability to defray the cost of publication, that new sources of income be tapped. It is to be hoped that every member who has the true interest of his profession at heart will take his share in the work of strengthening the position of the Institute.

ROLL OF THE INSTITUTE.

A substantial increase in the number of members on the Roll of the Institute is to be recorded. On December 31, 1931, the totals for the various classes of Membership were as follows :—

Honorary Members	5
Fellows	7
Ordinary Members	2146
Student Members	74
	2232

The following table shows the growth in the membership of the Institute during the past five years :—

	Dec. 31, 1927.	Dec. 31, 1928.	Dec. 31, 1929.	Dec. 31, 1930.	Dec. 31, 1931.
Honorary Members	4	4	5	5	5
Fellows . .	2	2	9	7	7
Ordinary Members	1792	1900	2035	2083	2146
Student Members .	105	97	73	65	74
	1903	2003	2122	2160	2232

OBITUARY.

Losses by death during the year were unusually numerous. Among the Original Members thus lost to the Institute were Sir Hugh Bell, Bart., the Hon. Sir Charles Parsons, and Colonel C. T. Heycock.

In addition to the above the deaths of the following were notified to the Secretary during the past year: Professor A. Barr; P. Brown; Thomas Brown; W. H. Colpitts; Sir Trevor Dawson; G. FitzBrown; W. C. Gray; W. J. Gregg; R. Jarry; A. Laing; Colonel R. Law; Sir James McKechnie; and Dr.-phil. L. R. J. Nowack.

GENERAL MEETINGS.

Three General Meetings of the Institute were held during the past year—one that was particularly notable in that it witnessed the first Autumn Meeting of the Institute to take place in Switzerland. At the Annual General Meeting, which took place in London on March 11 and 12, fourteen papers were presented, and Dr. Richard Seligman was re-elected President for a further year. The meeting was followed by a Dinner and Dance at the Trocadero Restaurant. At the second General Meeting of the year—the Twenty-first Annual May Lecture—a discourse was delivered by Mr. W. B. Woodhouse on "The Progress of Power Production." The Annual Autumn Meeting, which took place in Switzerland from September 13 to 18, was well attended by members from sixteen countries. No fewer than twenty-five papers, including the Autumn Lecture by Mr. U. R. Evans, M.A., on "Thin Films in Relation to Corrosion Problems," were presented. Following the reading and discussion of these papers at Zurich the members visited works in various parts of Switzerland, in the course of their journeyings passing through some of the most beautiful portions of the country. After leaving Switzerland a party of members visited Milan to take part in the International Foundry Congress and to visit the Exhibition arranged in connection therewith.

SPECIAL MEETINGS.

On February 20 an official visit of members was paid to the British Industries Fair, Birmingham, the party being entertained to luncheon by the Fair authorities.

On September 25 the Institute paid an official visit to the Shipping, Engineering, and Machinery Exhibition at Olympia, at which the visiting members were entertained to tea by the Exhibition organizers.

The first joint meeting of the Institute and the Manchester Metallurgical Society was held in Manchester on October 7, when the President of the Institute, Dr. Richard Seligman, was present in support of the Chairman of the Society, Mr. J. S. Glen Primrose. Four of the papers from the Zürich Meeting of the Institute were re-presented and discussed. It is the hope of the Council that similar joint meetings may be held in Manchester and elsewhere.

POSTPONED AMERICAN AUTUMN MEETING.

Throughout the year active preparations were continued in connection with the meeting which, as far back as 1928, had been planned to be held in the United States and Canada in the autumn of 1932. Last summer Dr. Foster Bain, the secretary of the inviting body—the American Institute of Mining and Metallurgical Engineers—visited London in order to assist the Council in giving final shape to the programme for the American Meeting. At the end of the year the disturbed financial and economic conditions prevailing in Europe and America made it necessary for the Council to postpone the American Meeting, which was to have been held jointly with the Iron and Steel Institute. The American hosts of the two Institutes, whilst sympathetically receiving the suggestion that the meeting be postponed, made it quite clear that they wished the visit to take place at the earliest opportunity. In the meantime, plans were set afoot by the Council with a view to hold the forthcoming autumn meeting in London jointly with the Iron and Steel Institute.

PUBLICATIONS.

The year 1931 will be memorable in the history of the Institute in that it witnessed the publication of the *Journal* in an entirely new form. Up to December 1930 forty-four volumes of the *Journal* had been published, these having appeared at half-yearly intervals since the foundation of the Institute in 1908. These volumes consist of two sections, of approximately the same number of pages, containing, in the first section, original papers and the discussions thereon, and in the second section, abstracts of the world's metallurgical literature. Since January 1931 the abstracts, together with an Editorial section, have been published monthly, the two half-yearly "Proceedings" volumes consisting entirely of papers and discussions. The year's publications include the issue of a third volume containing a re-issue, in bound form, of all the abstracts issued monthly during the year, together with a full index to these abstracts and the Proceedings. The Council has been glad to learn that this change in the method of issuing the *Journal* has met with the widely expressed approval of the members.

LOCAL SECTIONS.

Interest in the work of the six Local Sections has been stimulated as a result of the issue of the new monthly *Journal*, in which there has been published, in advance of each Local Section meeting, a synopsis of the paper to be presented, this being followed, after the paper had been read, by a summary of the paper and any discussion thereon. The particular thanks of the Institute are due to the Honorary Secretaries of the Local Sections for their co-operation in the work of collecting the material for these synopses and summaries. The Council is appreciative of the constant efforts made by the Committees and honorary officers of the several Local Sections to secure useful programmes of papers, the latter being planned particularly with a view to meet the requirements of those engaged in local industries. During the year the annual grant from the Institute's funds to the funds of the Local Sections was increased from £120 to £125.

LIBRARY.

In the last Report attention was directed to the increasing use that had been made of the Library facilities of the Institute, and to the fact that members, after studying the abstracts published in the *Journal*, were applying to the Library for the originals of those that interested them. With the publication of the monthly *Journal* this tendency has become much more marked. It has become customary for the Library to receive, a few days after the publication of the monthly abstracts, considerable demands for the originals of the articles abstracted.

During the past year the number of visits paid to the Library by members has increased, several members having come from the Continent to spend some days in the Library in order to consult literature which they were unable to obtain elsewhere.

The number of periodicals received in the Library has increased, and many valuable text-books have been added during the past year, these being noted in the Bibliography published in the monthly issues of the *Journal*, where the additions are marked with an asterisk.

Once again hearty thanks are offered to Sir Henry Lyons, F.R.S., Director of the Science Museum, for his courtesy in allowing the Institute to borrow for its members any book, or periodical, contained in the great Science Library at South Kensington. Much increased use has been made of these facilities during the past year. The attention of members is particularly directed to the fact that very few books or periodicals on scientific and technical subjects in which they are likely to be interested are now unobtainable for them. If they are not contained in the Institute's own special Library they will be secured from the Science Library through the Institute.

Overseas members are reminded that photostat copies can be obtained through the Institute's Library, but that a certificate must be sent with the application stating that the copies are not required for sale, hire, or distribution. The wording of the certificate is given on p. 443 of Volume XLIV (1930) of the *Journal*, and in the preface to the abstracts of previous volumes. The Institute does not possess photostat apparatus, so that copies have to be prepared by a commercial office; the charge made to members is that made to the Institute by the photostat office. At present, the Institute makes no charge for Library service beyond that coming under the headings " postages " and "fares" (to and from other libraries and photostat offices to obtain books and prints for members). As the work is growing very rapidly, however, it may be necessary to engage outside assistance, a proportionate share of the cost of which would be debited to each member concerned, thus enabling the Library service to be placed on an economic basis.

During the past year Miss L. Ornstein, B.Sc., was appointed to the post of Librarian of the Institute in the place of Miss C. Stenhouse, F.L.A., who left the Institute prior to her recent marriage.

JOINT BUILDING SCHEME.

In the appeal for a Central Building in London for Scientific and Technical Societies and Institutions, which was issued in February 1931 to the members of each of the constituent societies and institutions, it was stated that options had been secured for a limited period on a site near Westminster Abbey and that an estimated sum of £350,000 would be required to defray the cost of the complete building, including the purchase of leases. It was further mentioned that the options on the site would expire on June 24, 1931, and that to complete the purchase of the leases it would be necessary to secure £100,000 in cash by that date. Though a considerable response was received from the members of the constituent societies and institutions—amounting in all to £42,000—the sum available thus fell short of the £100,000 required, and after careful consideration of all the circumstances the Council of Management decided to allow the options on the leases to lapse. This involved the forfeit of the deposits and incidentals connected therewith, amounting to £3592 18*s.* 7*d.*—a sum that has been met substantially by amounts contributed specifically for the purpose of investigation.

The acute financial and industrial conditions prevailing during the past year have rendered it impossible to secure certain substantial contributions which it had been anticipated would have been received. The Council of Management, therefore, have had no alternative but to postpone a public appeal until national conditions have improved.

Although regretting the consequent delay in proceeding with the project—imposed by conditions beyond their control—the Council of Management will not relax their efforts to bring the scheme to fruition at the earliest possible moment, and it is hoped that financial and industrial conditions may improve and render it possible to proceed with the scheme in the near future.

REPRESENTATIVES.

Representatives of the Institute as follows were appointed by the Council:

Jubilee of the Society of Chemical Industry: Dr. Richard Seligman, President.

British Association Centenary: Dr. Richard Seligman, President.

American Society for Testing Materials (Committee on Die-Cast Metals and Alloys): Dr. W. Rosenhain, F.R.S., F.Inst.Met., Past-President.

Faraday Centenary Celebrations: Dr. Richard Seligman, President.

Empire Council of Mining and Metallurgical Institutions: Mr. A. H. Mundey, Member of Council, and Dr. Sydney W. Smith, A.R.S.M.

Henri Moissan Commemoration: Dr. R. S. Hutton, Vice-President.

Association of Scientific and Technical Institutions: Dr. Richard Seligman, President.

Professional Classes Aid Council: Mr. H. B. Weeks, Member of Council.

Ramsay Memorial Laboratory Advisory Committee: Dr. Richard Seligman, President.

British Non-Ferrous Metals Research Association, Institute of Metals Corrosion Research: Dr. Richard Seligman, President, Sir Harold Carpenter, F.R.S., F.Inst.Met., Past-President, Mr. H. B. Weeks, Member of Council.

Third International Conference on Bituminous Coal (Pittsburgh): Professor C. H. Desch, Member of Council, Dr. F. N. Speller, Member.

British Standards Institution:

Chemical Division.

Technical Committee C/3 Containers for Heavy Acids and Corrosives: Dr. Richard Seligman, President.

Technical Committee C/6 Chemicals and Chemical Plant for Electroplating: Dr. R. S. Hutton, Vice-President.

Engineering Division (Mechanical Section):

Technical Committee ME/22 Marking and Colouring of Foundry Patterns: Mr. A. H. Mundey, Member of Council.

Technical Committee ME/25 Testing of Metal Sheets and Strips: Dr. W. Rosenhain, F.R.S., F.Inst.Met., Past-President.

Non-Ferrous Section:

Non-Ferrous Metallurgy Industry Committee NF/–: Dr. W. Rosenhain, F.R.S., F.Inst.Met., Past-President; Mr. F. Tomlinson, Member of Council; Mr. H. B. Weeks, Member of Council; Mr. G. Shaw Scott, M.Sc., Secretary.

Technical Committee NF/1, Copper: Mr. F. Tomlinson, Member of Council; Mr. G. Shaw Scott, M.Sc., Secretary.

Technical Committee NF/2, Cast Brass: Mr. H. B. Weeks, Member of Council.

Technical Committee NF/3, Wrought Brass: Mr. F. Tomlinson, Member of Council.

Technical Committee NF/4, Cast Bronze: Mr. H. B. Weeks, Member of Council.

Technical Committee NF/6, Special Alloys of Copper: Mr. F. Tomlinson, Member of Council; Mr. H. B. Weeks, Member of Council.

Technical Committee NF/8, Zinc: Professor T. Turner, M.Sc., A.R.S.M., F.Inst.Met., Past-President.

CORRESPONDING MEMBERS TO THE COUNCIL.

Valuable services have continued to be rendered to the Institute during the year by the following Corresponding Members to the Council, to each of whom the Council desires to express its thanks: Mr. H. Norman Bassett (*Egypt*); Professor C. A. F. Benedicks, Ph.D. (*Sweden*); Monsieur L. Boscheron, O.B.E. (*Belgium*); Professor P. A. J. Chevenard (*France*); Mr. W. M. Corse, S.B. (*United States of America*); Professor J. N. Greenwood, D.Sc. (*Australia*); Dr.-Ing. Max Haas (*Germany*); Dr.-Ing. E. Honegger (*Switzerland*); Mr. R. Mather, B.Met. (*India*); Professor G. H. Stanley, A.R.S.M. (*South Africa*); Professor A. Stansfield, D.Sc., A.R.S.M. (*Canada*); and Professor K. Tawara, Sc.D. (*Japan*).

It was particularly gratifying to the Council that four of their abovementioned Corresponding Members were able to participate in a meeting of the Council that was held in Zürich in September 1931.

Signed on behalf of the Council,
RICHARD SELIGMAN, *President.*
HENRY FOWLER, *Vice-President.*
February 8, 1932.

G. SHAW SCOTT, *Secretary and Editor.*

APPENDIX.

LOCAL SECTIONS' PROGRAMMES, 1931–32.

BIRMINGHAM LOCAL SECTION.

Chairman: T. G. BAMFORD, M.Sc.

Hon. Secretary: R. C. READER, M.Sc., Ph.D., Service Castings Company, King's Road, Tyseley, Birmingham.

1931.	PROGRAMME.
Oct. 22.	SIR WILLIAM LARKE, K.B.E. Inaugural Address.
Oct. 31.	DINNER AND DANCE.
Nov. 12.	OPEN DISCUSSION on "Mechanical Testing." (Opened by W. A. BENTON.)
Nov. 26.	W. F. BRAZENER. "The Casting of Tough-Pitch Copper."
Dec. 10.	R. JACKSON. "Pulverized Fuel."
1932.	
Jan. 12.	J. H. G. MONYPENNY. "Recent Developments in Stainless Steels."
Jan. 21.	A. BURSTALL, D.Sc. "The Testing of Electric Welds."
Feb. 4.	N. P. ALLEN, M.Met. "The Dilatometer in the Study of Steels."
Mar. 3.	S. L. ARCHBUTT. "Gases in Metals."
Mar. 17.	R. GENDERS, M.B.E., M.Met. "The Extrusion of Metals."

The papers form part of a joint programme arranged by the Co-Ordinating Committee of the Birmingham Metallurgical Society, the Staffordshire Iron and Steel Institute, and the Birmingham Local Section of the Institute of Metals.

The Meetings are held in the Chamber of Commerce, New Street, Birmingham, at 7 P.M. (unless otherwise stated in the monthly notices).

LONDON LOCAL SECTION.

Chairman: W. T. Griffiths, M.Sc. *Hon. Secretary:* J. McNeil, A.R.T.C., The Mond Nickel Co., Ltd., Thames House, Millbank, S.W.1.

1931. Programme.

Oct. 8. W. T. Griffiths, M.Sc. Chairman's Address.

Nov. 12. W. J. P. Rohn, Dr.phil.nat. "Some Recent Advances in Rolling Plant." (Meeting at the Royal School of Mines, South Kensington, S.W.)

Dec. 10. G. L. Bailey, M.Sc. "Deoxidizers and Fluxes." (Joint Meeting with the Institute of British Foundrymen.)

1932.

Jan. 14. G. D. Preston, B.A. "X-Ray Examination of Alloys."

Feb. 10. H. Sutton, M.Sc. "Some Recent Advances in Protective Coatings on Metals." (Joint Meeting with the Electroplaters' and Depositors' Technical Society at the Northampton Polytechnic Institute, St. John's Street, at 8.15 p.m.)

Mar. 17. H. J. Gough, M.B.E., D.Sc., Ph.D. "The Efficacy of Testing Methods."

Apl. 14. Annual General Meeting. Open Discussion on "Welding, Brazing, and Soldering."

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

NORTH-EAST COAST LOCAL SECTION.

Chairman: J. W. Craggs. *Hon. Secretary and Treasurer:* C. E. Pearson, M.Met., Armstrong College, Newcastle-on-Tyne.

1931. Programme.

Oct. 13. J. W. Craggs. Chairman's Address.

Nov. 10. A. H. Mundey. "Die-Casting."

Dec. 8. J. T. Lowe. "Industrial Heat-Treatment Furnaces." (Joint Meeting with Society of Chemical Industry.)

1932.

Jan. 12. R. Dowson, B.Sc., S. G. Homfray, B.A., and A. Logan. "Defects in Non-Ferrous Castings."

Feb. 9. N. P. Allen, M.Met. "Some Causes of Unsoundness in Non-Ferrous Alloys." (Joint Meeting with Newcastle Branch of the Institute of British Foundrymen.)

Mar. 15. R. D. Burn, M.Sc. "Refining of Copper."
Annual General Meeting.

The Meetings are held in the Electrical Engineering Lecture Theatre, Armstrong College, Newcastle-on-Tyne, at 7.30 p.m.

SCOTTISH LOCAL SECTION.

Chairman: H. H. A. GREER, J.P. *Hon. Secretary:* HAROLD BULL, Messrs. Bull's Metal & Melloid Co., Ltd., Yoker, Glasgow.

1931. PROGRAMME.

Oct. 12. L. SHORT. "Some Random Reflections on Industrial Problems and Economics."

Nov. 9. W. L. GOVIER. "Experiences with Some Electric Furnaces for Melting Copper and Copper Alloys."

Dec. 14. J. ARNOTT. "New Alloys in the Brass Foundry."

1932.

Jan. 11. H. C. BIGGS. "Some Properties of Fire-Bricks."

Feb. 8. R. B. DEELEY, B.Sc., A.R.S.M. "Aluminium-Silicon Alloys—Their Properties and Some Applications."

Mar. 14. ANNUAL GENERAL MEETING.
J. STIRLING. "Some Notes on Condenser Tubes and their Packing."
J. W. DONALDSON, D.Sc. "Non-Ferrous Alloys in Marine Engineering—Some Recent Developments."

The Meetings are held in the Rooms of the Institution of Engineers and Shipbuilders in Scotland, 39 Elmbank Crescent, Glasgow, at 7.30 P.M.

SHEFFIELD LOCAL SECTION.

Chairman: E. A. SMITH, A.R.S.M. *Hon. Secretary:* H. P. GADSBY, Assoc. Met., 193 Sandford Grove Road, Sheffield.

1931. PROGRAMME.

Oct. 9. W. ROSENHAIN, D.Sc., F.Inst.Met., F.R.S. "Gases in Metals." (Conjoint Meeting with the Sheffield Society of Engineers and Metallurgists.)

Nov. 13. E. A. SMITH, A.R.S.M. "Engineering Silver Solders."

Dec. 1. SYDNEY WILKINSON. "The Technique of Enamelling."

1932.

Jan. 15. A. WRAGG, B.Sc. "Stresses in Metals."

Feb. 12. H. W. BROWNSDON, M.Sc., Ph.D., and E. H. S. VAN SOMEREN, B.Sc. "Spectrographic Methods of Chemical Analysis." (Conjoint Meeting with the Sheffield Society of Engineers and Metallurgists.)

Mar. 4. W. R. BARCLAY, O.B.E. "Defects in Spoon and Fork Blanks." (Conjoint Meeting with the Sheffield Technical Trades Society.)

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: A. M. KEMPSON. *Hon. Secretary:* ROOSEVELT GRIFFITHS, M.Sc., Metallurgical Department, University College, Singleton Park, Swansea.

1931. PROGRAMME.

Oct. 13. A. M. KEMPSON. Chairman's Address.

Nov. 10. PROFESSOR D. HANSON, D.Sc. "Some Causes of Unsoundness in Non-Ferrous Alloys." (Paper read by I. G. SLATER, B.Sc.)

Dec. 8. A. L. NORBURY, D.Sc. "Use of Cast Iron in the Non-Ferrous Industry."

1932.

Feb. 9. E. EVANS, B.Sc. "Zinc—the Utility Metal."

Mar. 8. ROOSEVELT GRIFFITHS, M.Sc. "Metallography in Industry."
ANNUAL GENERAL MEETING.

The Meetings are held at the Y.M.C.A. at 6.15 P.M., unless otherwise stated. Tea served before Meeting.

The PRESIDENT, in moving the adoption of the Report, said: It is customary for the President to move the adoption of the Report of the Council, and to say a few words on the salient points in it. I have noted three paragraphs to which to direct your particular attention. The most important, probably, is the second, which tells you that, in spite of everything which has occurred during the last year, we have been able to carry on our mission. That, I think, must be a source of gratification to all those who are connected with the Institute or who are connected with the much larger field which the Institute attempts to serve. I must at the same time emphasize the note of warning contained in the next paragraph, which points out that we have not yet felt the full weight of the terrible conditions existing in the world. Perhaps it may be safe to say that at the present moment one can just see a little light almost from beyond the horizon, and that we may hope that before very long the rim of the sun itself will be showing. I think that I am right in saying that the signs of improvement at present show only in this country; but that should be good news for everybody. I have never spoken on behalf of the Institute, either here or in other countries, without testifying to my belief that we, at any rate, can never benefit, nor can ever be happy or well, unless all other peoples are in the same happy condition as we would like to be. If that be true, it is even more true to say that unless this country and its institutions, and its Institutes perhaps, are thriving, none of the rest of the world can really be prosperous. Therefore I hope that all our many overseas members will feel that if we here are beginning to see the light, it will not be very long before it reaches them.

The next point to which I wish to direct your attention concerns the Autumn Meeting, remarks on which are to be found on p. 4. It is stated there that the Council had set about trying to organize a joint meeting in the Autumn with the Iron and Steel Institute. I am happy to be able to inform you that that is now assured. The two Institutes will meet together in September, and I am further able to say that, at a small meeting which has been held for the purpose, the organization was put on foot, and I think that there is every hope that we shall have a thoroughly successful joint meeting. I am particularly glad to be able to say this. It offers to all the members of both Institutes an opportunity to get together and to solve their problems together, which I think every member of the Institute of Metals will take, and will use to the fullest extent.

The next paragraph of the Report is one dealing with the Local Sections. The Local Sections are amazingly alive. I am particularly glad to be able to testify to this. It has been my good fortune to be able to be with all of them at least once during the year, and I can assure all members that their spirit continues in the fullest activity. I think that not only are the thanks of the Council due to the local secretaries and their committees, but that the thanks of the local members and the associates are especially due to those gentlemen. The associates are, as we all know, not regular members of the Institute, but we have very fraternal feelings towards them and I am glad to say that the Council has recently been considering some small steps which it hopes to be able to take to further their interest in the Institute and to help them in their daily work.

I now come to my last point, which is not in the Report, but which deals with the year's work. We have had on several occasions during the year, not demands but requests from hard-pressed members (and I am sorry to say there are many members who are hard-pressed at the present time) as to whether we could not ease the burden on them, either by reducing subscriptions or in some other way. We have listened with keen sympathy to such requests, but at present we see no means of complying with them. There are only two ways to my mind by which one can ease that burden, because, as the Treasurer's Report will show you very shortly, we have nothing to spare; on the contrary. One is to reduce our services to our members,—and that, I think, would be a very retrograde step for us to take—and the other is to try by all means to secure such collaboration between ourselves and other kindred societies as will enable us to stop some of the great amount of overlapping which goes on, and in that way constructively reduce the burden on our members. To that our attention is definitely directed, and although the road may be long I hope that ultimately we shall reach that goal.

Mr. H. Sutton, M.Sc., Member (Farnborough): I have great pleasure in seconding the motion for the adoption of the Report of Council, which I believe to be a particularly good one even in spite of difficulties which have been inordinately great during the present year. I am much impressed by the fact that we have on our Council a large group of men each of whom is individually very busy; and, if I might say a word to the Council as an ordinary member of the Institute, I would remark that you are making a great sacrifice in devoting your time, energy, and consideration so carefully and effectively to the interests of the Institute.

I was pleased as an individual to be called on to second this motion, because it gives me the opportunity to say one thing about the Institute of Metals which I have always felt very sincerely, and that is this: I belong, like most of you, to several societies, some British and some having their headquarters in other countries, but my ideals of the organization and conduct of a scientific society are more closely approached by the Institute of Metals than any other society I know.

There are three portions of this Report to which our President did not refer in detail. It is a splendid Report, and there are many things in it which are of great importance; but I should like to refer briefly to three sections which have interested me very much.

As regards the publications, the monthly issue of the abstracts has been of immense service to me personally. It is a nice little volume which goes comfortably in my bag and is carried with me on train journeys. I can read in the odd moments which are at my disposal, the various items of news of what other people are doing and I find it of real assistance.

As regards the Local Sections, I can see from the accounts in our own *Journal* and in the technical press that a very fine selection of practical papers has been given by members and others to the Local Sections. That is a very fine work. I am sure that we all feel that the Council is doing splendid work in encouraging it, even at some little expense.

Lastly, I would just mention the Library Service. I occasionally wish to refer to rather abstruse literature, and I have yet to beat the Institute of Metals' Library when in search of a remote journal. It is a very valuable service to those of us who are situated at some distance from the more important libraries, to be able to send a note to the Institute and to receive by post on the following morning some journal containing an article of special interest to us. That is a work which has been going on for a long time with increasing efficiency and importance.

I do not wish to say any more, except this—that I am purposely refraining from touching upon the financial situation. I have the impression that in normal times in any society which is busy with its own affairs, and is healthy and prosperous, the finances are all right.

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

Professor T. Turner, M.Sc., A.R.S.M., F.Inst.Met., Past-President and Chairman of the Finance Committee, then presented, in the absence of Mr. John Fry through a bereavement, the Report of the Honorary Treasurer :

REPORT OF THE HONORARY TREASURER

(Mr. JOHN FRY.)

For the Financial Year ended June 30, 1931.

The Accounts of the Institute for the twelve months ending June 30, 1931, are not quite so simple or so easy of explanation as they have been in previous years.

It is difficult, if not impossible, to make a fair comparison of the accounts for 1930–31 with those of the previous year because of the change that took place during the former period in the method of issuing the *Journal.* The inauguration of our new monthly *Journal* of " Metallurgical Abstracts " meant rather a revolution in our finances. We are now paying our printers' bill monthly instead of half-yearly; and there is also a lag in the receipts of advertisement revenue—a source of income that is steadily growing in magnitude—which temporarily dislocates the Institute finances. Our next set of accounts will still not be strictly comparable with those before you, and will show an apparent considerable excess of expenditure over income due to the new method of publishing—and paying for—the *Journal.* In fact, it will not be until we have ended the financial year 1932–33 that our accounts will begin to be directly comparable with those of future years.

Our excess of expenditure over income of £751 6*s.* 4*d.* is largely explained by what I have said above. The debit balance is also swollen by a non-recurring charge of £248 7*s.* 5*d.* representing legal charges in connection with our successful income tax appeal, an expenditure which has already been more than recouped by the amount that we should have had to pay for " back " years had we lost the appeal. If we had included—as we did until 1928–29 —in our Income and Expenditure Account the amount received for Entrance Fees—£429 8*s.* 5*d.* last year—our debit balance would have been still further reduced. As it is, that useful amount goes to the Entrance Fees Account and now shows in the Balance Sheet.

The Council is satisfied that we are not actually spending more money on the production of our *Journal* under the new method than previously. The transition stage will explain itself financially in due course.

Turning now to the Balance Sheet, reference has already been made to Entrance Fees. On the assets side, it will be noted that the stock of *Journals*, always conservatively valued, shows an increase of £356 12*s*. 6*d*., and also that a further £1,000 of War Loan was purchased. This was a temporary method of employing surplus cash. The stock has since been sold. Beyond these items there are only slight changes, with the exception of the *Journal* Account, which, as explained above, is in a state of evolution.

The Income and Expenditure Account shows that the annual subscriptions are down by £56. A substantial loss occurred on Australian subscriptions, which the Council accepted in depreciated Australian currency to assist members during a time of financial crisis.

Interest on War Loan is up by £50, on account of the increased investment, and for the same reason Bank interest is down by £29.

On the expenditure side, salaries are up by £163, due to staff additions necessitated by the Institute's ever-increasing activities.

Rent, Telephone, Lighting, and Insurance show an increase—of £71—reflecting the Institute's new activities and staff additions, whilst the item Subscriptions and Grants to local Sections, at £38, also shows a slight growth.

Printing and Stationery is down by £200, as this year we have refrained from reprinting the List of Members. Library Expenses are down by £26, and Expenses of Meetings are reduced by £12.

Other slight alterations are to be expected in the comparison of any annual expenditure, and do not call for special comment.

The Institute of Metals, like most institutions, has had an anxious time financially during the year under review. So far, it is weathering the storm moderately well, although the anxiety continues, and the Council invites all the support which members can possibly give.

Professor T. Turner, M.Sc., A.R.S.M., F.Inst.Met.: You will, I am sure, all feel deeply with Mr. Fry in the circumstances which have led to his absence to-day. The Report which he has prepared shows that the accounts of the Institute are not quite so simple or easy of explanation as they have been in previous years. I may say that I expect at the end of the present financial year that we shall have an even more disconcerting report than we have at the moment: but it is merely a question of cash and not of capital. In future years we believe that these things will adjust themselves.

Our excess of expenditure over income is £751, but of this £248 represents legal charges for the successful appeal against income-tax assessment, and this has already paid itself.

The Council is satisfied that we are not actually spending more money on the production of our *Journal* under the new method than previously. The transition stage will explain itself financially in due course.

We had temporarily invested money which we had in the Deposit Account and it was intended to sell this. We had to sell it at a bad time, and unfortunately we lost something like 7 per cent. on the sale, while we had been getting 5 per cent. interest in the meantime. The net result of what we thought was going to be a good investment was a loss.

Mr. H. B. Weeks, Member of Council, seconded the motion, which was put to the meeting and carried unanimously.

THE INSTITUTE OF METALS

BALANCE SHEET AS AT JUNE 30, 1931.

LIABILITIES.

	£	s.	d.	£	s.	d.
Sundry Creditors :						
For Accrued Expenses, less proportions in advance	431	18	10			
,, *Journal* Accounts	1,953	9	8			
,, Subscriptions paid in advance	821	10	7			
,, Entrance Fees paid in advance	—					
				3,206	19	1
Entrance Fees Account :						
Balance at June 30, 1930	460	6	11			
Amount receivable for Year to June 30, 1931	429	8	5			
				889	15	4
Woodhouse Fund Account				20	0	0
House Fund Account				1,049	19	2
Excess of Assets over Liabilities at June 30, 1930	6,526	10	10			
Less Excess of Expenditure over Income for Year ended June 30, 1931	751	6	4			
				5,775	4	6
				£10,941	18	1

ASSETS.

	£	s.	d.	£	s.	d.
Office Furniture :						
As at June 30, 1930				200	0	0
Library Books, &c. :						
As at June 30, 1930				100	0	0
Sundry Debtors :						
For Entrance Fees	17	17	0			
,, Subscriptions	324	5	8			
,, *Journal* Accounts, &c.	386	0	0			
,, Sundries	20	0	0			
				748	2	8
Stock of Journals :						
As per Secretary's Inventory and Valuation				2,755	5	0
Investments :						
£6,111 1s. 8d. 5% War Loan, 1929–47, at Cost				6,025	7	10
Cash :						
Balance at Bank—Deposit Accounts	51	2	4			
Current Accounts	18	19	6			
	70	1	10			
Less Petty Cash overspent	6	18	5			
				63	3	5
House Fund :						
£1,000 5% War Loan, 1929–47, at Cost	1,044	19	1			
Cash at Bank	5	0	1			
				1,049	19	2
				£10,941	18	1

RICHARD SELIGMAN } *Members of*
HENRY FOWLER } *Council.*

G. SHAW SCOTT, *Secretary.*

AUDITORS' CERTIFICATE.

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 affairs of the Institute of Metals, as on June 30, 1931, according to the best of our information, and from the explanations given to us, and as shown by the books, &c., of the Institute.

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

November 30, 1931.

THE INSTITUTE OF METALS

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED JUNE 30, 1931.

	£	s.	d.		£	s.	d.
To Salaries	2,143	6	8	By Annual Subscriptions	6,362	10	2
,, Wages and National Insurance	831	6	7	,, Interest on War Loan	305	11	0
,, *Journal* Account	2,393	0	2	,, Bank Interest	29	4	7
,, Rent, Telephone, Lighting, and Insurances	844	3	5	,, Sundry Donations	24	3	0
,, Printing and Stationery	309	10	7	,, House Fund Rent	50	0	0
,, Postages, Travelling, and Sundry Expenses	378	9	1	,, Income Tax refund	23	0	4
,, Library Expenses	62	16	5	,, Balance—Excess of Expenditure over Income for Year to June 30, 1931	751	6	4
,, Subscriptions and Grants to Local Sections	178	9	6				
,, Expenses of Meetings	100	2	9				
,, Repairs and Renewals	29	17	10				
,, Solicitors' Charges in connection with Income Tax Appeal, &c.	248	7	5				
,, Audit Fee	26	5	0				
,, Balance—Excess of Income over Expenditure	—						
	£7,545	15	5		£7,545	15	5

JOURNAL ACCOUNT FOR THE YEAR ENDED JUNE 30, 1931.

	£	s.	d.		£	s.	d.
To Stock of *Journals* at June 30, 1930	2,399	12	6	By Accounts owing at June 30, 1930	224	16	3
,, Sundry Debtors for *Journals* sold at June 30, 1930	106	3	3	,, Sales of *Journals* and Index, and Advertisements	1,345	2	9
,, Cost of production of *Journals* including Abstractors' Fees	2,644	18	9	,, Stock of *Journals*	2,755	5	0
,, Sundry Creditors	1,953	9	8	,, Sundry Debtors for *Journals* sold and Advertisements	386	0	0
				,, Balance transferred to Income and Expenditure Account	2,393	0	2
	£7,104	4	2		£7,104	4	2

"HOUSE FUND" ACCOUNT FOR THE YEAR ENDED JUNE 30, 1931.

	£	s.	d.		£	s.	d.
To Rent paid to the Institute of Metals	50	0	0	By Balance at June 30, 1930	1,049	19	0
,, Balance as at June 30, 1931	1,049	19	2	,, Interest on War Loan	50	0	0
				,, Bank Interest			2
	£1,099	19	2		£1,099	19	2

ELECTION OF OFFICERS FOR 1932–1933.

The SECRETARY read the following list of officers elected to fill vacancies on the Council for the year 1932–33:

President.

SIR HENRY FOWLER, K.B.E., LL.D., D.Sc.

Vice-Presidents.

W. R. BARCLAY, O.B.E.
H. MOORE, C.B.E., D.Sc., Ph.D.

Members of Council.

MAURICE S. GIBB, C.B.E., J.P.
R. LLOYD GIBBINS.
E. L. MORCOM, M.A.
JAMES STEVEN.
W. G. TURNER, O.B.E.
H. B. WEEKS.

VOTE OF THANKS TO THE COUNCIL.

Professor Dr.-Ing. GEORG SACHS, Member (Frankfurt-am-Main, Germany): The task has been allotted to me on this occasion of expressing on behalf of the members of the Institute our thanks to the Members of the Council for their services during the past year. I think that it is rare that one can congratulate the Council so sincerely as in this instance. In these days of general economic confusion and want of confidence in technical progress, it must be regarded as a great achievement to maintain an existing position. The Council of the Institute has not only accomplished this, but has succeeded in continuing the same astonishing rate of increase of membership as in the last decade, and in improving the scientific position of the Institute. We may take this as an indication that the fundamental ideas which have brought us together as an Institute will not only in the future maintain their strength, but will continue to increase in importance in regard to the other progressive branches of technology. In this sense we in Germany appreciate very much the efforts of the Council to promote international co-operation in metallurgical work, and I would like to extend once more to the Council the most cordial thanks of the members of the Institute, and especially the thanks of the overseas members.

The vote of thanks was then put to the meeting and carried unanimously.

The PRESIDENT: I thank Professor Sachs very cordially on behalf of the Council for the friendly words he has spoken, and you, ladies and gentlemen, for the way in which you have received his suggestion. The Council has undoubtedly had a very difficult task during the past year. That it has performed it to your satisfaction must be a source of satisfaction to them also. It is especially pleasing to us to feel that the thanks of the members can be voiced by one of its very distinguished overseas members. We shall never forget the fact that our province is the world, and it is pleasing to feel that our efforts to draw all metallurgists together are appreciated overseas. Just recently the Council has been in communication through me with every one of its German members, and it has been a real pleasure to receive from them replies encouraging us to proceed with our work. Professor Sachs has expressed his thanks to the Council. I think, if I may say so at this stage, that the thanks of the members are at least equally due to the staff of the Institute. The work they have done under the leadership of Mr. Shaw Scott and Mr. Guillan has been Herculean work. It has been "twenty-four hours a day work," if I may use a phrase which Dr. Hutton used a little while ago, and their only regret seems to be that there are not a few more hours in the day in which to work. Their duties have been very harassing and strenuous. They are carrying them out to the admiration of every member of the Council, and certainly to the admiration of those of us who are closely connected with the working of the Institute. Professor Sachs, I thank you very cordially for the friendly words you have spoken.

Election of Members and Student Members.

The Secretary announced that the following members and student members had been elected on October 29 and December 17, 1931, and January 21 and February 18, 1932.

Members Elected on October 29, 1931.

Baldwin, Tom	Rochdale.
Bent, Quincey, B.A.	Bethlehem, Pa., U.S.A.
Betterton, Jesse O.	Westfield, N.J., U.S.A.
Brown, William H., Ph.D.	Manila, Philippine Islands.
Davy, C. Humphrey	London.
Dawidenkow, Professor N. N.	Leningrad, U.S.S.R.
Francis, Edgar Llewellyn, M.Sc.	Stockport.
Heurtault, René	Paris, France.
Hill, Erle Gladstone, B.S.	Coatesville, Pa., U.S.A.
Iachino, Commander Angelo	London.
de Kruyff, Herman	Utrecht, Holland.
Lones, John Arthur	Birmingham.
Meuche, Hans Eugen	Wettingen (Aargau), Switzerland.
Mould, Albert Parton	Birmingham.
Sperk, Charles	Kladno, Czechoslovakia.
Swartz, Torrence Albert, M.S.	Prince Bay, N.Y., U.S.A.

Student Members Elected on October 29, 1931.

Browne, Charles Gordon Knight, B.A.	Oxford.
Flack, Eric Gordon	Glasgow.

Members Elected on December 17, 1931.

Anderegg, Charles G. A., Dipl.-Ing.	Zürich, Switzerland.
Asher, Samuel Bernard, A.R.S.M.	Johannesburg, South Africa.
Burningham, Arthur Charles James	Horley, Surrey.
Carman, W. Floyd	London.
Fairlie, James	Kenilworth.
Fennell, Charles Augustus Francis	Letchworth.
Grah, Fritz, Dipl.-Ing.	Hemer i/Westfalen, Germany.
Hagen-Torn, Vladimir Oscar	Leningrad, U.S.S.R.
Imai, Professor Hiroshi, D.Eng.	Port Arthur, South Manchuria.
King, Henry George	Erith.
Martin, William Milles	Bombay, India.
Oknoff, Professor Michael G.	Leningrad, U.S.S.R.
Roš, Professor Mirko	Zürich, Switzerland.
Scott, Murray Duncan	Enfield.
Taiana, Luis	Buenos Aires, South America.
Versell, Herman	Zürich, Switzerland.

Student Members Elected on December 17, 1931.

Gould, George Herbert	Coventry.
Hallett, Michael Mountjoy	Penarth.
Kasz, Frank	Manchester.
Matthewson, Albert William	Birmingham.
Whiley, Manning Hedges	London.

Members Elected on January 21, 1932.

Anthes, Lawrence Lee	Toronto, Ont., Canada.
Barr, Mark	London.
Bedinger, Margery, A.B.	Butte, Mont., U.S.A.
Center, Jakob Alexandrovich	Leningrad, U.S.S.R.
Crowell, Walter S., B.S.	Philadelphia, Pa., U.S.A.
Hunn, Sidney Charles	London.
Moir, Douglas Morton	Birmingham.
Otzen, Geh. Reg.-Rat. Professor Robert	Berlin-Dahlem, Germany.
Patrick, James	Milngavie, Scotland.
Ponisovsky, James, B.Sc.	Brussels, Belgium.
Rolleston, Patrick William, B.A.	Shawinigan Falls, P.Q., Canada.
Young, George MacDonald, B.Sc.	Montreal, Canada.

Student Members Elected on January 21, 1932.

Bailey, John Cleaver, B.Sc.	Birmingham.
Mehta, Faredoon Pirojsha, B.Sc.	Sheffield.
Plant, Wilfred	Tipton.
Sandford, Ernest Jack	Birmingham.
Saville, James Patrick	Birmingham.

Members Elected on February 18, 1932.

Brace, Porter Hiscock, B.S.	East Pittsburgh, Pa., U.S.A.
Clapham, Dorothy P., B.Sc.	London.
Harper, Charles Douglas	Chesterfield.
Hawkes, Arthur John	Wigan.
Ivano-Skobliekov, Nicolay Nicolayevich	Leningrad, U.S.S.R.
Kalling, Professor Bo Michael Sture	Stockholm, Sweden.
Kirkwood, David, Jr.	London.
Myers, Richard Harold	London.
Williams, Howell	London.

Student Members Elected on February 18, 1932.

Hamburger, Max	Birmingham.
Houdek, Vladimir	Brno, Czechoslovakia.
Taylor, Robert, B.A., B.Sc.	London.
Tremlett, Henry Frederick	Abingdon-on-Thames.

Re-Election of Auditors.

Dr. O. F. **Hudson**, Member (London), proposed and Mr. H. J. **Tapsell**, Member (Teddington), seconded, the re-election of the Auditors, Messrs. Poppleton and Appleby. The motion was put to the meeting and carried unanimously.

Induction of New President.

The **President**: I now come to the last task which I have to perform before retiring from the position to which you called me two years ago, and that is to induct our new President to the Chair.

It is customary on these occasions to give an outline of the activities of our future President, but in the case of a man with so many and such varied activities as Sir Henry that would occupy the rest of the morning. His interests range from heavy locomotives to light alloys and from Roman remains to international hockey! He is an engineer who has occupied posts of vast responsibility in peace and in war, not only national, but also international. That is a matter which must be of great value to the Institute over which we are now asking him to preside.

Further than that, he has had a long and diverse experience of just such duties as we are now seeking to impose upon him. He has been President of many big organizations, and I think that I am right in saying that this will not be the first time that he has actually occupied this Chair. That fact also, I think, must be very helpful to us.

Looking back, Sir Henry must be proud of the record which all that implies, but I have a feeling that if one could only look behind that genial countenance of his one would see that his greatest pride was in yet another thing—a little thing perhaps, but it is this: that he has not only been a student and a practitioner of metallurgy, but a teacher of metallurgy as well. And he has taught to some effect, because I find that one of our very distinguished members—a previous Vice-President—Professor C. A. Edwards, learned his first lessons in metallurgy from Sir Henry Fowler.

All these are attributes which many of us might envy him, but there are just two others from which, I believe, the Institute will derive the greatest possible value. One is that Sir Henry has a positive genius for the making of friends. He knows everybody everywhere who is anybody, and I think that I am right in saying that everybody, everywhere, whether anybody or nobody, knows him. I am sure that in the position he will occupy that will not only be helpful to him, but also very helpful to us.

His second attribute is this—that he has an unquenchable interest in the welfare of young men and young women, members of our Institute or not, to whom we look to carry on the work which we old fogeys have been doing up to now. That is another attribute which we must all welcome in a President of an Institute such as this.

Now, Sir Henry, I think that I have said much more than you feel comfortable to hear, and I now proceed to hand on to you the torch which my predecessor, Dr. Rosenhain, handed to me two years ago. I have tried to keep it burning through two very tempestuous years. I had hoped that I should have been able to hand it over when the storm had at last passed, but the Fates have willed otherwise. You, Sir, will feed it with very different fuel from that which I have used, but I am absolutely convinced that when the time comes for you to hand it to your successor you will do so with its flame unquenched, its brilliance undimmed.

Sir Henry Fowler then took the Presidential Chair.

The President (Sir Henry Fowler): I have occupied this Chair before, in point of fact, as President of two other Institutions, but I have never been placed in such a position as I am at this moment; that is to say, I feel unable to speak as I should like to do in thanking you, Dr. Seligman, and you ladies and gentlemen, for your kindness to me. But I do thank you very sincerely indeed. You have spoken, Dr. Seligman, about the flame of the torch of the Institute. I trust that there may never be any chance of the flame not burning with as clear a light as it has done throughout the whole of the time I have been associated with the Institute. I am placed in a very difficult position. If the staff has worked twenty-four hours a day, I would not like to say how long Dr. Seligman has worked on our behalf, and I do not know that it is possible for me to give the same close attention, because, after all, I am a provincial man. I ought to have looked up how many other provincial men you have had as Presidents; but I do know this—that no one could have given the time and the amount of serious thought and hard work to Institute affairs, which Dr. Seligman has given. But I must not anticipate what Sir Harold Carpenter will say later on. I express my hearty thanks to you for having elected me President of the Institute, and I assure you that, with that help which I know the Council and members will give me, I will do everything in my power to forward the interests of the Institute in every possible way.

VOTE OF THANKS TO THE PAST-PRESIDENT.

Professor SIR HAROLD CARPENTER, Kt., M.A., D.Sc., A.R.S.M., F.Inst.Met., F.R.S., Past-President: I must thank you very much for the privilege you have afforded me of moving a vote of thanks to our retiring President. The Institute has now entered on the twenty-fifth year of its life. As I speak I look at the portrait of our first President, the late Sir William White, who gave us a splendid start, due to his unrivalled experience and ability. In the early days of the Institute it was not particularly difficult for the President to leave his mark, because there were many questions to be settled and many policies to be considered. It is not so easy for the President to leave his mark in that way to-day. My own view is that no President has left a deeper mark on the Institute than Dr. Seligman. I do not think that I can describe his achievements better than in that sentence. Two years ago he put before us his hopes and aspirations in his Presidential Address, and substantially they have been realized. It was a large programme. It was a fine programme. It is not quite finished. Some of it has been finished, and all of it is on the way. The President's activities may be divided roughly into two categories. If I may speak colloquially, those that he does " on his own," and those that he does as the spear-head of the Council. I would just like to say a word about these two aspects of Dr. Seligman's work.

In the first category, without any hesitation I place his work in visiting and assisting our Local Sections. The headquarters of this body are situated in London. Its administrative work is done here, and there are, of course, many metallurgists who live and work in London; but as a body we represent non-ferrous metallurgy in the country and overseas, and everything which can be done to what I may call de-centralize the work of this Institute is, in my opinion, to the good. I think that we want to maintain this feeling—that we are as a body representing non-ferrous metallurgy as a whole, and I do not think there is a better way of doing that than for the President to go round and assure the local members and committees of his interest and sympathy in their work. Dr. Seligman has somewhat under-stated his work in this connection. He did say, I think, that he visited the Local Sections once or twice. I do not know how many times he has visited them, but he left something very important out, and that was that he gave them hospitality. I should like to emphasize that. I think that was a very nice feature of his visits—and I think that the Local Sections appreciated that too.

Then there was the Zürich meeting, which was essentially his creation. Those who had the privilege of attending that will always retain the happiest memories of one of our most successful overseas meetings.

With regard to his action as the spear-head of the Council's activities, reference has already been made to the new form of the *Journal*. That seems to me to be the outstanding event of his work during these two years. I also read the monthly *Journal*, but I do not always read the abstracts it contains. I read the news about " the other fellow," and I hope that everybody enjoys it as much as I do. But, speaking quite seriously, I think that they constitute a valuable annealing process in the life of the Institute; they keep us in good touch with one another, and they prevent any " work-hardening strains " from developing at any particular point with possible consequent danger to the Institute.

Our President has also represented us at many meetings. He has eaten many dinners. I hope that he looks upon that as as big a service as I do!

Then there is another event, and I am not sure that it is not going to prove ultimately the most important development of Dr. Seligman's two years' Presidency, and that is the fact that we are going shortly to hold a joint meeting with the Iron and Steel Institute. A number of us have had hopes for a long time of something of this kind happening. I think that I am right in saying that something like 300 members are common to both Institutes, and that at once suggests the question, Is it really necessary to have two organizations, and particularly two sets of subscriptions? I say that having regard particularly to the younger members. It is very difficult to-day for a young worker in metallurgy to start with a proper professional membership outfit, as it were, requiring two sets of entrance fees and subscriptions. That is a big hurdle to negotiate, and I will do anything in my power, as Treasurer of the Iron and Steel Institute, to facilitate the simplification of this.

Just one thing more. Valuable as have been the many activities of the President, and of his acts, on behalf of the Institute, he has done something still more valuable—valuable because to a great extent it has been unconscious. He has revealed himself to the Institute. The members of the Council knew something of his qualities before—not all of them, of course, because every man develops as President; but I am quite sure that I shall have your endorsement when I say that Dr. Seligman has unconsciously by his work during these two years revealed something of what he possesses—qualities of vision, energy, broad-mindedness, and high-mindedness. There is no President from whom we part with greater regret than Dr. Seligman. Fortunately we are not going to lose him. I am sure that he will not give up his splendid work on behalf of the Institute; but in thanking him I would like to assure him on your behalf, as well as on my own, of our gratitude, our admiration, and I think that I may add, our affection.

Dr. H. Moore, C.B.E., Vice-President: It might be thought that Sir Harold Carpenter has not left me very much to say, but I assure you that that is by no means the case, and that I could go on talking enthusiastically about Dr. Seligman's work for the Institute for a very long time. I do not propose to do so, but it is a great pleasure to me to be able to say very briefly what I really think about Dr. Seligman. The pleasure is tempered with the regret which we must all feel that this meeting marks the end of a very notable Presidency. In giving my impression of it, very briefly, I am bound to use terms which to those who have not seen Dr. Seligman's work at such close quarters as myself may seem extravagant. During these two years he has devoted himself heart and soul to the interests of the Institute. He has worked early and late and has never spared himself. We are delighted to see with us this morning Mrs. Seligman—by no means for the first time, and I am sure that Mrs. Seligman could speak very feelingly indeed about the countless hours that her husband has devoted to the work of the Institute. May I take this opportunity of saying how very much we have all appreciated Mrs. Seligman's presence at many of our meetings, and the charm with which she has taken a leading part in our social gatherings? Taken as seriously as Dr. Seligman has taken them the duties of a President of this Institute are multifarious and exacting, and give full scope to the abilities of even so many-sided a man as he is. Metallurgical research lost a most able worker when he turned his attention mainly to manufacture, but he is still far more of a man of science than he will ever admit. I even think that, in view of our usual practice, there might be some ground for extending Dr. Seligman's term of office for another two years, considering that he is so much a man of science as well as a man of business! This combination of business ability and scientific imagination has been singularly successful in the Presidential Chair. To these qualities Dr. Seligman adds an urbanity, a tact and a humour which make him an ideal Chairman at meetings of the Council and Committees, and on other occasions. I do not know whether he has succeeded in attending all the meetings during his two years as President which it has been physically possible for him to attend, but I am sure that he has made a very good try. Although Sir Harold Carpenter has mentioned the

Zürich meeting, I feel that I must say a word about the two autumn meetings at Southampton and Zürich. The easy dignity and distinction with which Dr. Seligman presided at those meetings made us all proud to have him as our President. Incidentally, I think that the Institute must be acquiring a reputation for having as its Presidents men who are at home in all the ordinary European languages.

But Dr. Seligman's great and lasting achievement has been the new monthly *Journal*, and the consequent great improvements which have accompanied it in our method of publication. The great amount of work involved in making the change cannot, I think, possibly be realized by the ordinary members of the Institute. Others have helped, in particular the secretary and the staff have done an enormous amount of additional work, but it has been the courage, the enthusiasm, the drive and the unremitting work of Dr. Seligman himself which have carried through the change, and carried it through so successfully.

May I conclude on a note which I hope is not too personal? During these two years I have come to regard Dr. Seligman not only with admiration and complete confidence, but also with a great deal of affection and I am sure that I speak for all those who have worked in close association with him. I have the greatest pleasure in seconding the vote of thanks to the retiring President.

The PRESIDENT: Dr. Seligman, it is with the greatest pleasure that I put this motion to the meeting. There never was a time when the Chair put forward a motion which it was known beforehand would meet with such hearty approbation from every member present. There is one way in which the Council and the members as a whole can show some small recognition to one who has served us as you have served us. One of our rules with regard to the members and membership says that: "*Fellows* shall be chosen by the Council. They shall be limited in number to twelve, and shall be members of the Institute who have, in the opinion of the Council, rendered eminent service to the Institute." This morning the Council have elected you, Dr. Seligman, a Fellow of the Institute.

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

Dr. RICHARD SELIGMAN: It seems only yesterday that I sat where you now sit, Sir, and heard Dr. Rosenhain say that we had not often seen him short of words, but that on that occasion he felt difficulty in finding them in replying to the thanks of the members which had then been accorded to him. I remember thinking then, as I think now, that if he felt that way, how much more must I feel it at this moment. To have this vote moved by Sir Harold Carpenter is in itself a matter of real gratification to me. I have always regarded Sir Harold as my father in metallurgy. He really first awakened my interest in the matter—an interest which has never ceased, and for him to come down here to move this resolution is in itself a matter for which I am profoundly grateful. He referred to the programme which I laid out for myself two years ago, and he said that much had been done and that other things remained to be done. Well, that is the way of the world. I have only put another brick or two on to the structure which those who went before me had built up—more particularly my immediate predecessor, Dr. Rosenhain. I leave lots of gaps in the brickwork for you, Sir, to fill. There was an old song which we used to sing when I was at school which related to the football field. We had a peculiar game at that school. The object was for a boy to take the ball down through the field as far as he could and then, just when he might have succeeded in getting a goal for himself, to give the ball to another. It is much the same in life; in fact, the old song said "The world is a scrimmage, and life is difficult run, but often a brother shall finish the work that we have begun."

That is just the case here. We are all trying to build this structure, one helping the other, one carrying on the work which the other has started.

Turning to the very friendly words which Dr. Moore has used, I must make an admission there. I did miss a Committee meeting. It is true it was on an occasion when there were two Committee meetings going on at the same time! Perhaps therefore it would count as one of those which I could not physically attend. Dr. Moore speaks really from the goodness of his own heart. He said one thing which must be more prized by anybody who has been allowed to preside over you than anything else—that is the feeling that he carries with him memories of good fellowship, of friendliness, and of the desire to help of all of his colleagues on the Council and the staff and the various Committees and the membership of the Institute.

You have done me, Sir, a very great honour to-day in electing me to a Fellowship of the Institute. It is a thing which I shall prize all my life, and which I hope and believe those who owe their being to me will prize long after me.

For that, and for the many other favours which have been accorded to me during the last two years, I give you my very heartiest thanks, and to Sir Harold Carpenter and to Dr. Moore I give my special thanks for their friendliness in voicing what you have been good enough to say is the opinion of the members of the Institute.

PRESIDENTIAL ADDRESS.

SIR HENRY FOWLER then delivered his Address (see pp. 27–36).

Professor T. TURNER, M.Sc., A.R.S.M., F.Inst.Met.: The honour of moving that "our best thanks be accorded to the President for the interesting Address which he has just delivered" has fallen to me, probably because, as he has mentioned, we have known each other for many years. He was a student in Mason College at the time when, as I tell him, he was a good-looking boy with a shock of curly light hair. He was one of the youngest students we had, because he had already shown unusual ability. I believe that there was no student at Mason College who entered at so early an age for a systematic course of instruction. He has found that the study of metallurgy has been of assistance to him in connection with his engineering work, and that, of course, is a matter which is now fully recognized by engineers. The work which he has done has already been briefly referred to, and is well known to most of us. One is pleased to know that metallurgy is of profit to the general student, apart altogether from its direct and technical value. One remembers, for example, that the study of metallurgy was not disadvantageous to one who afterwards became a Prime Minister; nor was it a disadvantage to one who is now the Chancellor of the Exchequer; or, going still further afield, it will be remembered, by some of the older ones among us, that the President of the United States of America was connected with the mining and metallurgical industry. We may therefore claim that the study of metallurgy is one which gives a man a broad and useful outlook upon things in general. It is true that modern metallurgy becomes more and more specialized and is connected intimately with certain branches of physics. The older metallurgy dealt more with the occurrence of the metals, with their extraction, and with economic questions dealing with their reduction and distribution. I think from that point of view the older metallurgy gave a broader outlook to the student than the more specialized subjects which we have at the present time.

We are very much indebted to Sir Henry Fowler, with his many duties and occupations, for coming to us as President and we feel that we have one here who can sympathize with the young, who can appreciate the scientific investigator, and who can also speak with experience from the practical side. We thank him for his Address. We look forward to a successful period of office, and we are, I am sure, willing to promise him our earnest and sincere support.

Mr. Maurice S. Gibb, C.B.E., Member of Council: I have been associated with Sir Henry Fowler on so many and varied occasions that I feel privileged in being allowed to second the vote of thanks for his Address.

Whenever I have come in contact with him in railway work, in the manufacture of shells, in the manufacture of gun equipments, or in the work of technical institutions, I have been impressed with his wide knowledge and the practical grip he takes of any subject with which he is concerned. I am not surprised, therefore, to hear from him such a delightful and valuable Address as that which he has given us.

As a mere user of metals, I thought that I would be fortified in the duty which I have to perform by being in the President's company as another user, but after listening to his Address I feel that he has left me high and dry. Certainly he has not left the ranks of the users, but he has disclosed a knowledge of metallurgy that should entitle him to be classed amongst the "red hats" of that eminent profession.

I am glad to see that the President has stressed the point that metallurgy is the basis of mechanical engineering, also that he pleads for closer co-operation between the scientist and the practical man—a term which he dislikes.

By a quotation from "Ecclesiasticus" he exhorts us to "observe the opportunity." May I quote from the same book in which that writer of 2000 years ago states when referring to practical men (Chap. 38):—

> "31. All these (*i.e.* practical men) trust to their hands and every one is wise in his work.
> 32. Without these cannot a city be inhabited; and they shall not dwell where they will.
> 34. But they will maintain the state of the world and their desire is in the work of their craft."

This is all perfectly true, even to-day, but when "Ecclesiasticus" states (Chap. 38, verse 24):—

> "The wisdom of a learned man cometh by opportunity of leisure and he that hath little business shall become wise"

we realize how conditions have changed since those times, for our President and other eminent engineers have become wise in their profession, not by opportunity of leisure, but by opportunity of work.

The amount of knowledge that has to be acquired nowadays by those engaged in all technical professions is so vast and so varied that some process of acquiring knowledge in tabloid form is almost a necessity: it is here that technical institutions can be of such service, particularly if they take to heart the advice given by the President to employ simple language when writing on technical subjects.

The President's plea for some better means of translating the investigations and research of the scientist into practical shape is very vital. It is true that more is being done in that direction to-day than ever before. But in these days of financial stringency it is well to avoid putting the whole machine out of balance by doing more research work than industry is able to absorb and turn to practical account.

The great progress in metallurgy during recent years, referred to by the President, has made possible the aeroplane, the motor-car, and other machines, which have caused many alterations in our mode of life.

The President has referred to the usefulness of this Institute. I have referred briefly to the achievements of metallurgists. I think, to be fair, that I must also refer to their deficiencies—or at least to the only deficiency I know. The mathematician has given us tables of areas, &c., and we have tables of the characteristics of steam, air, and water, but, although the art of metallurgy dates back to the Bronze Age, the metallurgist has not yet given us tables of the characteristics of the principal non-ferrous metals in the same way as the mathematician and the physicist have given us their tables.

It is true that some thirty years ago Thurston published in his "Materials of Engineering" some tables of alloys with their physical and mechanical properties, but these are not complete, and in any case are quite out of date.

I hope that this Institute will add further to its usefulness ultimately by so combining the activities of metallurgists that such tables may be available for users in some years to come.

I have much pleasure in seconding the vote of thanks to the President for his able Address, and I wish him a successful and pleasant period of office.

The motion was put and carried with acclamation.

The PRESIDENT: I need scarcely say that I appreciate your vote of thanks very much indeed. Not only has my metallurgical work been of benefit to me in my profession, but is has also been a source of very great happiness. I thank you very much indeed for the patient way in which you have listened to my Address.

COMMUNICATIONS.

The communications of the following authors were presented and discussed: J. Newton Friend; O. F. Hudson and J. McKeown; H. J. Tapsell and A. E. Johnson; R. Seligman and P. Williams; F. Bollenrath; Professor D. Hanson and E. Rodgers; and A. J. Sidery, K. G. Lewis, and H. Sutton. 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 Trocadero Restaurant, Piccadilly Circus, London, W.1, and was presided over by the President. Nearly 300 members and guests were present. A report of the speeches at the dinner was published in the April 1931 issue of the monthly *Journal*.

Thursday, March 10.

On the resumption of the meeting, communications by the following authors were presented and discussed: G. D. Bengough and L. Whitby; M. L. V. Gayler and G. D. Preston; C. F. Elam; W. H. J. Vernon; H. J. Gough and H. L. Cox; and H. O'Neill and H. Greenwood. A paper by Professor P. Saldau and M. Zamotorin was, in the absence of the authors, not discussed. In each case a hearty vote of thanks to the authors was proposed by the President and carried with acclamation.

A general discussion took place on the subject of "The Testing of Castings," an opening paper to which was contributed by Dr. W. Rosenhain, F.Inst.Met., F.R.S., Past-President.

CONCLUDING BUSINESS.

The PRESIDENT proposed and Dr. RICHARD SELIGMAN, Past-President, seconded, the following resolution, which was carried with acclamation.

"That the best thanks of the Institute be and are hereby tendered to the Council of the Institution of Mechanical Engineers for their courtesy in permitting the use of their rooms on the occasion of this meeting."

PRESIDENTIAL ADDRESS.

Delivered by SIR HENRY FOWLER, K.B.E., LL.D., D.Sc., Wh.Ex.,
on March 9, 1932.

It has become a custom, and I think a very wise one, for the presidency of this great Institute to be held successively by a producer, or manufacturer, of non-ferrous metals; by a member engaged in academic pursuits and investigation; and by one who is a user of the metals with which we are concerned.

I naturally feel very honoured to have been selected as President, and as a representative of the latter category. I am interested to note that three of the four previous "user" occupants of this chair have been eminent in our senior service, including as they do our first President. The other President, Sir John Dewrance, is one whose name is known throughout the world as a user of non-ferrous metals and as a manufacturer of engineering articles; his memory must ever be associated with the valuable but unostentatious work and assistance that he has always given to educational and research work. I am very proud to follow him here, as I was when I previously followed him in the presidency of another Institution dealing with engineering.

I represent the users, as exemplified in the manufacture and use of steam engines generally; nevertheless, as a railway mechanical engineer, I have been concerned with many phases of engineering work. Although this is so, and engineering represents my life work, I have always been drawn towards the metallurgical side of my activities. This I feel has been largely due to the interest in the subject which was instilled into me, very early in life, by my old teacher, our esteemed Past-President, Professor T. Turner. I am in this respect only one of many who have benefited by his instruction, and by the great facility that he possesses in being able to make those to whom he speaks interested in his subject.

I was doubly fortunate in my metallurgical education, for my second teacher was Mr. E. L. Rhead, another of our Original Members, who for many years taught metallurgy so successfully at Manchester Technical School (now the Manchester College of Technology).

As you will judge, those were times when the teaching of metallurgy was in its infancy, and it was a subject taught to engineers usually as an adjunct to chemistry. When surveying the facilities which exist now for the teaching of metallurgy and for research in the subject, it is difficult to realize the progress which has been made in this respect. There is no university or college at the present time which has not either a chair of, or classes in, metallurgy.

No engineer can be said to be properly equipped for his work unless he has some knowledge of metallurgy. As has so often been said, an engineer nowadays is required to deal with such a wide range of subjects and problems that his education covers so long a period that the age at which he can start his actual professional career has been and is still becoming much later than was formerly the case. This presents difficulties in many instances, but undoubtedly the broad base on which an engineering training should be built ought to include a course of instruction in metallurgy. This should not be ferrous only, since those non-ferrous metals and their alloys which are becoming of increasing practical engineering importance are developing in usefulness so rapidly that it is only the specialist who can hope to have an intimate knowledge of the properties of them all. One feels that a general knowledge of those most frequently met with and used should be obtained by all engineers; whilst when one begins to specialize, and to build on the broad foundation, if this is in the direction of design, and especially—as is so often the case—if the question of lightness or corrosion has to be considered, accurate knowledge of non-ferrous metals becomes essential.

It has been said that no great advance has ever been made in metallurgical knowledge but a corresponding advance in engineering practice has also taken place. This is undoubtedly true, whether it has been in the perfecting of metals and alloys which we have known and used for years, or in the development of new alloys, such as molybdenum steel, the light alloys, or the ternary alloys of lead. The work of the engineer is facilitated, and in some cases revolutionized, by the discoveries of the metallurgist.

This being so, and being myself an engineer, it is a source of gratification to me that during the past few years there has been a very definite tendency for my colleagues in the engineering profession to recognize that their interests and those of the metallurgists run parallel or even converge. Ever since the birth of the Institute it has counted on its roll a large number of engineers, and it is with the greatest regret that we have to record the recent death of two of the most eminent of these—Sir Charles Parsons and Sir Alfred Yarrow.

It is pleasing to note that the names of several distinguished engineers have lately been added to the list of our members, and that two who have long been connected with the Institute have recently been added to our Council.

I do indeed trust that the interest shown in the work of our Institute by engineers may grow during my period of office. Not only must the Institute derive great and increasing benefit from the activities of our "user" members, but they also must gain, both directly and indirectly —directly by the additional knowledge which they will obtain of the metals that they are called upon to use, and indirectly by their contribution to our knowledge.

The literature of metallurgy in those days of which I have spoken—more than forty years ago—was very meagre in this country, especially so far as non-ferrous metals were concerned. Many of us will remember the illustrations of processes—so crude and so often copied from German publications. One can imagine that the three of our founders (as referred to by my predecessor in his recent article on our Origin and Objects)—the late Mr. W. H. Johnson, the late Sir William White, and Sir Harold Carpenter—may have been especially urged to found the Institute by their appreciation of this lack, for they aimed—as stated in the third of our original rules—" To advance the knowledge of metals and alloys, *e.g.*, by publication of a journal containing both original papers and abstracts of publications relating to these subjects, and in any other way." Dr. Richard Seligman refers in his article to the important position which the *Journal* has achieved during the past twenty-three years. It is not necessary for me to dwell at any length on this matter before such an audience as I am addressing. The *Journal* speaks for itself, supplemented as it now is by our new monthly publication. I feel that of our two thousand odd members, there are very few indeed who do not read some portion, at all events, of the *Journal*. Although I am naturally writing before I have the opportunity of addressing the members personally, past experience teaches me that it will be a very much smaller percentage of our total membership that will hear this address than will read it in the *Journal*. The comparatively small number of members who attend our meetings shows that we have not progressed as one would have liked in the direction of achieving that personal contact between members which is of such value in every way. I do, however, feel that we are happy in the loyalty of some of our friends, for I remember that at the first meeting, in 1908, which I was privileged to attend, papers were read by W. Rosenhain, C. H. Desch, G. D. Bengough, and O. F. Hudson, amongst others. Our Past-President's name was on the list of authors a few months later, and we are so glad to know that he is at this meeting—with all of those I have mentioned, three again being contributors of papers.

Without in any way disparaging the great value of the papers read at our meetings, one would like to direct particular attention to the growth of the abstracts, which first appeared in our second volume, then occupying 41 pages. In the last *Journal* in which they were incorporated they occupied (with their index) 436 pages—truly a prodigious growth. By this alone one can judge, even after allowing for the now closer touch with additional journals, of the increase of information available. It is not too much to say that these abstracts have been found—all over the world—to be an invaluable index of non-ferrous information. It must be a source of the greatest satisfaction to our immediate Past-President to know that during his year of office the monthly *Journal*, the appearance of which, I believe, he has keenly desired for so many years—and which Dr. D. Hanson advocated in 1926—has become an actuality. No one could leave a greater memorial of work accomplished than this monthly *Journal* furnishes. It has, I know well, meant an immense amount of work to Dr. Seligman and to our Secretary and Editor, Mr. Shaw Scott, and one feels that their greatest reward is in the success our new publication has already achieved. In so many ways it is of the greatest use in fulfilling, even more completely than before, the objects which our founders had in view; and already it seems to be extending its scope, as fresh items are being inserted to increase its usefulness. May I make an appeal to members to assist still further in adding to that usefulness by sending to the Editor letters on points of interest of which they may see or hear, and by personal notes that may help to increase our knowledge of one another?

It should be remembered that more than 1,000 periodicals, in about twenty languages, are searched for matter suitable for abstracting for our *Journal*.

The fact that these abstracts are now published monthly, instead of half-yearly, adds very materially to their value to every metallurgist who wishes to keep up to date as regards what is going on in the wide field covered. I heard with regard to one or two of the early numbers of our "*Metallurgical Abstracts*" some complaint of the slight delay in certain cases between the date of publication of articles and the appearance of the corresponding abstracts. I felt, however, that the magnitude of the work had not been fully appreciated. Now—as was stated in the *Journal* for January 1932—it is hoped that, in the case of abstracts from all important sources, they will be published within four to six weeks of their appearing in the original publication.

When one remembers that the number of abstracts which have been published in the *Journal* in the last twelve months is more than 4,000—the work of an enthusiastic band of more than thirty highly qualified abstractors—one can appreciate the work that has been done, and done so smoothly. One feels satisfied that such an undertaking is unique as the work of one Institute.

In a paper I read recently on research, the writer mentions as an essential to anyone about to start a research the necessity (often, alas! neglected) of ascertaining what has previously been done on the subject. With our abstracts at his disposal, no investigator could say that there is difficulty in this respect, at all events so far as concerns work published since the Institute of Metals began its invaluable abstracting service nearly a quarter of a century ago.

It may be well to look for a short time at the practical object of our Institute. I take it that it will be agreed that an ultimate aim—it will be appreciated that I speak as an engineer—is to ascertain and to point out the uses that non-ferrous metals may have for the world generally. It is oftentimes necessary to go a long way back in the investigation of the properties of metals in order to do this. We have to look very closely into the influences of small percentages of other metals and impurities to ascertain how metals and alloys are affected by heat-treatment, ageing, cold-working, and those various processes which alter and affect the properties of the metal being investigated.

One feels that every encouragement must ever be given to fundamental research. Whilst in the United States of America a short time ago, I took advantage of the opportunity to visit a number of research laboratories connected with large manufacturing establishments. I found that in one of these a considerable number of researchers of high scientific ability were employed on problems which they themselves had selected. They worked unrestrainedly at these problems, the results of which, if thought suitable, were published. The work might have no direct connection with the firm's manufactures, although the atmosphere of the laboratory itself might give it a tendency in that direction.

What we are able to do, it should never be forgotten, is very largely due to the fundamental work that has been carried out in purely scientific laboratories, and every assistance should be given to them. Although I fully appreciate the advantage of pure research, and the wonderful and often unexpected results that are frequently revealed, I feel that we as an Institute should always keep in view the ultimate goal to be reached. At the same time, I would remind the so-called practical man that no advance in our knowledge of the properties of metals should ever be looked upon as useless. We may not be able to see any direct application to-day, but such knowledge may be invaluable to some future investigator. It undoubtedly opens up paths, as does the work of the pioneer in any sphere, for those who follow after.

One of the great problems of the day is the "marrying up"—if one may use the term—of research with the practical application of the results obtained. Very considerable attention has recently been called to this in many directions. In 1922, the late Dr. William Maw, in his presidential address to the Institution of Civil Engineers, dealt shortly with this question. He pointed out that during the war a very large amount of research work had been done, and that this was not being used in industry as widely as it might be. I, as a one-time member of the Advisory Committee on Aeronautics, and Chairman of its Light-Alloys Sub-Committee, realized this very fully. As recently as September last, Mr. A. P. M. Fleming gave an address to Section "F" (Economics—Department of Industrial Co-operation) of the British Association on "Bridging the Gap between the Birth of an Idea and its Industrial Applications." Sir Josiah Stamp, in his presidential address to the Institute of Transport in 1929,* also spoke of this when dealing with "Scientific Research in Transport." On p. 16 of a pamphlet published by the British Non-Ferrous Metals Research Association in May 1931,† there are very pertinent remarks on "the interpretation and application of research results." Lord Rutherford, in the Report of the Advisory Council of the Department of Scientific and Industrial Research,‡ says in the conclusion: "Throughout the report we have been emphasizing the need for scientific method in industry. . . . At the same time, we feel that there must be many who with the best will in the world to apply the results of scientific research are in some doubt as to the means to be adopted in their particular case." In *The Engineer* of January 15, 1932, there is a leading article dealing with this report from an engineer's point of view. There are, in fact, many who are urging us to follow the advice of a writer who lived at least 2,000 years ago and said, "Observe the opportunity." §

There is no question that, as I have already stated, our Institute has been and is now placing before its members the fullest information on what is being done throughout the world in our particular sphere. The papers read at our meetings lay before our members, and all interested, fresh knowledge of the metals with which we deal.

I have hesitated considerably before touching on the subject of the application of the knowledge we possess, owing to the matter having been recently dealt with by so many writers. I feel, however,

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* *J. Inst. Transport*, 1929, 2, 1.

† "Ten Years of Research for the Metal Industries, British Non-Ferrous etals Research Association," London: 1931.

‡ *Dept. Sci. Indust. Research, Report for* 1930–31, p. 19

§ *Ecclesiasticus* iv. 20.

that I must say a few words on the subject. In the first place, no one will deny that we have advanced very much in the past few years towards a better understanding between the scientific and the so-called practical man. There is no doubt that the increased facilities for metallurgical education, as well as the growing importance of metallurgy generally, have helped to bring this about. Societies like our own have contributed largely to the progress made in this direction.

Although one does not now hear the complaints one formerly heard of the language (scientific and theoretical) employed by the research man, and of the ignorance of the practical user, there is, I believe, still room for them to get even closer together. What faults there may be are decidedly not all on one side. It is still difficult to place oneself wholly in the position of the "other fellow," even in a case like this. A very interesting paper on "Research Methods" was read by our Vice-President, Dr. H. Moore, at the Oxford Conference of the British Non-Ferrous Metals Research Association in January, 1927,* in which the importance of accurate and concise recording of research methods was emphasized. This is akin to a matter of urgent practical significance—namely, the mode of expression of scientific and technical reports for the use of industry. It has truly been said that we cannot expect an experienced business or practical man with no scientific knowledge to speak scientific language correctly. If he cannot speak it, he probably cannot understand it. I would therefore urge, as has often been done before, that all scientific papers and reports should be written in the very simplest of language. If any highly scientific explanations are required, they should be put in an appendix, where they can be referred to by those properly qualified to appreciate them. On this particular point another excellent paper was presented at the Oxford Conference—on the "Writing of Reports," by Professor C. F. Jenkin. This paper provoked an excellent discussion, to which Mr. N. Garrett Smith made a noteworthy contribution, closing with the words "the value of the paper . . . will rest entirely on how clearly the answer is given to the question 'How can I reap the benefit of the work?'"

But, after all, as I have said, the blame, if blame there be, is not by any means all on one side. One may often feel that the so-called practical man (and how I dislike the term!) is not ready or anxious to "observe the opportunity." Here again it may seem that he "won't see." Especially at times like the present, this may be due to the financial advantages not being sufficiently attractive to him when the situation is considered as a whole. There is no doubt, however, that

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* *Brit. N.-F. Metals Res. Assoc., Bull.* No. **19**, 1927, 10–22.

many of us are intensely conservative when it comes to adopting new ideas, and perhaps nervous of adventure in this respect. It may appear strange in an address to you to turn to an advertisement in a daily newspaper, even if that paper be *The Times*, but what I would say is expressed better than I can possibly do in the issue of that paper of December 11, 1931. In it, "Callisthenes," of Messrs. Selfridge & Co., deals with "The Reaction to a New Idea." I cannot quote it in full, but it will be found not only in the newspaper, but also in the *Bulletin of the British Non-Ferrous Metals Research Association* No. 39, 1931. "Callisthenes" deals with the inertia of the mind, the element of cowardice in shouldering responsibility (by adoption of a new idea), and a feeling sometimes of injured vanity that someone else has thought of something before ourselves.

In addition to these, there are other difficulties. One is the hesitation, probably quite mistaken, to allow the results of research to be applied early to a practical test. One can readily understand that, often when nearing what he hoped to be the conclusion of his work, the scientific investigator may see some better way of approach to the problem, or may have his attention directed to some new method or material. If circumstances allow, he naturally wishes to perfect his work as fully as he can before it is applied practically, although the results so far achieved may lead to something much in advance of what is already being done. In this way time is lost. He may feel, too, that it is not right to publish anything which is not as perfect as it can be made. How true is the French proverb "The better is often the enemy of the good"!

Although one appreciates very fully the great care which is taken in research experiments, one feels that there are cases where the practical results can be properly obtained only in actual commercial use. Not only so, but the time required to test in actual use may be long. This is the reason why I urge that practical tests should be put in hand as early as possible, especially as many engineering articles require years to test out. My friend and old colleague, Mr. H. A. Treadgold, and I were working nearly twenty years on research into the best material for a portion of a locomotive before the results showed that we could approximately double its life. I am hoping to be able shortly to finish a practical experiment which was started in 1912, and which I believe may confirm certain views I hold on a metallurgical point. To take another case which bears on the effect of the introduction of a small quantity of a non-ferrous metal into steel: in 1922 I heard incidentally a suggestion that a small quantity of copper increased the corrosion-resisting properties of steel. I was anxious to try this on the smoke-box and ashpan plates of locomotives. Owing, I take it, to the story I used to hear, when a student, that if a puddler wished to get a fellow-worker into trouble he threw a penny into the puddling furnace, we had difficulty in getting an order placed for the material we required. Finally Sir Robert Hadfield accepted an order for a small cast of what we now call "copper-bearing steel," and we received the necessary plates. Owing, however, to the relatively long life that the ordinary steel gave, it was six or seven years before we could say that we were obtaining better results from the new material.

I feel, therefore, that one of the objects which should always be borne in mind is to get the improvement we think we are able to make put to a practical test as early as possible. If necessary, let it be clearly understood that one hopes something better still may shortly be available.

The above is perhaps somewhat unnecessary as far as we are concerned, for, after all, we and our Institute are probably in a much better position than any other similar body as regards the means that we have to hand for bringing our knowledge before those interested in its application.

I believe that the Research Associations, of which twenty-eight are enumerated in the Report of the Department of Scientific and Industrial Research for 1930–31, are peculiarly British organizations. Although it is less than fifteen years since the inception of the first of these organizations, they have become a prominent feature in many industries. This is nowhere more marked, perhaps, than in the work with which we are associated. Such associations form one of the best means of bringing together those who are directly engaged in industry and those who are conducting research. A glance at the names of the members of the Council of the British Non-Ferrous Metals Research Association will show how catholic it is, with representatives of those interested in non-ferrous metals from every point of view. It is not necessary for me in such a meeting as this to speak of Dr. R. S. Hutton, the Director of the Association, and one who has served so long and so faithfully on our Council and assists us in so many ways. The connection between the Institute and the Association is very close—may it ever remain so—and we have been glad to be of service to it on many occasions, acting as the medium by which the work of the Association, at the appropriate time, is published to the world generally. One can scarcely appreciate the debt the industry is under to the Association for the work it has done since its commencement in January 1920. Not the least valuable of its work has been the opportunity it has given to so many research workers to get into touch with the actual problems existing in the works.

It is with considerable trepidation that I venture for a short time on to the not too clearly defined line which separates non-ferrous from ferrous metals.

In the past year we have been celebrating the Centenary of that remarkable man, Michael Faraday, and Sir Robert Hadfield has made a close investigation into the small box which contained the results of his metallurgical work.* This box, which is only 9 × 5¼ × 5¼ in., contained seventy-nine specimens, of which there were twelve metallic elements alloyed with iron. Of these, seven were so-called "noble metals." The work of Faraday was the beginning of an appreciation of the use of non-ferrous metals for alloying—with such remarkable results—with what some may call the "predominating partner," iron. The use of these metals in this respect is growing, and one of the first thoughts one has when one hears of the commercial production of a metal previously designated as "rare," is what effect it will have when incorporated with iron or steel. Of recent years benefit has accrued from the use in this way not only of nickel, tungsten, and chromium, but also of vanadium and molybdenum, among a host of others.

In concluding, may I make an appeal for the continued interest in the Institute of those to whom we already owe so much for the wonderful progress it has made? I trust also that our more recent members may be encouraged by the example of those who have helped the Institute in past years to carry on the tradition so finely established by our founders.

One appeals, too, for an increase of personal interest from the members of some firms. There are one or two conspicuous examples of firms who have a number of their staff as members of the Institute, but in many cases large firms have only one representative member. As I have already pointed out, the attendance at our meetings and the personal contact that this leads to is one of the greatest benefits which can be derived from societies such as our own.

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* *Trans. Roy. Soc.*, 1931, 230. "A Research on Faraday's Steel and Alloys."

THE THERMAL CONDUCTIVITY OF SOME NON-FERROUS ALLOYS.*

By Professor D. HANSON,† D.Sc., Vice-President, and
C. E. RODGERS,‡ M.Sc., Member.

Synopsis.

This paper describes the results of thermal conductivity tests on a series of aluminium–copper alloys, and also the effects of aluminium, nickel, iron, phosphorus, and arsenic on the thermal conductivity of copper.

This short paper describes the results of some tests on the thermal conductivity of some copper and aluminium alloys. It was originally intended to investigate the whole series of the alloys of aluminium and copper, but difficulties were experienced with the brittle alloys containing from 20 to 70 per cent. of copper, principally owing to the difficulty of machining suitable specimens. The tests have therefore been confined to alloys at each end of the system. Tests have also been made with copper containing small additions of nickel, iron, phosphorus, and arsenic.

A "guard-tube" method was used on the recommendation of Dr. Ezer Griffiths, F.R.S. The test-bar and guard tube were attached to an electrically heated copper block which acted as the source of heat. The opposite ends of the test-bar and the guard tube were soldered into water-jackets, by means of which the flow of heat could be regulated. Independent streams of water from a constant-level tank were passed through these water-jackets, the rate of flow being adjusted to give the same fall of temperature along both the specimen and the guard tube. The object of this arrangement is to prevent loss of heat from the surface of the test-bar, and this was further assisted by filling the intervening space between bar and tube with Silocel, an efficient heat insulator. The guard tube itself was surrounded by asbestos lagging. Iron–Constantan thermo-couples were inserted at appropriate positions in the specimen and the tube, by means of which the fall in temperature could be measured. When the conditions are suitably

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* Manuscript received January 19, 1932. Presented at the Annual General Meeting, London, March 9, 1932.

† Professor of Metallurgy, The University, Birmingham.

‡ Metallurgist, Buncher and Haseler, Ltd., Birmingham.

arranged, all the heat imparted to the test-bar travels along it to the water-jacket, and by measuring the temperature of the ingoing and outgoing water, the actual amount of this heat can be determined. In practice, it was found necessary to insert a small spiral water-jacket between the water-jackets on the specimen and tube, since the temperature of the last two was not always identical when the heat gradient in specimen and guard tube were the same, and a very small transfer of heat would otherwise have occurred between the two water-jackets. The thermal conductivity—that is, the number of calories passing per second through one cm. cube of the metal when there is a difference in temperature of 1° C. between opposite faces—can quite simply be calculated if the dimensions of the specimen, the fall in temperature per unit of length, and the amount of heat transferred are known.

TABLE I.—*Composition of the Test-Bars.*

Bar No.	Copper.	Aluminium.	Iron.	Nickel.	Arsenic.	Phosphorus.
0	nil	remainder				
1	0·18	,,				
2	0·52	,,				
3	1·01	,,				
4	2·60	,,				
5	5·06	,,				
6	7·20	,,				
7	9·50	,,				
8	11·51	,,				
9	15·46	,,				
10	20·08	,,				
11	25·60	,,				
12	30·46	,,				
25	remainder	12·78				
27*a*	,,	8·45				
28	,,	5·10				
30*a*	,,	1·75				
32*a*	,,					0·083
33*a*	,,					0·135
34	,,					0·229
35	,,					0·406
36	,,				0·070	
37	,,				0·144	
38	,,				0·302	
39	,,				0·495	
41	,,			0·78		
42	,,			1·57		
43	,,			2·76		
44	,,			4·90		
45	,,		0·29			
46	,,		0·50			
47	,,		1·07			
48	,,		0·20			

The aluminium used for the above alloys contained 0·21 per cent. of iron and 0·29 per cent. of silicon; the copper was high-grade electrolytic wire-bar, impurities being present only in traces.

TABLE II.—*Thermal Conductivity of Copper–Aluminium Alloys.*

Composition Copper. Per cent.	As Cast.		Annealed for 24 hrs. at 500° C. Cooled in the Furnace.	
	Thermal Conductivity.		Thermal Conductivity.	
	30°–100° C.	60°–270° C.	30°–100° C.	60°–270° C.
nil	0·513	...	...	...
0·18	0·493	0·512	0·497	0·518
1·01	0·433	0·503	0·492	0·511
5·06	0·390	0·451	0·463	0·473
7·20	0·406	0·433	0·453	0·465
11·41	0·363	0·405	0·441	0·446
15·46	0·362	0·375	0·437	0·420
20·08	0·346	...	0·418	0·422
25·6	...	...	0·394	0·405
30·46	...	...	0·388	0·381

TABLE III.—*Thermal Conductivity of Copper Alloys.*

Composition. Per cent.	Thermal Conductivity. 60°–270° C.	Composition. Per cent.	Thermal Conductivity. 60°–270° C.
Aluminium.		*Phosphorus.*	
1·75	0·405	0·083	0·708
5·10	0·256	0·135	0·504
8·45	0·219	0·229	0·398
12·78	0·169	0·406	0·292
Nickel.		*Arsenic.*	
0·78	0·655	0·070	0·695
1·57	0·562	0·144	0·504
2·76	0·425	0·302	0·398
4·90	0·310	0·495	0·292

Composition. Per cent.	Thermal Conductivity. 60°–270° C.	
	Quenched 1000° C.	Quenched 650° C.
Iron.		
0·20	0·702	0·713
0·29	0·640	0·603
0·50	0·505	0·580
1·07	0·342	0·570

Test-bars were cast in iron moulds 7 in. long and $\frac{9}{16}$ in. in diameter; from these bars, specimens 6½ in. long and ½ in. in diameter were machined; thermo-couple holes $\frac{1}{16}$ in. in diameter and $\frac{3}{16}$ in. deep were drilled 12 cm. apart. Similar corresponding holes were drilled in the guard tube, the relative positions to one another and to the heated end of the specimen being fixed by means of the steel template.

Table I gives the composition of the various bars, whilst in Tables II and III are given the results of the conductivity tests and the temperature ranges to which they refer. Details of the heat-treatment applied to the specimens are also given in these tables. Each figure is the mean of about sixteen readings. After the apparatus had attained a steady state, eight sets of readings were taken at intervals of about 5 minutes, and a further eight sets after an interval of an hour or two. As a rule, good agreement was obtained. Occasionally the second set of readings did not agree with the first; this was due to maladjustment of the temperature gradients within the apparatus, and in these instances the experiment was repeated.

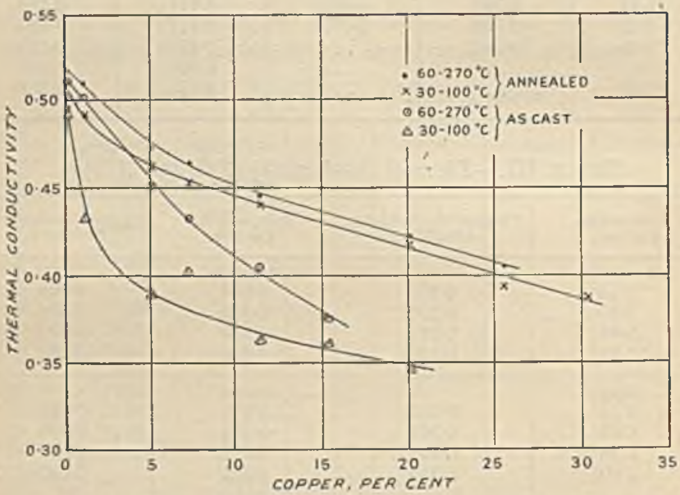

Fig. 1.—Thermal Conductivity of Copper–Aluminium Alloys. The annealed bars were heated for 24 hrs. at 500° C. and cooled in the furnace.

Discussion of Results

The results of the tests on copper–aluminium alloys are summarized in Fig. 1. The lower curves refer to alloys in the "as cast" state, and the upper curves to the same alloys after annealing at 500° C. for 24 hrs. and cooling in the furnace. Bars in the "as cast" state have a much lower conductivity than annealed bars. This is probably due to the retention of a greater amount of copper in solution in the chill castings. On annealing, much copper would no doubt be precipitated during cooling in the furnace. Considerable difficulties were experienced in determining the conductivities of the annealed bars, as it was found that the value increased slowly while the specimens were in the apparatus. At the time the tests were carried out, this result could not be explained. It is now thought to be due to a further precipitation of copper from solution at the testing temperature. Ordinary rates of cooling in a small furnace are now known to be insufficient for the attainment of equilibrium in these alloys, and it is likely that further precipitation would occur at the temperature at which these conductivity tests were carried out. The "as cast" bar containing 7·2 per cent. of copper, tested over the range 30°–100° C., gave an abnormal result. This bar was inadvertently over-heated in the apparatus before the conductivity was measured, and the high figure is probably due to precipitation of copper resulting from this over-heating. The big difference between "as cast" bars tested at 30°–100° C. and the same bars tested at 60°–270° C. is probably also due to precipitation of copper during the course of the test at the higher temperature, which is known to be within the range of temperature at which such precipitation readily occurs. It is clear that the thermal conductivity of copper–aluminium alloys is greatly affected by the heat-treatment to which they are subjected, and further work on this subject is required.

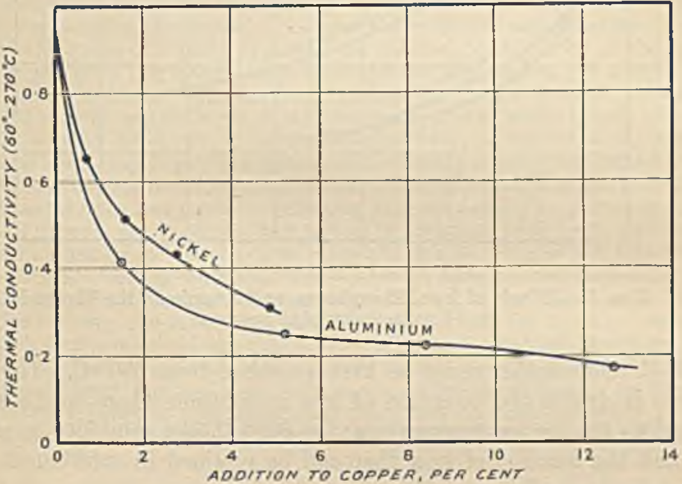

Fig. 2.—Effects of Nickel and Aluminium on the Thermal Conductivity of Copper.

Fig. 2 shows the influence of aluminium and nickel on the thermal conductivity of copper. The specimens were tested in the annealed state, the annealing temperatures being 500° C. in the case of the aluminium alloys and 900° C. in the case of the nickel alloys. Fig. 3 shows the effect of iron, phosphorus, and arsenic on the thermal conductivity of copper. The effect of iron is influenced by the thermal treatment to which the metal is subjected; one series of tests was carried out on samples quenched in water after heating for 1 hr. at 1000° C. and another series on bars quenched from 650° C. The difference is due to the retention of iron in solution when the bars are heated to the higher temperature; at 650° C. the solubility is much less and the amount of iron that can be retained in solution is correspondingly smaller.

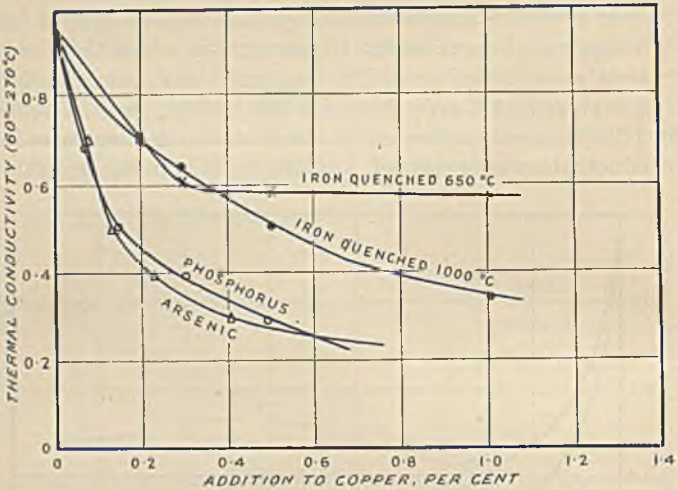

Fig. 3.—Effects of Iron, Phosphorus, and Arsenic on the Thermal Conductivity of Copper.

DISCUSSION.

Dr. W. Rosenhain,* F.Inst.Met., F.R.S. (Past-President): This is not a paper which lends itself to controversial discussion. We have a series of interesting determinations which are useful. Indeed, I have already been able to make use of them for practical purposes since this paper appeared in proof.

There are two points to which I should like to refer. One is that a short time ago Schofield and some of his colleagues at the National Physical Laboratory made an elaborate investigation of the thermal and electrical conductivity of alloys and found that the Lorentz law, by which the electrical and thermal conductivities are proportional to one another, holds for these alloys. That has made me doubt whether it is necessary to worry much about determinations of this kind unless they are required to be of a high degree of accuracy, because, for all practical purposes, if you know the electrical con-

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* London.

ductivity you also know the thermal conductivity—sufficiently, at any rate, for most purposes. That would possibly be a way out with regard to these brittle metals which are so difficult to handle. Of course, one would like to have measurements for both, because, in the case of a law of this kind, one would like to see it confirmed for every alloy and for every condition of heat-treatment. The fact to which Professor Hanson referred when introducing the paper, that in the copper–aluminium alloys the effect of solubility and the effect of what one might call artificial ageing or over-ageing at the higher temperatures make themselves felt in the thermal conductivity, warrants the assumption that it has a similar effect on the electrical conductivity also; the parallelism of the two is probably preserved.

From the practical point of view there is one remark I should like to make —namely, that possibly one is inclined to attach too much importance to the thermal conductivity of the material which is used for many purposes, particularly where heat transfer is concerned, because, if one takes the over-all thermal resistance between the source of heat and the substance which is to be heated on the other side of a plate of metal, the thermal conductivity of the metal itself is probably not a very large factor of that resistance. It is the losses which occur in passing the heat from the heating medium into the metal and out of the metal into the medium which is being heated which largely affect it, so that a small difference of thermal conductivity, as, for instance, in a tea kettle, is not a very important matter, and certainly is not so important as one might be inclined to imagine. For instance, the question of whether the surface of the metal has great power of reflecting heat may easily be more important than its thermal conductivity, and factors of that kind have to be considered. One sometimes hears these points raised by people who do not understand what they are dealing with, and who say that a certain alloy cannot be used because it has only half the thermal conductivity of the pure metal, but in practice not only can it be used, but it sometimes lasts ten times as long. It is foolish to reject its use on that theoretical ground. I think, therefore, that this knowledge is very important and very useful, but one must not jump to conclusions from the fact that there is a considerable difference in thermal conductivity between two materials; the effect on their efficiency in any particular heating devices in which they may be employed will not necessarily be in proportion.

Colonel N. T. BELAIEW,* C.B. (Member): With reference to Fig. 3 and to the solubility of iron quenched at 650° and 1000° C., I should like to know whether the authors mean that, when the alloy with iron is quenched from 1000° C., the iron is in the γ-state, or most of it is in the γ-state, and that when quenched from 650° C. it is in the α-state. What is said in the paper is: "The difference is due to the retention of iron in solution when the bars are heated to the higher temperature." Is it, as it were, the result of an allotropic state of iron?

Dr. RICHARD SELIGMAN,† F.Inst.M. (Past-President): I am very tempted to follow Dr. Rosenhain on to the byways of heat exchange, but I will resist the temptation except so far as to say this, that with modern methods of heat exchange, where those other resistances of which he speaks have been reduced to their utmost limit, the conductivity of the metal begins to play a part, and in commercial practice—unfortunately, I have a great deal of experience in this matter—the lower conductivity of an otherwise suitable alloy may be determinative in causing one to reject it.

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* Paris, France.

† Managing Director, The Aluminium Plant and Vessel Co., Ltd., London.

Dr. A. L. **Norbury** * (Member): Dr. Rosenhain has rather anticipated what I was going to say. I was going to suggest to the authors that it would be very useful if they would also determine the electrical conductivities of the alloys the thermal conductivities of which they have measured. The relationship between the two properties is probably a very simple one in the case of similar alloys such as, for example, the copper-rich solid solutions, and the data so obtained would help to define the relationship more accurately, and would make it possible to calculate the thermal conductivities of many other copper-rich alloys the electrical conductivities of which are well known.

The **President**: Dr. Rosenhain has reminded me that the experiments carried out during the War by the Light Alloys Sub-Committee have been published. I remember that the point which he has raised occurred then, when we were discussing certain small variations in conductivity. One of our friends pointed out that there was plenty of "path" for any heat we were producing to go along, which is a fact we sometimes forget.

Professor **Hanson** (*in reply*): Dr. Rosenhain referred to the possibility of calculating the thermal conductivity from the electrical conductivity. I think that I agree with everything that he said there; it is probably quite possible. One object in actually presenting these results to you was to direct attention to that particular point, or at least to direct attention to the profound effect which small amounts of an added element can have on the thermal conductivity of a pure metal. I had hoped that we should be able to contribute something to the verification of the Lorentz law, but we tried to use the values for electrical conductivities obtained at the National Physical Laboratory for pure samples of alloys, and, using those and comparing them with the thermal conductivities of our own specimens, we did not get sufficiently close agreement to justify any conclusions. We should have published them had the agreement been good, but it is not fair to make a comparison with someone else's experiments. We ought, as Dr. Norbury has suggested, to determine the electrical conductivity of our own specimens. I have the specimens still, and as soon as an opportunity occurs I must do that, and carry it a little further.

I do not think that I can contribute anything to the discussion of the importance of thermal conductivity in relation to the problems of heat transfer. It seems quite impossible to make any general statement on that question, and the different cases must be taken on their merits, and clearly there are other factors.

In reply to Colonel Belaiew, I may say that the iron is in solution in the copper bars that are quenched from 1000° C. I do not know now whether he wants me to say whether it is in the γ-state or in the α-state. In the bars containing more than 0·4 per cent. of iron quenched from 650° C., part of the iron is in the form of separate crystals of iron. If I had the diagram before me, I could tell whether it was in the α- or γ-condition, but without reference to that diagram I cannot do so.

CORRESPONDENCE.

Dr. J. W. **Donaldson** † (Member): I have read this paper with considerable interest in view of the work which I have carried out on the thermal conductivity of metals and alloys, using a somewhat similar apparatus to that

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used by the authors—a type of apparatus which I consider gives very satisfactory results.

In testing copper containing 0·389 per cent. of arsenic I obtained a thermal conductivity value of 0·512 at 100° C., the material being in the rolled, drawn, and annealed condition. Compared with the authors' results this value appears to be rather high, and possibly this was due to the heat-treatment. Williams and Bihlman obtained for copper containing 0·231 per cent. arsenic, when measured over a range 100°–230° C., a value of 0·52 in the hard-drawn state and of 0·50 in the annealed state, which indicates the effect which treatment, thermal or mechanical, has on the heat-conducting property. I have also tested two alloys of copper containing nickel, one containing 30 per cent. nickel and the other Monel metal containing nickel 67, copper 29, iron 3, and manganese 1 per cent. and both showed the influence of nickel in lowering the thermal conductivity of copper in a marked manner, values of 0·075 and 0·069 being obtained at 100° C.

The authors found that bars tested in the "as cast" state usually had a much lower thermal conductivity than annealed bars. I have obtained similar results with cast iron, higher values being obtained after heat-treatment at 550° C., and prolonged heat-treatment was necessary to produce stable conditions. I consider that those changes in cast iron were due to precipitation of free carbon from the combined carbon, and I am therefore in agreement with the authors' suggestion that the changes which they found were due to the precipitation of copper. Considerable difficulties are always experienced in testing cast iron in its "as cast" or partly heat-treated condition, unless stability is obtained, and no doubt similar difficulties will be found with other alloys which react to temperature in a similar manner.

Dr. C. S. SMITH * (Member): I am glad that the authors place such great emphasis on the importance of heat-treatment on thermal conductivity, and particularly on the effects of precipitation which may occur during the actual determination. It is to be regretted that an "instantaneous" determination of thermal conductivity cannot be made, for the considerable range of temperature needed to obtain sufficient flow of heat to be measured accurately frequently renders it impossible to make determinations in the most interesting range.

In connection with the theory of the metallic state, it is of great interest to compare the electrical and thermal conductivities throughout an alloy series, and I would suggest that the value of the paper would be considerably increased if the authors could provide electrical conductivity measurements, either at room temperatures or preferably at the mean temperature of the thermal conductivity determination. There is some evidence to indicate that the Wiedemann–Franz ratio increases considerably with the first small additions of alloying elements and remains fairly constant thereafter. Curves of the Wiedemann–Franz ratio would be very interesting for the series studied by the authors, particularly the α solid solutions of arsenic, phosphorus, iron, nickel, and aluminium in copper, and I hope that the authors will be able to supply these values.

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OBSERVATIONS ON THE PRESSURE OF FLUIDITY OF ANNEALED METALS.*

By HUGH O'NEILL,† M.Met., D.Sc., MEMBER, and HUBERT GREENWOOD,‡ M.Sc.

SYNOPSIS.

The pressure of fluidity at room temperatures has been designated as the stress at which a loaded rigid punch continuously penetrates a block of ductile metal. Examination of such a partly-punched specimen by hardness tests after sectioning, reveals that the most highly strained regions have a (Meyer) ball index value of $n = 2{\cdot}0$ and a resistance to indentation equal to the pressure of fluidity. The value of the latter for a given specimen can therefore be determined by a cone or ball test after cold-working the material to the greatest possible extent, *e.g.* by rolling. Furthermore, it appears that the minimum pressure required to extrude a metal through a die under certain conditions is equal to the pressure of fluidity, and very roughly equal (in most cases) to twice the Brinell number of the annealed metal.

The suggestion is made that the condition of "critical plasticity" observed by Tresca, Kick, Coe, and others, in the course of compression tests, corresponds with the condition of "necking" in tensile tests. "Necking" commences at the point of maximum *load*, and tensile diagrams on Stead's principle indicate that the true *stress* on the section from this point (P_M) to that of fracture, has a linear relation to the decreasing diameter of the test-piece. Extrapolation then gives a stress (P_a) at which theoretically the diameter would be reduced to zero by tensile straining. The available experimental evidence suggests that approximately: $P_a = 3P_M =$ the pressure of fluidity. Tensile, compression, indentation, and punching tests have thus all been related to the pressure of fluidity.

1 mm. ball tests have been made on annealed metal wires, and on the same specimens after heavy cold-rolling. In this way their pressures of fluidity were determined. The minimum stress required to draw the wires at a speed of 0·001 in. per minute through tungsten carbide dies giving 20 per cent. reduction of area was then measured. The pressures of fluidity prove to be about 25 times the magnitude of the minimum drawing stresses for these conditions, but if the wires are placed in a series of increasing values for each of these two tests, then the sequence in each series is the same.

FOR some time past one of the authors has been interested in the plastic flow of ductile metals at high pressures and room temperatures, and certain points of interest have arisen which seem worthy of attention. They refer particularly to the correlation of results obtained from com-

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‡ Metallurgical Dept., The University, Manchester.

pression, extrusion, indentation, and tensile tests, together with a consideration of flow effects in wire-drawing.

COMPRESSION TESTS.

The pioneer work upon the "fluidity" of metals in compression appears to have been performed by Tresca, and he introduced the term "pressure of fluidity" to designate the true stress (on the enlarged area) necessary to induce a certain critical condition of plasticity. Values of Tresca's pressure have been measured by means of simple compression tests on short cylinders of various metals, and some of them are recorded in Table I. Unwin [1] has described the procedure, and quotes results obtained by Tresca and by Kick, whilst in recent years further experiments have been reported by Coe,[2] by Sachs [3] and by others. The mean values for eight metals are given in the last column, and will be referred to here as "compression fluidities."

TABLE I.—*Tresca Pressures of Fluidity in Simple Compression.*

Metal.	Results given by Unwin. Tons/in.^{2}.	Results given by Coe. Tons/in.^{2}.	"Compression Fluidity." Kg./mm.^{2}.
Lead	0·75	1·17 (No. 6)	1·5
Tin	...	1·34 (No. 3)	2·1
Aluminium	10·5	7·0 (No. 13)	14
Zinc	...	9·45 (No. 9)*	15*
Silver	...	17·3 (No. 15) 13·4 (No. 16)	24
Copper	22	20·3 (No. 19)†	33
"Wrought iron" . . .	45 approx.	...	71
"Mild steel" . . .	50	...	79

* Behaved abnormally.

† Cold-drawn metal; this test chosen, as Sachs and others give a concordant value.

These compression results will be discussed later in connection with Bridgman's experiments.

INDENTATION TESTS.

A second method of studying the "fluidity" condition of solid metals is by means of indentation tests. It was suggested in 1922 [4] that when a Brinell ball indenter is loaded sufficiently to give "immersion" in a specimen up to its equator ($d = D$), then the imposition of a slightly higher load will cause continuous penetration of the ball. For *annealed* metals this does not appear to be exactly true, but experiment indicates that when a pressure of perhaps 1·5 times that of the "immersion" stress is applied ($P_u \times 1\cdot5$), then penetration proceeds. The effect was made evident by Ackermann's punch tests,[5] for when a rigid cylindrical punch was loaded against specimens of metal, a stress could be applied under which penetration proceeded comparatively rapidly. This stress Ackermann also called the "pressure of fluidity." After further consideration one of us suggested [6] that a metal which has been cold-worked to its utmost extent (as shown by having a Meyer value of $n = 2{\cdot}0$) should deform plastically under indentation at a stress (P_p) which must be equal to Ackermann's "pressure of fluidity." A ball or cone test made on such a metal yields a mean pressure $\left(P_m = \frac{4L}{\pi d^2}\right)$ hardness value which is independent of the load, and should theoretically represent the flow stress of the specimen. The available experimental results show that this suggestion is true, and the averages of some values obtained by the two methods are given in Table II, and will be referred to as "indentation fluidities."

TABLE II.—"*Indentation Fluidities*" *by Punch Tests and Ball Tests* (*kg./mm.*^{2}).

Metal.	Ackermann's "Pressure of Fluidity."	Ball Test. $P_p = P_m$ value when $n = 2$.	"Indentation Fluidity."
Lead	7·8	8·4	8·1
Tin	13·7	12·5	13
Aluminium . . .	40·2	42	41
Zinc	77·6*	38/61†	69 ±
Copper	109	106	108
Iron (Krupp soft) . .	133‡	131	132

* Behaved abnormally; specimen fissured.
† Published results show two ranges of values.
‡ Riedel's perforation test.

The figures for these ball tests and those of Table V have been obtained after a search of the literature. They represent the average values of many results by different experimenters using sometimes rather different loading ratios and loading times. Soft metals, such as thallium, lead, tin, cadmium, magnesium, and zinc, present curious difficulties in testing, especially in the cold-worked condition, for then age-hardening effects, combined with spontaneous softening, make the procedure somewhat uncertain. By taking the mean of many different results, it is believed that the values reported in this paper are reliable for purposes of general comparison. The flow test on Krupp iron was carried out by Riedel [7] on a plate of the material, a hard steel punch being increasingly loaded until it pushed out a wad of the iron. It appears from Riedel's paper that steady flow of the metal was taking place at the stress indicated in Table II. The test differs from Ackermann's in that the specimen was supported on a base-plate having a hole situated directly under the punch.

The "indentation fluidities" are much higher than the "compression fluidities" given in Table I. In the compression method all the metal which is being impressed by the machine is free to flow laterally, being hindered only by the friction of the plates. Under the punch or ball, however, the locally stressed material is enclosed by the body of the specimen, and is thus confined in practically all directions. For unit deformation in the latter case greater stress will therefore be required, and this point is dealt with later.

EXTRUSION TESTS.

The case of metal flowing under a loaded punch whilst confined and supported by surrounding metal resembles somewhat the state of affairs in an extrusion press. For a comparison of the stresses required in each case to give fluidity, resort may be had to the extrusion and Brinell results of Kurnakow and Schemtschushny.[8] They made a screw press which forced a die with a cylindrical hole against an enclosed cylindrical specimen of the metal, and the stress to give extrusion was measured. More recently, Pearson and Smythe [9] have studied the extrusion of a few metals, but were not concerned with the precise stress corresponding to "fluidity." Their work does, however, give the rate of flow obtained with various applied loads, hence by extrapolation the load required to cause unit rate of extrusion can be found. This will have to be taken as the fluidity load, which when divided by the sectional area of the container (diameter 1·25 in.) should give an approximate value of the pressure of fluidity. Extrapolation of their Figs. 30 and 31 for 17° C. and the "inverted" process gives extrusion loads for lead of 3·80 tons, tin 7·41 tons, and bismuth 13·2 tons. Cadmium was not tested below 106° C., but at that temperature required 11·3 tons for unit rate of flow. Now bismuth at 107° C. gives a value of 5·60 tons, so on a proportional basis a very rough estimate for cadmium at room temperature would be $\frac{11{\cdot}3 \times 13{\cdot}2}{5{\cdot}6} = 27$ tons.

Schischokin [10] has also carried out researches on the extrusion and hardness values of metals, and some of his results, together with those of the other workers, are given in Table III. His die was, however, complex, and the operation corresponded with that of the "direct" process, which is known to require higher pressures. Consequently, in arriving at the mean values for "minimum extrusion pressure," his results have not been included.

TABLE III.—*Minimum Extrusion Pressures* ($kg./mm.^2$).

Metal.	Schischokin "Direct" Process.	Kurnakow and Schemtschushny "Inverted Process."	Pearson and Smythe "Inverted Process."	"Minimum Extrusion Pressure" (mean).	"Indentation Fluidity" (Table II).
Thallium . .	9·9	5·8	...	5·8	4·3*
Lead . . .	10	8·8	4·9	6·9	8·1
Tin . . .	15	10·5	9·5	10	13
Bismuth . .	44	21	17	19	14 †
Cadmium . .	48	31	(35)	31	31 ± ‡
Zinc . . .	...	75	...	75	69 ±

* Nicolardot, 10/10/5 seconds.

† Communicated privately by Dr. J. A. Smythe that the highest Brinell number (10/100/30 seconds) found 24 hrs. after extrusion of a bismuth billet was 13·8. $P_m = 14{\cdot}2$ $kg./mm.^2$.

‡ 42 Molnar; 25 Greenwood; 25 Hargreaves. Mean = 31.

Considering probable differences in the purity of the metals and the geometrical differences of the two pieces of apparatus, there is a reasonable measure of agreement between the two extrusion tests. The mean of the results agrees sufficiently well with the "indentation fluidities" to confirm the view that, within the range considered, the two values refer to the same property of a metal.

So far, then, it has been demonstrated that the stress corresponding with the sinking-punch fluidity is the same as the maximum work-hardness pressure by indentation test, and is approximately equal to the minimum extrusion pressure as determined under the conditions stated.

THE BRINELL HARDNESS AND THE PRESSURE OF FLUIDITY.

In the course of some indentation tests one of the authors noticed that the standard Brinell number of an unstrained metal was roughly about half the mean-pressure ball hardness value of the same material in the completely cold-worked state (*i.e.* having $n = 2{\cdot}0$). Examples are given in Table IV, some of the indentations having been made on the region of the fracture of large tensile test-pieces. It must not be supposed, however, that the effect here observed would apply to metals undergoing a phase change with deformation; *e.g.* austenitic steels will probably harden to more than twice the original Brinell number. Furthermore, for specimens having a very high capacity for work-hardening (*e.g.* $n > 2{\cdot}40$), the P_p value may be about three times the original Brinell hardness.

This approximate doubling of the Brinell number can only be empirical, since the Brinell number itself is a purely arbitrary value and varies with the indenting load and sometimes with the period of

TABLE IV.—*Increase of Hardness by Heavy Cold-Working.*

Specimen.	Brinell Hardness Number in Unstrained Condition.	P_p. Mean Pressure Hardness Number when $n = 2{\cdot}0$. Kg./mm.^{2}.	Ratio.
Aluminium, cold-rolled	23 (10/250/30)	46	2·0
Decarburized mild steel cold-rolled (Mn 0·44%, Si 0·02%)	69 (1/10/120)	142	2·06
	78 (1/30/120)		1·82
Copper, tensile test-piece	49 (1/5/30)	111	2·26
Steel (0·3% C) tensile test-piece	151 (1/30/15)	...	...
	145 (120° cone 30 kg.)	327	2·16

loading. For various metals, however, loading conditions generally fall within certain limits of variation, and the test is becoming standardized in this respect. (For annealed metal, the mean-pressure P_m hardness value is only a little higher numerically than the Brinell number of the same indentation.) It has been shown earlier in this paper that the indentation hardness pressure corresponding with $n = 2{\cdot}0$ represents the pressure of fluidity; consequently it is now implied that the standard Brinell number of the unworked metal is roughly half the numerical value of the pressure of fluidity. This is an independent observation; but it is important to note that Kurnakow and Schemtschushny found that the minimum extrusion pressures were just about double the Brinell number of their specimens.

In Table V the pressures of fluidity previously given are recorded, together with a careful average of published indentation data.

For the range of metals considered here, with the exception of cadmium and zinc, it may be concluded that by doubling the Brinell number one arrives at a figure which is approximately equal to the pressure of fluidity. This may prove to be a useful method of determining roughly the pressure required to extrude an annealed metal at room temperature. If some such relation holds for indentation tests conducted at elevated temperatures, then for an extrusion machine of given maximum available pressure the temperature at which the billets must be worked could be determined in the laboratory.

HARDENING UNDER A SINKING PUNCH.

A study has been made of the distribution of strain-hardening in a metal subjected to impression by a rigid punch at the pressure of fluidity. Thanks to the courtesy of Mr. A. Ackermann, the authors were able to secure the cylindrical piece of copper, 70 mm. in diameter and 70 mm. high, which he had used for the determination of his pressure of fluidity. The face of the cylindrical vertical steel punch was 10 mm.

TABLE V.—*Brinell Hardness Number of Annealed Metal and Pressure of Fluidity.*

Metal.	Brinell Hardness Number. H_B.	Pressure of Fluidity (p). Kg./mm².				Ratio. p/H_B.
		Ball Test.	Punch Test.	Extrusion Test.	Mean Value.	
Thallium . .	2·9	4·3	...	5·8	5·1	1·8
Lead . . .	3·9	8·4	7·8	6·9	7·7	2·0
Tin . . .	6·1	12·5	13·7	10	12	2·0
Bismuth . . .	8·4	14	...	19	17	2·0
Cadmium . .	19·7	25/42	...	31	31	1·6
Aluminium . .	22	42	40	...	41	1·9
Zinc . . .	33	38/61	78	75	38/71	2·2/1·2
Silver . . .	30	72	...	...	72	2·4
Copper . . .	49	106	109	...	108	2·2
Iron (Krupp soft) .	73	131	133	...	132	1·8
Nickel . . .	118	237†	...	...	237	2·0
Wrought iron* .	118	210	...	...	210	1·8
Mild steel* . .	130	255	...	...	255	2·0

* Goerens.

† Nickel seems to show a considerable range of published values. This result is from Kurth and from Schwarz.

in diameter, and with a pressure of 109 kg./mm.² it had commenced to flow readily into the copper. The specimen was afterwards sawn in two, parallel to its vertical axis, and a plane surface carefully prepared which included that axis. The metal was finished with 00 emery paper, and then indented with a sharp polished 120° diamond cone in various places. The load on the cone was 10 kg. maintained for 30 seconds, and mean-pressure hardness values were calculated $\left(H_c = \frac{4L}{\pi d^2}\right)$. By using a cone the hardness results for metal of varying degrees of cold-working remain truly comparable. Their distribution may be seen in Fig. 1. It appears that a stagnant cap of metal forms under the punch, the outer layer of which is hardened-up to the same hardness-stress as the pressure of fluidity. The geometrical form of this cap cannot be stated precisely, but appears to be something between a hemisphere and a cone, and is softer in the interior than on its outer layers. It probably acts like the built-up edge on a lathe tool, and when the pressure of fluidity has been reached, fluid slip takes place over the surface of the cap. The lateral displacement of the body-metal causes hardening throughout the whole cylinder, with the possible exception of an annulus near the top surface shown in section as region A. The punch probably produces tensions in this region, and there may thus be a certain balancing of stresses. The reaction of the base-plate on the lower part of the cylinder is evident in Fig. 1, and the concentration of strain hardening at the centre of the lower face is to be ascribed partly to the existence of a slight projection on that face.

1 mm. ball tests were then made at three places on the sectioned

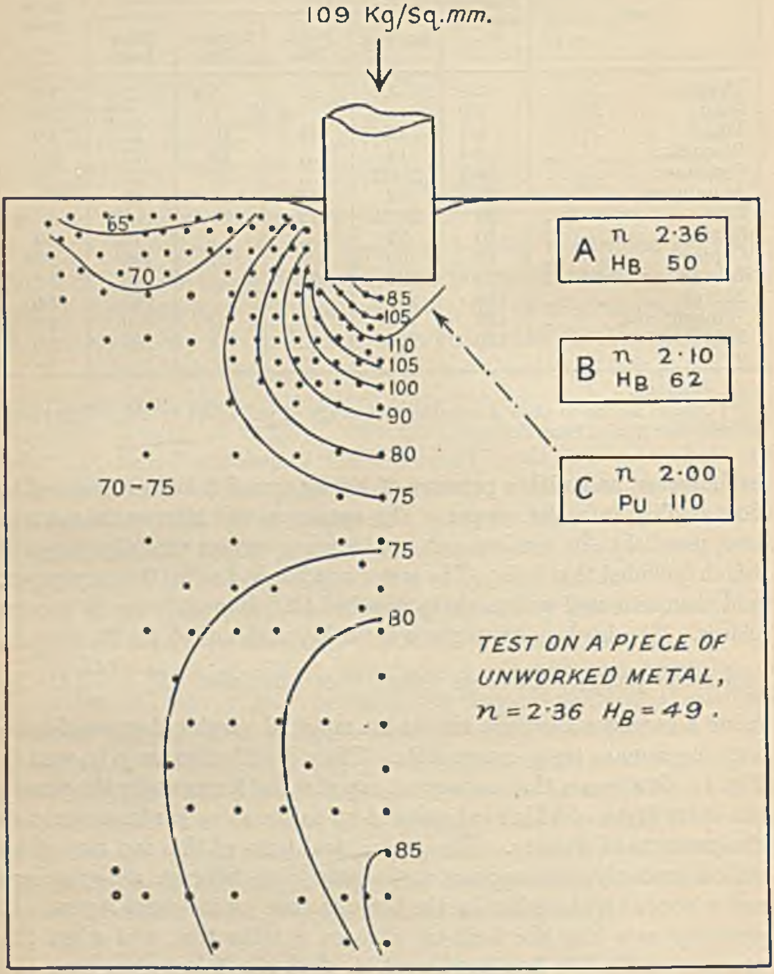

Fig. 1.—Exploration of Punch Test-specimen with 120° Cone to show Distribution of Strain-hardening (Mean-pressure Cone Numbers in kg/mm.²).

specimen, and also on a piece of the unworked metal. They are recorded in Table VI.

This last experiment shows that the copper along the face of the stagnant cap has reached the $n = 2{\cdot}0$ condition and has a resistance to

TABLE VI.—*Ball Tests on Copper Cylinder.*

Location of Indentations.	Meyer n Value.	P_u, i.e. P_m, for $d = D$.	Brinell Hardness Number. H_B.
Region A (Fig. 1) . . .	2·36	75	50 (1/5/120) 54 (1/10/120)
Region B ,, . . .	2·10	74	62 (1/5/120) 63 (1/10/120)
Built-up edge C . . .	2·00	110	107 (1/10/120)
Unworked metal . . .	2·36	75	49 (2/20/120) 51 (2/20/30)

pressure equal to the pressure of fluidity. The body metal immediately adjacent to the cap is similarly work-hardened, and at this critical pressure presumably they both flow over each other, but, for geometrical reasons, the cap maintains its position in front of the punch. The experiment, moreover, furnishes another example of the Brinell number of the unworked metal being about half the numerical value of the pressure of fluidity, whilst it also suggests the further comparison with the simple compression test which follows in the next section.

FURTHER CONSIDERATION OF COMPRESSION TESTS—BRIDGMAN'S EXPERIMENTS.

When a metal cylinder is being subjected to a simple compression test it is generally believed that conical bodies develop within it, having as their bases the flat faces of the specimen. As the stress and deformation increase, the body-metal slips over these cones and is extruded laterally. The condition of "critical plasticity," as Coe calls it, is reached, and the metal then flows more readily under stress. This stress of ready-flow will be smaller in magnitude than that when a punch experiment is made, because of the lateral support of the body of the specimen in the latter case. Assuming a condition of plasticity and various other geometrical effects, Prandtl[11] has suggested that the relation between these two stresses will be given by:

$$\text{Punch-flow stress} = \text{Plain compression-flow stress} \times \left(1 + \frac{\pi}{2}\right)$$

$$= \text{Plain compression-flow stress} \times 2{\cdot}6.$$

Now taking the mean values for pressure of fluidity in Table V as values of punch-flow stress, we may compare them with the Tresca compression stresses given in Table I. The ratio between the two is recorded in Table VII.

Disregarding the values of the ratio for lead and tin—these metals are so soft that variations of temperature and speed of compression are

TABLE VII.—*Tresca's Compression Fluidity and Punch Fluidity.*

Metal.	"Compression Fluidity" (Table I).	Mean Pressure of Fluidity (Table V).	Ratio.
Lead	1·5	7·7	5·1
Tin	2·1	12	5·7
Aluminium	14	41	2·9
Zinc	15	38/71	2·5
Silver	24	72	3·0
Copper	33	108	3·3
"Wrought iron"	71	210	3·0
"Mild steel"	79	255	3·2

liable to influence the results—there is evidence of a constant relation between the fluidity stresses determined by the two tests. It appears that the "pressure of fluidity" is roughly three times the "compression fluidity," a ratio which is somewhat higher than that suggested by Prandtl.

Compression tests in which the metal would receive lateral support during straining suggest the application of hydrostatic pressures. Experiments of such a nature have been carried out by Bridgman [12] in connection with high-pressure gauges. Hollow *thick* cylinders of metal had their ends fixed rigidly within a chamber, and hydraulic pressure was applied against their external surfaces. The metal yields and flows, and the internal diameter of the cylinders decreases. "After flow has once started," Bridgman says, "the relation between internal diameter and true hydrostatic pressure is approximately linear." Eventually a pressure may be applied which causes the cylinder walls to collapse inwards uniformly to zero internal diameter, and this pressure is independent of the initial diameter of the cylinders. In this type of experiment only two metals were tested by Bridgman, but the values of the hydrostatic collapse pressures strongly resemble the pressures of fluidity so far as the furnished description of the metals permits of comparison.

Perhaps a more remarkable experiment of Bridgman's consists of fixing a solid cylindrical specimen of metal into a pressure chamber with its ends passing through stuffing-boxes, but otherwise unsupported. The conditions resemble the reverse of those in the ordinary tensile test, and the results are similar. As the external chamber pressure increases, a stage is reached at which the ductile test-piece "necks" and fractures, the two severed pieces being violently shot out of the chamber through the stuffing-boxes. The stress at which this fracture occurs has a value approximating to the breaking stress in pure tension.

TABLE VIII.—*Pressure of Fluidity and Bridgman's Hydrostatic Collapse Pressures* (*kg./mm.*^{2}).

Bridgman's Hydrostatic Collapse Pressure.		Pressure of Fluidity (Table V).	
"Copper"	about 100	Copper . . .	108
"Bessemer mild steel" . .	,, 200	"Mild steel" . .	255

FLUIDITY AND THE TENSILE TEST.

The production of the phenomenon of "tensile necking" by radial compression suggests a correlative study of the two processes in connection with the fluidity property. When the point of maximum load has been reached in a tensile test-piece, uniform elongation ceases and localized reduction of area proceeds. A perfectly plastic test-piece would show no uniform elongation, but should commence to "neck" as soon as its yield stress had been applied. The point of maximum load is therefore a critical one as regards plastic flow, and Stead [13] has shown that the stress–strain diagram may be plotted in such a way that true stress is directly proportional to plastic strain when once this point has been reached. The linear portion of such a "stress-diameter" ($P - d$) diagram was represented by Stead according to the expression $P = a - bd$, where bd is interpreted as the hardening due to the cold-working of the test-piece during straining. A perfectly plastic material should not work-harden, in which case this term becomes zero and $P = a$, i.e. a is the stress which will draw the material down to zero diameter as true plasticity requires. We therefore believe that a is a measure of the pressure of fluidity of a metal,[6] but we prefer to write it "P_a" to prevent confusion with the term "a" in Meyer's ball test relation.

Stead did not carry out any tests on copper, but for comparison purposes the necessary data can be obtained from a "stress–reduction" diagram published by Körber.[11] This is reproduced in Fig. 2, and consists of a curved section up to the point of maximum load ($P_M = 31$ kg./mm.^{2}), followed by what is apparently a linear portion terminating at the breaking point stress P_B. Körber extrapolates this linear portion to a point P_0, which he finds to be twice the value of P_m, and which should represent the stress to draw a cylinder down to 100 per cent. reduction of area, or zero diameter. Now since Körber's abscissæ are $\left(1 - \frac{d_0^2}{d_1^2}\right)$ and Stead's abscissæ $\left(\frac{d_0}{d_1}\right)$, then for a given percentage reduction of area x, $\left(\frac{d_0}{d_1}\right)$ is given by $\sqrt{1 - \frac{x}{100}}$. Values have been interpolated from Körber's curve, re-calculated, and then plotted in Fig. 2 to give a

Stead diagram for copper. It will be seen that after P_M has been reached this graph is linear, as Stead's principle requires, and may be extrapolated to P_a, giving an a value for this copper of about 90 kg./mm.^{2}. The latter is reasonably near to values of pressure of fluidity previously given, especially as Stead sometimes found that the inclination of his diagrams increased a little in the region of fracture.

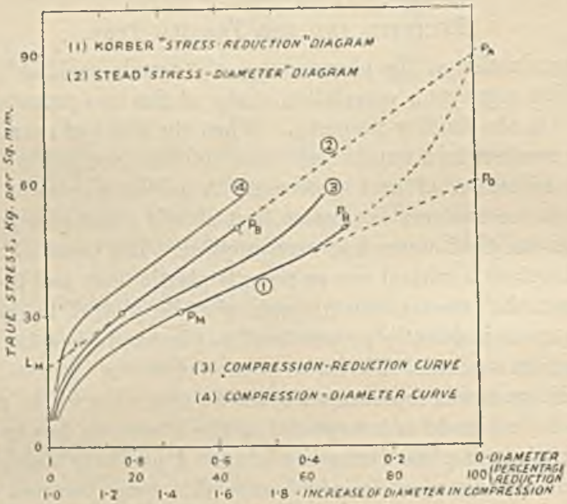

FIG. 2.—Tensile and Compression Tests of Copper.

In Table IX values of a have been recorded as determined for a few metals by the graphical method, using published Körber diagrams as

TABLE IX.—*Stead's Tensile Value "a" and the Pressure of Fluidity.* (*kg./mm.^{2}*).

Metal.	Tensile Tests by:	P_M.	Values of "a."	Pressure of Fluidity (Table V).
Aluminium	Ludwik [15]	14·5	43	41
	Körber and Roland [16]	13·7	40	
Copper	Körber	31	90	108
	Körber and Roland	32·75	94	
Nickel	,, ,, ,,	75·4	222	237

a source of data. The results lead the present authors to believe that Stead's principle is correct, and that a is—as it would be expected to be—a measure of the pressure of fluidity.

Incidentally, extrapolation to the ordinate $d = 1$ gives the value (L_M) of the nominal maximum stress.

If Stead is right, however, Körber's extrapolation to P_0 is unjustified. Considering the abscissæ in the two diagrams, the portions after the point of maximum load cannot *both* be linear. Since it appears that Stead's diagram *is* linear, Körber's must be parabolic. In Fig. 2 the authors have plotted the portion from P_E to P_a of Körber's curve by calculating back from Stead's linear diagram, and it will be noticed that the deviation from the P_M–P_0 line which is nearly always found near the point of fracture in Körber diagrams lies along the parabolic curve. By thus showing that Körber's diagrams are parabolic and not truly linear, there has been removed the inconsistency which would exist by having the rival claimants P_0 and P_a as representatives of the pressure of fluidity.

It seemed likely that a stress-compression diagram could be dealt with along these lines and yield something of interest. In Fig. 2, curve 3 represents results obtained by Sachs [3] during the compression of cylinders of copper having diameters twice their heights. Assuming that the metal remains cylindrical during compression, the mean increase of diameter can be calculated from Sach's abscissæ of percentage reduction of height. This has been done, and the results are plotted in curve 4. The resulting "compression–mean diameter" diagram will be seen to resemble Stead's tensile diagram in form, consisting of an initial curved portion which apparently becomes linear after a stress equal to the P_M value of copper has been passed. Since the value of diameter increases to infinity (corresponding with 100 per cent. reduction of height), it is not known what form the compression–diameter curve will ultimately take. It is also necessary to point out that friction and "barrelling" are always liable to vitiate results obtained by this treatment of compression data, so that exact agreements are unlikely.

It is noteworthy, moreover, that the linear portion of curve (4) begins at the known maximum-load stress (P_M) of copper. This stage must therefore mark the beginning of an inverse "necking" effect in compression, and such a view seems reasonable, since the two processes are comparable, the one being the reverse of the other. Reflection upon Bridgman's experiments supports this view, for his "necked" fracture took place at a compressive stress approximately equal to the tensile maximum stress. The authors are therefore led to believe that the Tresca or "compression fluidity" value corresponds with the condition where "necking" begins. But if so, since it was found that the experimental results suggest a ratio of about 1 : 3 between "compression fluidity" and "pressure of fluidity" (Table VII), in tensile tests a similar ratio between maximum-load stress (P_M) and Stead's "a" value would be expected, since the latter is the pressure of fluidity.

Such a ratio has never yet been demonstrated, but the data for steels contained in Stead's original paper enable an examination of the point to be made.

To obviate calculation, the values of maximum-load stress for twelve specimens have been interpolated from Stead's published diagrams, and are given with the corresponding maximum "*a*" values in Table X.

TABLE X.—*Relation between "Maximum-Load" Stress and Stead's* "a" *for Steels.*

Specimen No.	Carbon Content and Condition.	Maximum-Load Stress × 10^3lb./in.^{2}.	"*a*" × 10^3lb./in.^{2}.	Ratio.
1A	0·16	73·5	209	2·8
2A	0·28	93·5	255	2·7
3A	0·34	97	267	2·8
4A	0·44	106	288	2·7
5A	0·51	108	290	2·7
6A	0·55 normalized	121	320	2·7
1C	same steels heat-treated	81	249	3·1
2C		108	302·5	2·8
3C		110	303	2·8
4C		122	329	2·7
5C		128	327 (?)	2·6
6C		136	348	2·6

The last column gives the ratio between the two, and it is apparent that there is a fairly constant relation involved. It is of the order of 1 : 3, but the figures for steels suggest a value round about 1 : 2·75. The data given in Table IX gives P_a/P_M ratios of 3·0, 2·9, 2·9, 2·9 and 2·9.

It must be remembered that the point of maximum load is not easy to determine, and also that the values in the necking portion of the test appear to be affected somewhat by the speed of straining. Consequently the authors hold the view that $\frac{P_a}{P_M}$ in Stead's tensile diagram has a value of about 3; and further that the "compression fluidity" $= P_M = \frac{P_a}{3}$, approximately.

A check upon these views would now be furnished by taking values of the true tensile stress of different metals at the maximum-load point, multiplying them by 3, and comparing the product with values of pressure of fluidity given in Table V. This has been done in Table XI, in so far as data will permit, and the result may be considered as satisfactory.

Deformation by torsion could doubtless be applied to the study of

TABLE XI.—*Tensile Stress at Maximum-Load and Pressure of Fluidity (kg./mm.^{2}).*

Metal.	" Maximum-Load " Stress (P_M).			Mean P_M × 3.	Mean Pressure of Fluidity (Table V).
	Ludwik.	Körber and others.	Mean.		
Lead . . .	1·95	...	1·95	5·9	6·9
Tin . . .	4·55	...	4·55	13·6	12·1
Cadmium . .	7·75	...	7·75	24	31
Aluminium . .	14·3	13·7	14	42	41
Zinc . . .	11·9	...	11·9	36	38/71
Copper . .	33·5	32·8	33	99	108
Iron (Krupp soft) .	42·5	42·3	42	126	132
Nickel . . .	66·5	75·4	71	213	237

metals along the lines dealt with in this paper, for the torsion specimens also show the " necking " phenomenon. Data are not very plentiful, however, and this section of the subject will not be pursued here.

EFFECT OF COLD-WORK.

It has been shown by Möllendorf and Czochralski,[17] and also by Müller,[18] that if " stress–reduction " diagrams be prepared of increasingly cold-worked copper specimens, then the P_0 value is independent of the initial cold work. This means that the P_a value is also constant, *i.e.*, the *pressure of fluidity of a specimen is independent of its initial condition as regards work-hardening.* Stead showed the same result for a mild steel when he proved that his *a* value did not change if the specimen were strain-hardened before testing. One of the authors [6] has also shown that ball indentation tests can lead to the same conclusion, and it is one which in any case would be expected.

It is therefore obvious that the Brinell number will not serve as a guide to the value of the pressure of fluidity in metals which have been strain-hardened.

THEORETICAL CONSIDERATIONS.

Since the word " fluidity " has been used repeatedly in the foregoing account, it is perhaps natural to inquire whether the metal does in fact become amorphous and liquid when deformed at a stress equal to the " pressure of fluidity." It will be recalled that the well-known studies of Beilby led him to believe that the stress involved during polishing produced an amorphous layer on the surface of the metal being polished.

Recent experiments by G. P. Thomson [19] on electron-diffraction at polished surfaces have shown that this flowed layer is amorphous, or at least extremely micro-crystalline, and to this extent Beilby's views are confirmed. Secondly, there is the Beilby theory—at present unpopular—that amorphous material forms on the glide planes of a crystal during plastic deformation. It has been suggested by J. Johnston [20] that the pressure at suitable points on the glide planes is sufficient to lower the melting point of the metal at those points and cause actual fusion during slipping. This view was reached by Johnston after calculating the pressure supposed to be required to make the metal melt at room temperatures. The expression deduced for this purpose is of the form:

$$p\,(\text{atmospheres}) = 95{\cdot}1\ \text{Q.D.}\log\frac{T}{\theta}$$

where p = flow pressure (pressure of fluidity), Q = heat of fusion per grm., D = density of the metal at room temperatures, T = ordinary melting point (abs.) of the metal, and θ = temperature (abs.) of melting under a flow-pressure p. Table XII gives the flow-pressures calculated by Johnston for a temperature of $\theta = 27°$ C. (300 K.), whilst experimental values of pressure of fluidity taken from Table V are included for purposes of comparison.

TABLE XII.—*Calculated Flow-Pressure to Induce Melting at* 27° C. (*Johnston*).

Metal.	Q.	D.	p.		Pressure of Fluidity (Table V). Kg./mm.².
			Atmospheres.	Kg./mm.².	
Lead . . .	5·4	11·37	1,760	18	8
Tin . . .	14·1	7·29	2,200	23	12
Bismuth . .	12·5	9·80	3,000	31	17
Cadmium . .	13·7	8·64	3,300	34	31
Aluminium . .	42·0*	2·60	5,100	53*	41
Zinc . . .	28·0	7·1	6,900	71	38/71
Silver . . .	23·0	10·5	14,000	145	72
Copper . .	43	8·93	24,000	250	108

* Most tables give $Q = 77$, whence $p = 93$ (authors).

Although the values in the last column are about half those of Johnston's melting pressures, yet the fact that they are both of the same order of magnitude is interesting. A third point of significance is also to be found in the quantitative study of slip made by Russell.[21] He suggested that the evidence permits of the belief that during gliding on the slip planes of an iron crystal the temperature rises to above 1500° C., and thus there is a partial melting of the metal. Finally it is to be noted that in considering the fatigue failure of lead, Haigh and Jones, and Waterhouse,[22] regarded it as not impossible that some kind of melting takes place.

In spite of these observations, the authors are not convinced that the true liquid phase is produced during stressing at the pressure of fluidity. The production of an amorphous or extremely micro-crystalline phase or condition, however, still appears to be a possibility. The authors have discussed Johnston's equation with Dr. J. C. M. Brentano of the Department of Physics, and it does not appear that the reasoning is sound. It is known that under increasing hydrostatic pressures the melting point of metals—except in the case of bismuth—is raised, and thermodynamic reasoning involving the Clausius–Clapeyron equation can legitimately be applied only to conditions of hydrostatic pressure. Johnston, however, proceeds to deal with "unequal pressures," *i.e.* conditions where shear is involved and the compressed metal flows and escapes, and to apply thermodynamic argument to these conditions. Furthermore, it seems doubtful whether the assumption is justified that the latent heat of fusion has a linear relation with the specific volume at increasing pressures. At present, therefore, the authors prefer to envisage the fluidity process as producing metal in a form having a submicroscopic crystal grain-size such that clear diffraction patterns are not produced by X-rays or by electron beams.

WIRE-DRAWING AND PRESSURE OF FLUIDITY.

If it so happens that the stress in metal situated within a wire-drawing die is highly concentrated at a certain annular zone, it seems likely that the condition for flow through the die might be related to the pressure of fluidity of the metal. Experiments were therefore made to determine the minimum drawing load of various annealed wires when reduced 20 per cent. in area by tungsten carbide dies. The movement of the wire through the die was followed by means of an autographic magnifying recorder,[19] and a load was applied to the carefully lubricated wire sufficient to produce a substantial rate of flow. This load was then reduced by successive amounts until drawing only just continued (generally at a speed of about 0·001 in./minute), the final weight being taken as the minimum drawing load under the conditions stated.

The pressure of fluidity could have been readily determined by melting down lengths of wire into small ingots and carrying out some of the tests mentioned earlier in this paper. It was decided, however, to use the 1-mm. ball indentation test, and to determine both the Brinell number of the undrawn wire and the P_p value after it had been heavily cold-rolled into strip.

The Brinell testing of wires 0·071 in. in diameter needs considerable care. The authors found that a simple way of mounting such wires for indentation is to cement them on to a small ebonite plate by embedding in warm plastic shellac, worked with a warm spatula. When the shellac had hardened, the wire and mounting-medium were rubbed down on emery until a longitudinal section of the wire was exposed. This was then indented on an Alfred Herbert small ball machine, the minimum load of which is 5 kg. The authors modified this machine by replacing the transverse member holding the weight-tray and suspension rods by a wooden member bearing suspenders of aluminium strip. This gave a minimum load of 2·8 kg., which was desirable for testing the aluminium wire.

To make sure that the hardness of the supporting mount did not affect the Brinell testing of small wires, preliminary tests were made on a piece of nickel–brass strip about 2·5 mm. in thickness. This was indented with a 10 kg. load when supported on a slab of (*a*) rubber, (*b*) lead, and (*c*) hard steel. The mean diameters of the indentations produced were (*a*) 0·409 m., (*b*) 0·408 m., and (*c*) 0·409 m., respectively, indicating that for this thickness the nature of the support has no serious effect on the Brinell results.

Samples of the same wires were next carefully cold-rolled to a thickness of approximately 0·017 in. in order to cold-work them as much as possible. They were afterwards indented with a hard steel base plate as support and without any special mounting. Meyer analysis was conducted on both the undrawn and the rolled wires, to ensure that the latter had approached to the $n = 2{\cdot}0$ condition. The results are given in Table XIII and plotted in Fig. 3. The minimum drawing load has been converted to a stress by dividing it by the original area of the wire.

Fig. 3.—Wire-Drawing Experiments.

The results indicate that if annealed wires be arranged in the order of their minimum drawing stresses, then this order holds for their pressures of fluidity. To some extent the same may be said regarding their standard Brinell numbers, austenitic materials like Staybrite being excepted. The authors do not conclude, however, that the minimum drawing stress is always directly related to the pressure of fluidity, as a further experiment shows this to be improbable. The minimum drawing load of a specimen of initially cold-drawn aluminium wire

TABLE XIII.—*Tests on Annealed Metal Wires* 0·071 *in. in Diameter.*

Specimen.	Minimum Drawing Load (lb.) for 20% Reduction. Tungsten Carbide Dies of the following Angles:			Mean Drawing Stress (kg./mm.².) $= \frac{\text{Minimum Load}}{\text{Original Area}}$.	1 mm. Ball Tests.	
	2·5°.	6°.	8°.		Brinell Hardness Number.	Pressure of Fluidity after Heavy Cold-Rolling.
Aluminium . .	8	9·5	9	1·56	21†	46
Copper . . .	...	13*	...	2·3	43†	112
Cupro-nickel . .	35	38	37	6·6	81†	160
Brass . . .	39	41	41	7·2	71‡	192
Mild steel . .	45	40	40	7·5	101§	216
18% Nickel-brass .	51	48	49	8·8	90‡	222
30% Nickel-brass .	...	72	71	12·9	134‡	256
Monel metal . .	74	73	71	13·1	134‡	260
0·3% Carbon-steel .	85	82	85	15·1	164§	300 ‖
Staybrite . .	...	103	...	18·5	161§	445

* This load gave a speed of 0·025 in./min. True minimum is probably lower.
† $L/D^2 = 5$. ‡ $L/D^2 = 10$. § $L/D^2 = 30$. ‖ Value probably low, as $n = 2{\cdot}05$.

was determined, and proved to be about 20 lb., as compared with 9 lb. for the annealed metal. For 20 per cent. reduction, therefore, it appears that initial cold-working increases the load required to make the metal flow through the die. The authors believe, however, that in general the pressure of fluidity is independent of cold-working, and consequently the two values cannot always have the same relation.

SUMMARY.

(1) A general examination of the results of different workers obtained by certain deformation tests of metals suggests that there are simple relations between such tests. So far, this examination has not been made under very precise conditions. The metals considered have Brinell hardness numbers not exceeding about 130, whilst the samples of a given metal tested by the various experimenters probably differ in purity. Furthermore, the deformations quoted may not always be strictly comparable, on account of departures from the principle of geometrical similarity.

Allowing for these effects, however, it appears that there is an important fundamental static stress value (p) for a metal, which is aptly called its "pressure of fluidity." This stress is equal to:

(*a*) The stress at which a loaded rigid punch will just steadily penetrate a block of the metal.

(*b*) The resistance to ball or cone indentation offered by the metal when fully cold-worked, *i.e.* when it has a Meyer value of $n = 2$.

(*c*) The true tensile stress which theoretically would reduce a cylindrical tensile specimen down to zero diameter at fracture, *i.e.* $p =$ the tensile value "a," as determined by Stead's method of straining.

(*d*) The mean true compressive stress which under ideal conditions would give 100 per cent. reduction of height of a cylindrical compression specimen.

(*e*) Bridgman's hydrostatic collapse pressure for thick hollow cylinders of the metal.

(*f*) The minimum pressure which just maintains extrusion of the metal through an orifice.

The stress for any one of the above conditions of deformation may therefore be determined by an experiment made under any of the other conditions.

(2) Within the range examined, *i.e.* from 3 to 130 Brinell, the Brinell number of an *annealed* metal is very approximately equal to half its pressure of fluidity. This may be of practical utility in determining the suitability of a metal or alloy for extrusion.

(3) Within the range examined, the true compressive stress corresponding with Tresca's "fluidity" is approximately equal to the true stress at the point of maximum load in the tensile test. Both these stresses appear to be approximately one-third of the value of the pressure of fluidity.

(4) The apparently straight portion of the well-known stress-strain diagram associated with the name of Körber is not truly linear, but forms part of a parabola. Linear extrapolation of this portion is therefore not justified, and leads to the computation of erroneous values of true stress for limiting conditions of strain.

(5) Tests made on annealed wires indicate that their minimum drawing stresses for 20 per cent. reduction of area are of the same order as that of their pressures of fluidity, though of course much smaller numerically.

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DISCUSSION.

Mr. A. S. E. Ackermann: This subject interests me, although I have not had time to do any work on it since 1923. It arose out of my work on the physical properties of clay. I was trying to separate the friction on the side of a pile from the supporting force on the end of a pile, and the obvious thing to do was to take away the sides of the pile. This left a disc at the bottom, and a vertical rod by means of which to apply a load to the disc.

As so often happens in research work, something occurred which I did not expect and was not on the look-out for. When a certain load on the disc is reached, and after it has penetrated into the clay a distance about equal to the diameter of the disc, the latter starts penetrating rapidly and apparently indefinitely. When what I have called the pressure of fluidity is reached, the speed of penetration is about ten times what it is before the critical load is reached. In the case of copper and the other plastic metals, I was not able to determine the increase of speed so readily, but it was obviously much greater when the pressure of fluidity was reached than before that stress was attained. When first this phenomenon occurred, I thought that there must be an air-pocket in the clay, so I packed it again carefully to make sure that there was none. The same thing happened again when the critical stress was reached. The experiments were repeated with great variations in the diameters of the discs and the critical stresses were in each case almost identical.

It seemed to me that what happened in clay would happen in plastic materials, so I tried first with lead and then with aluminium, copper and so on. Before I published anything, O'Neill and Thompson published * a formula which they had evolved by combining that of Meyer with that of

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* *Nature*, 1922, **110**, p. 773.

Brinell, and gave the interpretation of it, namely, that if the load on the 1 cm. diameter ball reached a certain amount, the formula indicated that the ball would penetrate into the metal indefinitely. They had not made this experiment, but by the formula had predicted it, while I had in fact obtained the result experimentally with clay and lead, and my letter appeared in *Nature* * saying that I not only agreed with the formula but had previously obtained the result it indicated—a pleasing result to all of us concerned.

There is one point on the first page of the paper where the authors refer to twice the Brinell number. I can scarcely imagine that Dr. O'Neill has overlooked it, but when the formula which he and Thompson evolved was used, the stresses I found were exactly twice those calculated by the formula, and I searched through my calculations for a dropped 2. Then it occurred to me that the Brinell number is the load divided by the surface of a hemisphere, which is equal to two great circles, whereas I was dividing the load by the area of the disc, *i.e.* one great circle; hence one result being twice the other.

I see that under my name in Table II there is a result given for Krupp soft iron. In my fifth paper † I gave the method of calculating the pressure of fluidity from the ultimate shear and tensile stresses of the material. Given the shear stress and tensile stress of the metal, I was able to calculate the pressure of fluidity, but the result always came out 30 per cent. too much; that is, if 30 per cent. were deducted from the calculated result, the experimental result was obtained very closely. Doing that, I calculate the pressure of fluidity of mild steel to be 221 kg./mm.^{2}. I did not obtain that result experimentally, as we did not get a punch which would stand the necessary load. In the last column in Table II, I take " Indentation fluidity," to be the mean of the results in the other two columns.

Dr. O'Neill: Yes.

With regard to the cap of hard material under the punch shown at p. 54, I placed various coloured beads in layers in the clay immediately under the disc. After the experiment the surrounding clay was carefully excavated and the beads were looked for. They were all underneath the disc, showing that the cap of clay immediately under the disc travels down with it.

Dr. O'Neill (*in reply*): With regard to Mr. Ackermann's figure " 2," his " 2 " is not the same as the one mentioned in the paper. One can determine from the Meyer constants of the metal, the stress at which a Brinell test-ball will become immersed up to its diameter in the specimen, and we thought in 1922, that this stress was such that if it were exceeded the ball would then begin to flow right into the metal. Experiment shows that this is not always so. If the specimen is in the annealed condition, the load to cause immersion to the diameter is not sufficient to cause it to flow right through; a greater stress is needed, one (the pressure of fluidity) which seems to be approximately twice the standard Brinell number. That is where our " 2 " comes in; but Mr. Ackermann was comparing the projected area and the spherical area of an indentation. The ratio between these at immersion is exactly equal to 2, but we were not dealing with that point.

For the punching of the mild steel a hard steel punch was used, and if Mr. Ackermann calculated it to be 221, he appears to be in the right region, because mild steel is somewhat harder than Krupp soft iron.

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* *Nature*, 1923, 111, p. 17.

† *Trans. Soc. Eng.*, 1923.

THE PROPERTIES OF COPPER IN RELATION TO LOW STRESSES.*

THE EFFECT OF COLD-WORK, HEAT-TREATMENT, AND COMPOSITION.

PART I.—TENSILE AND COMPRESSION TESTS UNDER SHORT-TIME LOADING.

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

SYNOPSIS.

Some results of previous research carried out by the British Non-Ferrous Metals Research Association on the subject of locomotive fire-box stays and plates (*J. Inst. Metals*, 1929, **42**) had demonstrated the marked improvement in the elastic properties of copper, containing small amounts of added elements, by work-hardening followed by low-temperature heat-treatment. That work also demonstrated the beneficial addition of small amounts of some foreign elements, such as silver, tin, &c., in raising the temperature limit at which loss of elasticity and softening occurs. The present paper gives the results of further investigation, having in mind the potential wider application of copper with such improved elastic properties and resistance to permanent deformation.

Five types of copper have been studied, namely H.-C. copper; arsenical copper with and without the addition of silver (0·05–0·1 per cent.); copper containing about 0·1 per cent. silver, without arsenic, and copper containing about 1 per cent. tin and about 0·02 per cent. silicon. Rods of these materials with known amounts of cold-work have been subjected to heat-treatment for various times at different temperatures, and tensile and compression tests have been made. Tensile tests were carried out at room temperature and at 300° C., and compression tests were made at 300° C. and also at 350° C.

The tensile tests have shown that all the materials tested possess a certain limit of proportionality due to the applied cold-work, and that this limit of proportionality can be considerably raised by suitable heat-treatment.

The amount of permanent deformation due to stresses not greatly exceeding the limit of proportionality has been measured in tension at ordinary temperatures and in compression at 300° C. and 350° C. The results have shown the superior resistance to deformation brought about by cold-work and suitable heat-treatment, and have also demonstrated the greater resistance to deformation conferred on copper, particularly at elevated temperatures, by the presence of a very small percentage of silver and also by the presence of tin and silicon.

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

INTRODUCTION.

COPPER is used so extensively as a material of construction that it is somewhat surprising to find how little attention has been paid, until recently, to its elastic properties and its resistance to deformation when subjected to comparatively low stresses, and to the possibilities of the control and improvement of these properties by suitable mechanical and thermal treatment and additions of other elements.

It is well known that fully annealed copper shows no proportionality between stress and strain in either tensile or compression tests, and also that when hardened by cold-work it is found to have a measurable limit of proportionality which rises as the amount of cold-work is increased. In some previous work by one of the authors jointly with other investigators,* the marked effect of work-hardening followed by low temperature heat-treatment on the elastic properties has been demonstrated. In the paper in which this work was reported the beneficial influence of the addition of quite small amounts of silver and other constituents in raising the temperature limit at which loss of elasticity and softening occur was also demonstrated.

The recognition of the potential wider application of copper with such improved properties has led to further work, and appears to the authors to justify the present publication.

The work described deals with the effect on the tensile properties, especially the elastic limit (limit of proportionality), and on the resistance to tensile and compressive stresses at moderately elevated temperatures, always in relation to the influence of pre-treatment by cold-working and low-temperature heat-treatment, together with the influence of the composition of the copper.

In this connection, copper containing fractional percentages of arsenic and silver separately and together, and copper containing approximately 1 per cent. tin, together with a fraction of 1 per cent. of silicon, have been examined. Comparison tests have also been made on H.-C. copper.

PREVIOUS WORK.

Reference has already been made to the report of work on this subject previously carried out by the British Non-Ferrous Metals Research Association.† In that paper the knowledge then available was briefly reviewed, and since that date the most notable publication bearing

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* "The Properties of Locomotive Firebox Stays and Plates. The Oxidation of Arsenical Copper and Effects of Small Quantities of Added Elements on the Softening Temperature and Mechanical Properties of Copper," by O. F. Hudson, T. M. Herbert, F. E. Ball, and E. H. Bucknall, *J. Inst. Metals*, 1929, 42, 221–300.

† *Loc. cit.*

directly on the subject of the present investigation has been the paper by Jones, Pfeil, and Griffiths,* in which are given the results of a study of the effects of heat-treatment of cold-worked cupro–nickel containing 2 per cent. nickel (amongst other cupro–nickels). Apart from this paper the authors have been unable to discover in the recently published work (since 1929) dealing with the mechanical properties of copper any results giving limits of proportionality of cold-worked and treated copper. Although no fresh results on determinations of softening temperature are included in the present paper, reference may be made to two recent papers, the one by O. Dahl † and the other by A. Burkhardt.‡ In the latter the notable influence of small additions of silver, silicon, and tin in raising the softening temperature is demonstrated.

MATERIALS USED.

Particulars of the materials used for the present tests are given in Table I. The figures given for the degree of cold-working are percentage reductions of area in the final operation, which was carried out on fully annealed material. The alloys were made from high-grade material, and the composition is given in Table I.

TABLE I.

Material.	Mark.	Diameter of Rod. In.	Degree of Work. Per cent.	Composition.					
				Copper.	Arsenic.	Silver.	Tin.	Silicon.	Oxygen.
H.-C. Copper.	GC	$\frac{7}{8}$	7	99·94	nil	nil	...	...	0·030
Arsenical copper.	X	$\frac{7}{8}$	7	99·52	0·31	...	...	...	0·12
	NA	$\frac{3}{32}$	5	99·57	0·34	...	...	...	0·067
Silver–arsenical copper.	SA	1	5·7	99·55	0·33	0·10	...	...	0·001
	SA	$\frac{7}{8}$	7						
	SA	$1\frac{1}{32}$	5	99·41	0·34	0·095	...	...	0·084
	NS	$\frac{3}{32}$	5	99·56	0·31	0·072	...	...	0·025
Silver–copper.	H	$\frac{7}{8}$	10	99·81	...	0·098	...	...	0·045
Tin–silicon–copper.*	E	$\frac{7}{8}$	10 and 50	98·87	...	...	1·02	0·019	0·002
	" alloy 2 "	$1\frac{1}{32}$	5	99·15	...	...	0·86	0·017	0·002

* Alloys of this kind are widely known as " silicon–bronzes."

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* *J. Inst. Metals*, 1931, **46**, 423–440.

† *Wiss. Veröff. Siemens-Konzern*, 1929, **8**, (2), 157–173; see also *J. Inst. Metals*, 1929, **42**, 307–409.

‡ *Metallwirtschaft*, 1931, **10**, 657–659; for abstract see *J. Inst. Metals*, 1931, **47**, 650.

APPARATUS AND METHODS OF TESTING.

Tensile Tests.

(a) *Extensometers.*—Lamb's roller extensometers were used in both room-temperature tests and elevated-temperature tests for the determination of limit of proportionality, a standard 2-in. gauge instrument * being used for room-temperature tests, and for elevated-temperature tests one designed on the lines of the extensometer in use at the National Physical Laboratory.†

The scale distance used with both extensometers was such that 1 cm. on the scale represented a strain of 1×10^{-4} on the 2-in. gauge length of the specimen. The reading of the scale could be estimated to 0·2 mm., and actual readings were taken to the nearest 0·5 mm., thus giving accurate strain measurements to $0{\cdot}5 \times 10^{-5}$ (*i.e.* $\frac{1}{100,000}$ of an inch on the 2-in. gauge length).

The load could be applied from the commencement of the test with an accuracy of at least 0·01 ton.

(b) *Test-Pieces.*—The test-pieces used, except in a limited number of tests on unturned rod, were made to the dimensions of the standard British Engineering Standards Association test-piece with screwed ends and diameter 0·564 in. on the parallel length, the gauge-length of $4\sqrt{\text{area}}$ being 2 in.

(c) *Determination of Limit of Proportionality.*—The stress on a specimen was raised by steps of 0·2 ton/in.^{2} at definite time intervals of 30 seconds each, the scale-reading corresponding with any given load taken immediately before the next higher load was applied. The effect of time of application of load was not noticeable until well beyond the limit of proportionality. The scale-readings were plotted against corresponding stresses, and a straight line was drawn through the early points. The limit of proportionality was determined as the highest value of the stress at which definite proportionality existed between stress and extension, the extension corresponding with the next higher stress being such that the point on the curve lay to the right of the elastic line by an amount equal to the least count of the extensometer, namely $\frac{1}{2}$ mm. or $0{\cdot}5 \times 10^{-5}$ strain. The limits of proportionality recorded in this paper are consequently those obtained under the specified conditions of testing.

(d) *Determination of Ultimate Tensile Strength, &c.*—When the first definite indication of visible creep showed in a test, the extenso-

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* E. H. Lamb, *Engineering*, 1922, **113**, 684.

† E. G. Batson and G. H. Hyde, "Mechanical Testing." Volume I, p. 367. Second edition. London: 1931.

meter was removed from the specimen and the remainder of the test proceeded with, the rate of pulling being standardized at 0·1 in. per minute. The maximum load, percentage elongation on $4\sqrt{\text{area}}$, and reduction of area at break were determined in the usual manner.

(e) *Heat-Treatment.*—Treatments at 200° C. were carried out in an oil-bath, the remainder in an electric resistance-tube furnace, except those at 650° C. and 750° C., which were carried out in a gas muffle or in an electrically-heated muffle furnace. The temperature of the oil-bath was determined by means of mercury thermometers, and that of the electric furnaces and gas muffle by means of thermocouples. For long time treatments of more than 2 hrs.' duration thermostatic control was used.

(f) *High-Temperature Tests.*—In tests at elevated temperatures the specimen was heated in an electric resistance-tube furnace, supported vertically in the frame of the testing machine, and controlled by hand through a series of adjustable resistances. The temperature of the specimen was measured at the centre of the gauge length by an iron–Constantan thermocouple wired on at that point.

Compression Tests.

The specimens used for these tests were turned up from bars of the different materials which had been previously heat-treated, and their ends were accurately ground parallel. The length of a specimen was approximately 1 in. and diameter 0·798 in., thus giving an area of cross-section of 0·5 in.^2.

Each test consisted in applying a definite load to the specimen and holding that load for 1 hr. The temperature of the specimen was raised to the required value and steadied at that value before the load was applied, and then kept constant within ± 3° C. throughout the time of the test.

The specimens were measured in a constant-temperature room, being kept in this room for at least 24 hrs. before measurements were taken. The length of a specimen was measured at five different points by means of a micrometer reading directly to one ten-thousandth of an inch and by estimation to one hundred-thousandth of an inch.

The furnace used in these tests was an ordinary type of wire-wound electrical resistance-tube furnace, temperature measurements being made by means of a thermocouple and millivoltmeter, and control being effected by hand through variable resistances in series with the furnace circuit.

The importance of correct alignment of the specimen for central loading was recognized, and this was effected in the following manner:

The specimen was compressed between two steel extension pieces having accurately ground ends. One end of each extension piece was centrally located on a compression block of the machine by means of a steel slipper with a central hole fitted to the piece, while the other end was provided with a brass thimble locating the specimen by a hole tapered slightly outwards. Since both compression blocks had spherical seatings, complete alignment of the specimen and the two extension pieces was secured by means of a steel sleeve fitting fairly freely on the latter for about half their length.

RESULTS OF TESTS.

Tensile Tests at Room Temperatures.

The results of the tensile tests are collected in Tables II–VI, in which a few of the results previously published have been included for the sake of completeness, and a selection of stress/strain diagrams is given in Figs. 1 and 2. In discussing the results of the tests under consideration here, it is well to remember that the different materials, although in most cases specially supplied by the makers for this work, were all made and drawn under ordinary works conditions. They were also supplied at different times, and not all by the same maker. They may

TABLE II.—*H.-C. Copper.*

Mark.	Cold-Work. Per cent. (area).	Treatment.	Limit of Proportionality. Tons/in.^{2}.	Ultimate Tensile Strength. Tons/in.^{2}.	Elongation on $4\sqrt{\text{area}}$. Per cent.	Reduction in Area. Per cent.
GC 1	7	As received	1·0	14·7	51	69·5
GC 2	7	2 hrs. at 100° C.	1·8	14·7	51	69·5
GC 3	7	2 hrs. at 200° C.	2·4	14·7	51	69·5
GC 4	7	2 hrs. at 300° C.	2·3	14·5	52	69·5
GC 5	7	2 hrs. at 350° C.	1·9	14·4	55	70·5
GC 6	7	20 hrs. at 100° C.	2·0	14·7	49·5	69·5
GC 7	7	20 hrs. at 200° C.	1·8	14·7	49	69·5

TABLE III.—*Arsenical Copper.*

Mark.	Cold-Work. Per cent. (area).	Treatment.	Limit of Proportionality. Tons/in.^{2}.	Ultimate Tensile Strength. Tons/in.^{2}.	Elongation on $4\sqrt{\text{area}}$. Per cent.	Reduction in Area. Per cent.
X 71 R	7	As received	2·8	15·0	46	52·5
X 73	7	2 hrs. at 200° C.	5·0	14·9	44·5	54·5
X 74	7	20 hrs. at 200° C.	4·6	14·9	35	42
X 75 L	7	100 hrs. at 200° C.	4·4	14·9	42	50
X 72	7	2 hrs. at 300° C.	4·6	14·8	46·5	61·5
X 76	7	2 hrs. at 350° C.	2·3	14·7	49·5	59

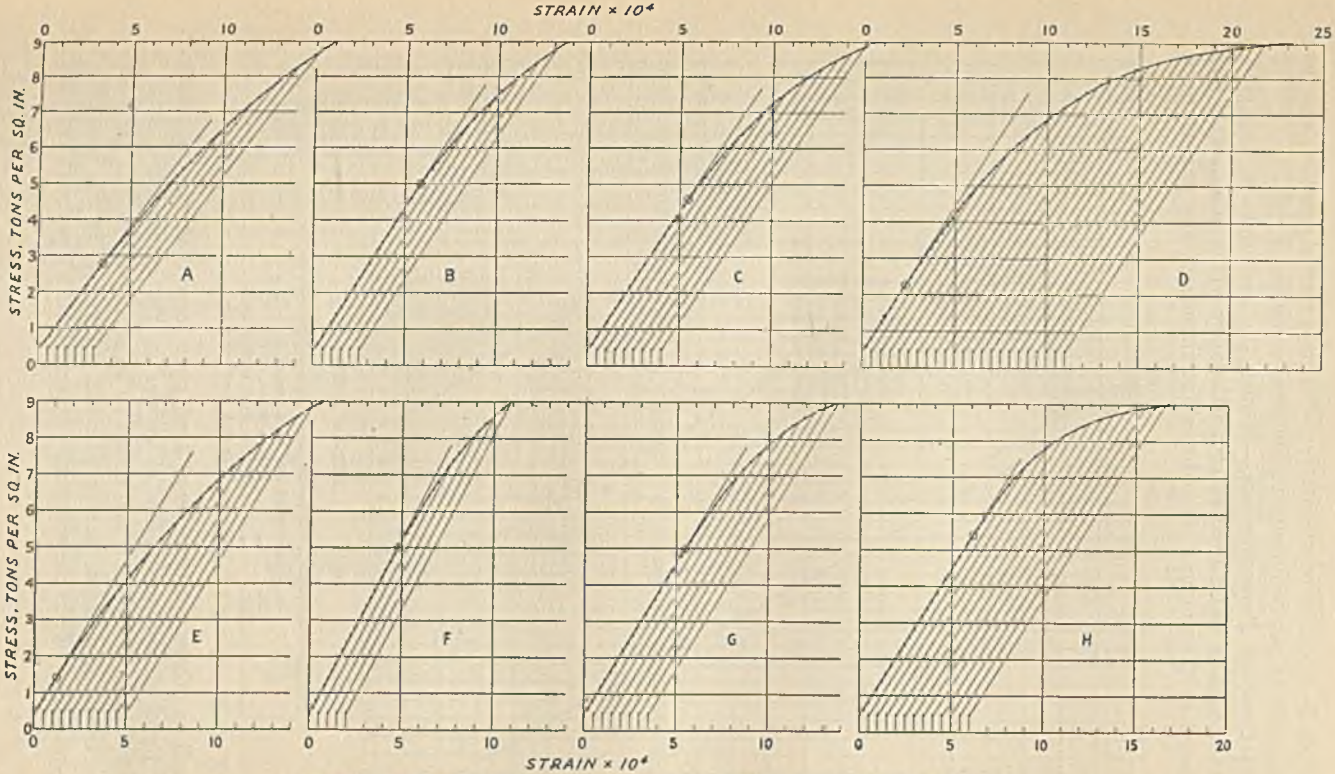

FIG. 1.—Stress/Strain Curves of Arsenical Copper and Silver-Arsenical Copper Specimens.

A. Arsenical Copper, cold-worked (7%), as received.
B. " " " " + 2 hrs. at 200° C.
C. " " " " + 2 hrs. at 300° C.
D. " " " " + 2 hrs. at 350° C

E. Silver-Arsenical Copper, cold-worked (7%), as received.
F. " " " " " + 2 hrs. at 200° C.
G. " " " " " + 2 hrs. at 300° C.
H. " " " " " + 2 hrs. at 350° C.

therefore be taken as representative of normal works' practice, and the results such as can be obtained from good commercial rods.

(a) *Limit of Proportionality.*—Whilst the materials in the cold-drawn condition had a limit of proportionality which in a general way increased as the amount of cold-working increased, the present tests, as well as others not considered here, gave somewhat varying results. The limit of proportionality of copper in the cold-worked state is usually rather ill-defined, and seems to be sensitive to small variations in methods of manufacture or to small differences in the amount of cold-working. Thus the arsenical–copper rod with 7 per cent. reduction

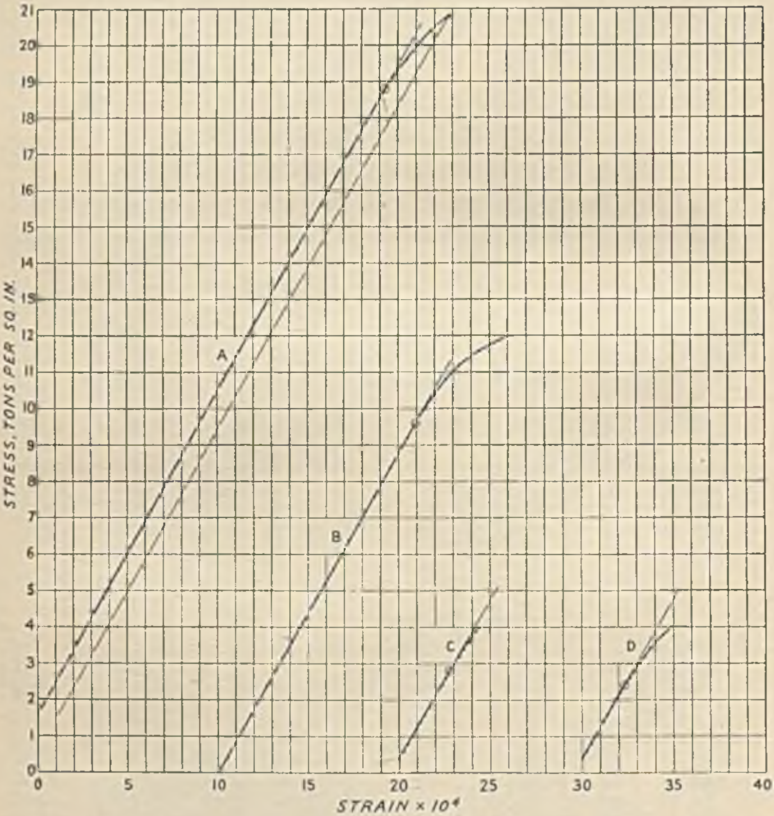

FIG. 2.—Stress/Strain Curves of Tin–Silicon–Copper Specimens.

A. Cold-worked 50% + 9 hrs. at 350° C.
B. „ 10% + 2 hrs. at 350° C.
C. „ 50% + ½ hr. at 650° C.
D. „ 50% + ½ hr. at 750° C.

Table IV.—*Silver–Arsenical Copper.*

Mark.	Cold-Work. Per cent. (area).	Treatment.	Limit of Proportionality. Tons/in.^{2}.	Ultimate Tensile Strength. Tons/in.^{2}.	Elongation on $4\sqrt{\text{area}}$. Per cent.	Reduction in Area. Per cent.
SA	5·7	As received	1·2	15·7	34 *	...
SA	5·7	2 hrs. at 300° C.	5·6	...	...	...
SA	5·7	650 hrs. at 300° C.	6·4	...	...	...
SA 71	7	As received	1·4	16·0	47	61
SA 7	7	As received	1·2	...	...	...
SA 75	7	20 hrs. at 100° C.	2·0	15·9	48	62
SA 73	7	2 hrs. at 200° C.	5·0	16·0	46	62
SA 74	7	20 hrs. at 200° C.	5·4	15·9	47	62
SA 75 L	7	100 hrs. at 200° C.	6·6	15·7	46	62
SA 77	7	2 hrs. at 300° C.	5·0	15·7	51	66
SA 72	7	2 hrs. at 350° C.	5·4	15·8	49	64
SA 2 †	5	As received	2·8	15·9	51 (39)	...
SA 10 †	5	2 hrs. at 300° C.	4·6	16·0	51	...
SA 11 †	5	2 hrs. at 325° C.	4·6	15·8	51 (40)	...
SA 6 †	5	2 hrs. at 350° C.	4·8	15·8	53 (41)	...
SA 8 †	5	2 hrs. at 375° C.	4·8	15·7	53 (40·5)	...
SA 9 †	5	2 hrs. at 400° C.	3·3	15·7	52	...

* The figure for elongation is abnormal, owing to flaw in rod.

† 1$\frac{1}{32}$-in. diameter rods made to specification of 0·3–0·5 per cent. arsenic with silver not less than 0·05 per cent. and to be given a final cold-drawing to give a reduction of approximately 5 per cent. (on area). The tests were made on lengths of unturned rod using ordinary V grips. The figures for elongation given in parentheses refer to percentage elongation on 8 in.

Table V.—*Silver–Copper.*

Mark.	Cold-Work. Per cent. (area).	Treatment.	Limit of Proportionality. Tons/in.^{2}.	Ultimate Tensile Strength. Tons/in.^{2}.	Elongation on $4\sqrt{\text{area}}$. Per cent.	Reduction in Area. Per cent.
* H 1	10	As received	1·2	15·4	51	...
H 11	10	As received	1·2	15·4	52	...
H 13	10	2 hrs. at 200° C.	2·0	15·5	51	...
H 14	10	5 hrs. at 200° C.	2·2	15·7	48	...
H 15	10	20 hrs. at 200° C.	2·8	15·6	45	...
H 12	10	2 hrs. at 300° C.	3·2	15·3	51	...
* H 19	10	2 hrs. at 300° C.	3·6	15·3	51	...
* H 20	10	2 hrs. at 490° C.	nil	14·2	66	...

* Results previously given in *J. Inst. Metals*, 1929, **42**, 295–299, Table XV.

by cold-work gave a limit of proportionality of 2·8 tons/in.^{2} and the silver–arsenical rod, with nominally the same amount of cold-work, one of 1·4 tons/in.^{2}, a difference that is scarcely likely to be due to the presence of 0·05–0·1 per cent. silver or to small variation in the

TABLE VI.—*Tin–Silicon–Copper* (1 *per cent. Tin*, 0·02 *per cent. Silicon*).

Mark.	Cold-Work. Per cent. (area).	Treatment.	Limit of Proportionality. Tons/in.^{2}.	Ultimate Tensile Strength. Tons/in.^{2}.	Elongation on $4\sqrt{\text{area}}$. Per cent.	Reduction in Area. Per cent.
* E 11	10	As received	1·6	18·7	51	...
* E 111	10	2 hrs. at 350° C.	9·6	18·4	55	...
* E 51	50	As received	4·0	26·3	20	...
* E 59	50	2 hrs. at 300° C.	20·4	27·2	26	...
E	50	9 hrs. at 350° C.	18·4	25·8	28	...
E	50	⅓ hr. at 650° C.	2·8	...	...	...
E	50	⅓ hr. at 750° C.	2·4	17·3	65	84
Alloy † No. 2	5	2 hrs. at 325° C.	5·7	18·0	56 (42·5)	...
,,	5	2 hrs. at 350° C.	8·1	17·7	56 (43)	...
,,	5	6 hrs. at 350° C.	8·7	17·9	56 (42·5)	...
,,	5	2 hrs. at 400° C.	6·9	17·5	58 (44·5)	...

* Results previously given in *J. Inst. Metals*, 1929, 42, 296–299, Table XV.

† $1\frac{1}{32}$-in. diameter rod. Tests made on unturned test-pieces held in ordinary V grips. Figures for elongation given in brackets refer to percentage elongation on 8 in.

arsenic content. After heat-treatment, however, the limit of proportionality was much more clearly defined, and the value of the raised limit brought about by the treatment was apparently not dependent on the limit of proportionality in the cold-worked condition.

(1) *H.-C. Copper.*—From the test results given in Table II it will be seen that the limit of proportionality is raised by heat-treatment. For the 2 hrs.' treatments a maximum of 2·4 tons/in.^{2} was obtained after 2 hrs. at 200° C.; the value was only slightly less after treatment at 300° C., but was definitely reduced after the treatment at 350° C. Longer time of heat-treatment (20 hrs.) showed an improvement in the limit of proportionality when the temperature of treatment was 100° C., but a definite fall for treatment at 200° C.

(2) *Arsenical Copper.*—The test results given in Table III refer to one degree of cold-work only—namely, 7 per cent. For treatments for a constant time of 2 hrs. the maximum improvement in limit of proportionality was obtained after the treatment at 200° C. (5 tons/in.^{2}). Treatment at 300° C. gave almost as good a result—namely, 4·6 tons/in.^{2}—but after treatment at 350° C. softening was very noticeable in the fall of the limit of proportionality to 2·3 tons/in.^{2}, a value lower than that given by the cold-worked rod. The effect of time up to 100 hrs. at 200° C. is not very marked, but there is a tendency for a lowering of the limit of

proportionality, the specimen treated for 100 hrs. having a limit of only 4·4 tons/in.^{2}.

In comparison with H.-C. copper, the arsenical copper gave a higher limit of proportionality after treatment, but in both cases the maximum value for 2 hrs.' treatment was obtained after heating at 200° C.

(3) *Silver–Arsenical Copper.*—Considering the results obtained by treatment of rod which had had a final 7 per cent. reduction of area by cold-work (Table IV), it will be seen that for a constant time of 2 hrs. a slightly higher limit of proportionality was on the whole obtained with this alloy than with the plain arsenical copper. It is important to note that 2 hrs.' treatment at 350° C. caused no lowering of the limit, as in the case of arsenical copper, a result in accordance with the known effect of silver in raising the softening temperature of copper. With regard to the effect of time at 200° C., the limit of proportionality showed a decided tendency to increase with time of treatment, indeed, the highest value for the limit of proportionality in this series (6·6 tons/in.^{2}) was obtained after 100 hrs.' treatment at 200° C. It was also found that a long time treatment at 300° C. produced an increase in the value of the limit of proportionality. Silver–arsenical copper which had received 5·7 per cent. reduction in area by a final cold-drawing operation gave a limit of proportionality of 1·2 tons/in.^{2} in the "as received" condition; after 2 hrs.' treatment at 300° C. it gave 5·6 tons/in.^{2}, and after 650 hrs. its limit of proportionality was still further raised to 6·4 tons/in.^{2}.

Included in Table IV is a series of tests carried out on $1\frac{1}{32}$-in.-diameter rod (5 per cent. cold-work) in the unturned condition, the tests, with the exception of the determination of limit of proportionality, being made in accordance with general commercial testing practice. For this series it will be seen that for treatments of 2 hrs.' duration the limit of proportionality was maintained up to 375° C., and showed a decided fall only at 400° C. These results, in comparison with those for plain arsenical copper, further emphasize the strong effect of silver in raising the softening temperature.

It may be noted that material of the 1-in. diameter and $\frac{7}{8}$-in. diameter rods (5·7 and 7 per cent. cold-work) was almost oxygen-free (de-oxidized), whilst the material of $1\frac{1}{32}$-in. rods contained 0·084 per cent. oxygen. The de-oxidized material, on the whole, gave somewhat higher values for limit of proportionality than the material containing oxygen, although having a lower value in the "as received" condition; otherwise the results of the tests were very similar.

(4) *Silver–Copper.*—The limits of proportionality obtained after treatment from the rods of this material used for the present tests (Table V) were lower than those given by the coppers containing arsenic and somewhat higher than those for H.-C. copper. The maximum proportional limit was 3·6 tons/in.² in a rod annealed for 2 hrs. at 300° C. Another sample which had 5 per cent. cold-work gave the following results (not included in Table V) for limit of proportionality: "as received," 1·6 tons/in.², 2 hrs. at 300° C., 3·6 tons/in.², 7 hrs. at 300° C., 4·8 tons/in.². In still another series of tests made on 1-in. rod (unturned test-pieces) which had been heat-treated in the works, after 5 per cent. reduction by cold-work, the material gave a limit of proportionality of 4·7 tons/in.², and this figure was maintained after a further 2 hrs.' treatment at 350° C. The limit of proportionality was, however, lowered to 3·5 tons/in.² by 2 hrs. at 375° C., and to 1·75 tons/in.² by 2 hrs. at 400° C. While, therefore, on the whole the presence of silver to the extent of not more than 0·1 per cent., in the absence of arsenic, does not give quite such high limits of proportionality as silver–arsenical copper or even plain arsenical copper, the limit appears to be retained at the higher temperatures of heat-treatment almost as well as in the case of the silver–arsenical copper, and certainly better than in the case of the plain arsenical copper or that of H.-C. copper.

(5) *Tin–Silicon–Copper.*—From the results given in Table VI it will be seen that this alloy, after suitable heat-treatment following cold-work, gave very much higher values for the limit of proportionality than any one of the other three materials dealt with, limits of proportionality of about 20 tons/in.² being obtained on annealing at 350° C. after 50 per cent. cold-work and of 8–9 tons/in.² on annealing at 350° C. after 5 per cent. cold-work. The softening temperature of this alloy is somewhat higher than that of silver–arsenical copper, and 2 hrs.' treatment at 400° C. resulted only in lowering the limit of proportionality to 6·9 tons/in.². It is of particular interest to note that reheating to temperatures of 650° C. and 750° C. for ½ hr. did not destroy all the elastic properties, the alloy in this condition still giving a limit of proportionality of about 2·5 tons/in.².

(b) *Permanent Deformation* ("*Proof Stresses*").—On the stress/strain diagrams given by specimens of arsenical copper and silver–arsenical copper (7 per cent. cold-work) lines were drawn parallel to the elastic

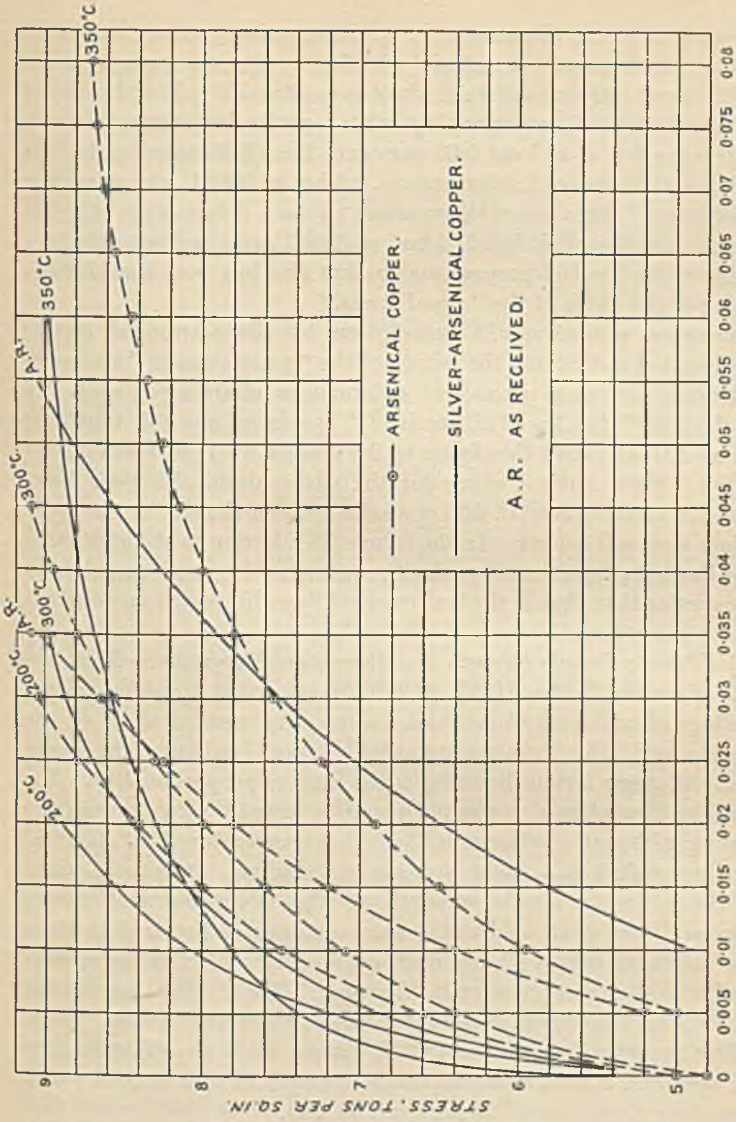

FIG. 3.—Relation between Permanent Deformations and Stresses ("Proof Stresses") immediately above the limit of proportionality for specimens annealed for 2 hrs. at the indicated temperatures or "as received."

line from 0·005, 0·01, 0·015, &c. percentage deformation. The stresses at which these lines cut the stress/strain curve were taken as "proof stresses," corresponding with the given small amounts of deformation. Curves of "proof stress" and corresponding percentage permanent deformation are given in Fig. 3.

Considering first the curves for plain arsenical copper, it will be seen that treatment of the material with 7 per cent. cold-work for 2 hrs. at 200° C. not only raised the limit of proportionality, but also raised the "proof stress" corresponding with a particular deformation up to a deformation of at least 0·03 per cent. (from 8·65 tons/in.^{2} to 9·05 tons/in.^{2} at 0·03 per cent. deformation). 2 hrs. at 300° C. also raised the "proof stress" for a given deformation up to a deformation of 0·024 per cent. On the other hand, 2 hrs. at 350° C. resulted not only in a lowering of the limit of proportionality, but also in a very considerable lowering of the value of the "proof stress."

Somewhat similar results were given by silver–arsenical copper specimens, but in this case the raising of the "proof stresses" was more pronounced, *e.g.* at a permanent deformation of 0·02 per cent. the "proof stress" for the "as received" specimen was 6·5 tons/in.^{2}; 2 hrs. at 200° C. raised this figure to 8·9 tons/in.^{2}. It is worth noting that the "proof stress" curve for the silver–arsenical copper heat-treated for 2 hrs. at 350° C. differs markedly from the similar curve for the plain arsenical copper. In the former, in addition to the high value for the limit of proportionality, the "proof stress" for a given deformation is greater than that in the "as received" condition up to a deformation of 0·052 per cent.

(c) *Ultimate Tensile Strength and Percentage Elongation.*—From the results given in Tables II–VI it will be seen that low-temperature annealings of cold-worked material had no very marked effect on the tensile strength, which was not appreciably lowered so long as the copper did not suffer any serious lowering of the limit of proportionality. The percentage elongation also was not greatly affected by low-temperature annealing, although treatment at the higher temperature (300°–350° C.) generally resulted in a slight increase of ductility. It may be noted that the ultimate tensile strength of the silver–arsenical copper specimens (7 per cent. cold-work) were consistently better than those of the arsenical copper (7 per cent. cold-work), which, in turn, were somewhat better than those for H.-C. copper. The excellent mechanical properties of the tin–silicon–copper are also worth noting. Thus the alloy annealed for ½ hr. at 750° C. gave a limit of proportionality of 2·4 tons/in.^{2}, and an ultimate tensile strength of 17·3 tons/in.^{2}, with a percentage elongation of 65 per cent. on 2 in.

It should be pointed out that the majority of the tests which are considered here have been made with material which has been comparatively lightly cold-worked (5–10 per cent.). Heat-treatment of such material gives a substantial limit of proportionality, combined with a ductility which is not seriously lower than that of the soft, annealed material. With greater amounts of cold-work (cf. results for tin-silicon–copper in Table VI) higher limits of proportionality may be obtained, but at the expense of a seriously lowered percentage elongation, whilst at the same time the more severely cold-worked material is more readily softened.

Tensile Tests at 300° *C.*

The results of these tests are given in Table VII. Comparing the plain arsenical copper with the silver–arsenical copper, both pretreated materials gave a definite limit of proportionality which was higher in the case of the latter than in the former. The ultimate tensile strength was lowered in both materials to about 11 tons/in.^{2}, compared with 15–16 tons/in.^{2} at room temperature. The ultimate tensile strength of the fully softened specimens was about the same as that of the heat-treated specimens.

TABLE VII.—*Tensile Tests at* 300° *C.*

Material.	Cold-Work. Per cent. (area).	Treatment Prior to Test.	Limit of Proportionality. Tons/in.^{2}.	Ultimate Tensile Strength. Tons/in.^{2}.	Elongation on $4\sqrt{\text{area}}$. Per cent.	Reduction in Area. Per cent.
Arsenical Copper.	10	2 hrs. at 300° C.	2·4	11·5	43	54
	50	10 minutes at 650° C.	nil	10·5	58	65
Silver–Arsenical Copper.	5·7	2 hrs. at 350° C.	3·6	11·1	27 *	19 *
	50	10 minutes at 650° C.	nil	11·2	49	50
Tin–Silicon–Copper.	10	2 hrs. at 350° C.	4·4	16·0	39	66
	10	650 hrs. at 300° C.	4·6	15·9	50	81
	50	10 minutes at 650° C.	2·2	15·4	52	61
	50	½ hr. at 650° C.	2·0	15·1	55	79

* The figures for elongation and reduction in area are probably abnormally low in this specimen owing to a defect in the rod.

In the case of the tin–silicon–copper the heat-treated specimens gave a limit of proportionality of about 4·5 tons/in.^{2} and specimens previously annealed at 650° C. a limit of about 2 tons/in.^{2}. It may be noted that the ultimate tensile strength is well maintained at this temperature; thus the specimen heat-treated for 2 hrs. at 350° C. following 10 per cent. cold-work gave 16·0 tons/in.^{2} at 300° C., compared with 18·4 tons/in.^{2} at room temperature. The tests at elevated temperatures also show that the ductility is not seriously lowered at 300° C.

Compression Tests at Elevated Temperatures.

The results of these tests, which were made to determine the amount of permanent deformation at 300° C. and 350° C. due to the application for a definite time of compressive stresses slightly in excess of the limit of proportionality (by tensile tests), are given in Tables VIII–XI, and some of them are expressed graphically in Fig. 4.

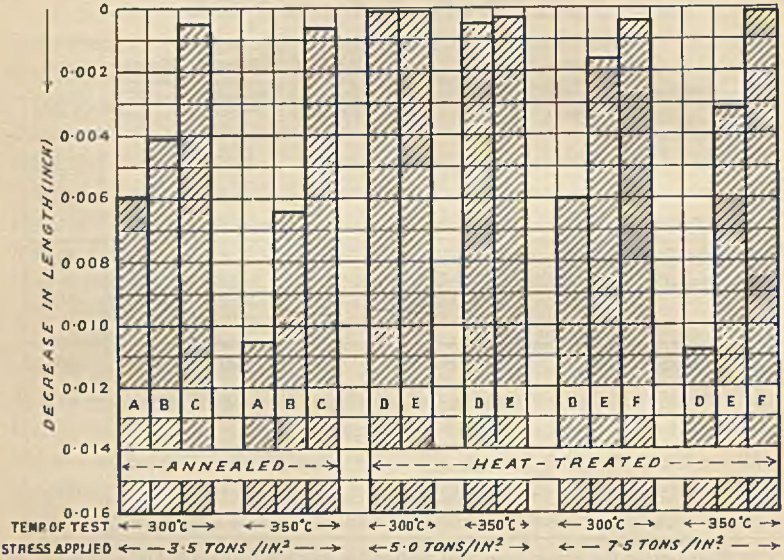

FIG. 4.—Permanent Deformation in Compression at Elevated Temperatures. Stress Applied for 1 hr.

A. Arsenical Copper (see Table VIII). Annealed 10 minutes at 650° C.
B. Silver–Arsenical Copper (see Table IX). Annealed 10 minutes at 650° C.
C. Tin–Silicon–Copper (see Table X). Annealed ½ hr. at 650° C.
D. Arsenical Copper (see Table VIII). Pre-treated for 2 hrs. at 300° C. after 10% cold-work.
E. Silver–Arsenical Copper (see Table IX). Pre-treated for 2 hrs. at 350° C. after 10% cold-work.
F. Tin–Silicon–Copper (see Table X). Pre-treated for 2 hrs. at 350° C. after 10% cold-work.

Compression tests were carried out on three materials only—namely, plain arsenical copper, silver–arsenical copper, and tin-silicon–copper. The arsenical and the silver-arsenical test-pieces were taken from the rods NA and NS respectively of Table I. These rods were also used for the creep tests described in Part II. On referring to Fig. 4, in which comparative results of application of stresses for 1 hr. are expressed graphically, it will be seen that in both the annealed condition and the

TABLE VIII.—*Compression Tests on Arsenical Copper Cold-Worked* 5 *per cent.*

Treatment before Test.	Temperature of Test. °C.	Stress Applied. Tons/in.².	Total Decrease in Length (in.) after each Application of Stress for 1 hr.			
			1st.	2nd.	3rd.	4th.
10 minutes at 650° C.	300	3·5	0·0059	0·0085	0·0099	0·0117
10 minutes at 650° C.	350	3·5	0·0105	0·0128	0·0147	0·0157
2 hrs. at 300° C.	300	5·0	0·0001	0·0001	0·0002	0·0003
2 hrs. at 300° C.	350	5·0	0·0005	0·0004	0·0004	0·0007
2 hrs. at 300° C.	300	7·5	0·0060	...	...	...
2 hrs. at 300° C.	350	7·5	0·0103	...	...	...

TABLE IX.—*Compression Tests on Silver–Arsenical Copper, Cold-Worked* 5 *per cent.*

Treatment before Test.	Temperature of Test. °C.	Stress Applied. Tons/in.².	Total Decrease in Length (in.) after each Application of Stress for 1 hr.			
			1st.	2nd.	3rd.	4th.
10 minutes at 650° C.	300	3·5	0·0041	0·0046	0·0058	0·0070
10 minutes at 650° C.	350	3·5	0·0064	0·0073	0·0085	0·0109
2 hrs. at 350° C.	300	5·0	0·0001	0·002	0·004	0·0003
2 hrs. at 350° C.	350	5·0	0·0003	0·002	0·005	0·0005
2 hrs. at 350° C.	300	7·5	0·0016	...	...	...
2 hrs. at 350° C.	350	7·5	0·0032	...	...	...

TABLE X.—*Compression Tests on Tin–Silicon Copper, Cold-Worked* 10 *per cent. and* 50 *per cent.*

Treatment before Test.	Temperature of Test. °C.	Stress Applied. Tons/in.².	Total Decrease in Length (in.) after each Application of Stress for 1 hr.			
			1st.	2nd.	3rd.	4th.
50 per cent. cold-work						
½ hr. at 650° C.	300	3·5	0·0005	...	...	...
½ hr. at 650° C.	300	5·0	0·0072	...	...	...
½ hr. at 650° C.	350	3·5	0·0006	...	...	...
½ hr. at 650° C.	350	5·0	0·0079	...	...	...
10 minutes at 650° C.	300	3·5	0·0001	0·0002	0·0002	...
10 minutes at 650° C.	350	3·5	nil	nil	nil	0·0001
10 per cent. cold-work						
2 hrs. at 350° C.	300	7·5	0·0004	0·0009	0·0012	0·0016
2 hrs. at 350° C.	350	7·5	0·0001	0·0004	0·0008	0·0010

TABLE XI.—*Permanent Deformation of Different Materials under Compressive stresses at* 300° *C.*

Material.	Condition.	Stress. Tons/in.^{2}.	Deformation 1 in. per 1 in. after Application of Stress for 1 hr.
	5–10 per cent. cold-work.		
Arsenical copper	10 minutes at 650° C.	3·5	0·0059
Silver–arsenical copper	10 minutes at 650° C.	3·5	0·0041
Tin–silicon–copper	$\frac{1}{2}$ hr. at 650° C.	3·5	0·0005
Tin–silicon–copper	$\frac{1}{2}$ hr. at 650° C.	5·0	0·0072
Arsenical copper	2 hrs. at 300° C.	5·0	0·0001
Silver–arsenical–copper	2 hrs. at 350° C.	5·0	0·0001
Arsenical copper	2 hrs. at 300° C.	7·5	0·0060
Silver–arsenical–copper	2 hrs. at 350° C.	7·5	0·0016
Tin–silicon	2 hrs. at 350° C.	7·5	0·0004

heat-treated condition the tin–silicon copper had a much greater resistance to deformation than either the arsenical copper or the silver–arsenical copper, and that the silver–arsenical copper was decidedly superior to the arsenical copper, except at 300° C. under 5 tons/in.^{2}, when both heat-treated materials showed practically no deformation. The superiority of the silver–arsenical copper over the arsenical copper was most marked at the higher temperature of test and under the higher compressive stresses. This is particularly noticeable for the stress of 7·5 tons/in.^{2}.

CONCLUSIONS.

(1) Four different varieties of alloyed copper, together with H.-C. copper, have been tested in tension to determine the effect of re-heating, after known amounts of cold-work, on the limit of proportionality.

(2) In the case of two of the coppers—namely, arsenical copper and silver–arsenical copper—the resistance to small permanent deformation has been investigated.

(3) Three of the materials have been tested at elevated temperatures in both tension and compression; in the tensile tests to determine the limits of proportionality at 300° C., and in the compressions tests to determine the amount of permanent deformation at 300° C., and 350° C. due to applications for 1 hr. of stresses not much beyond the limit of proportionality (in tension).

(4) The limit of proportionality of cold-worked copper, including H.-C. copper, is raised by suitable low-temperature annealing.

(5) Arsenical copper rod (0·3–0·5 per cent. arsenic) which has been cold-worked by a final draw giving a reduction of area of 5–10 per cent., has a small limit of proportionality, generally not more than about

2·5 tons/in.^{2}, and sometimes less. This limit of proportionality is raised by re-heating at low temperatures, *e.g.* for 2 hrs. at 200°–300° C. to a value of about 5 tons/in.^{2}. Treatment, however, for 2 hrs. at 350° C. results in a lowering of the limit of proportionality to less than 2·5 tons/in.^{2}.

(6) Similarly, cold-worked silver–arsenical copper (*i.e.*, copper containing 0·3–0·5 per cent. arsenic and about 0·1 per cent. silver), when re-heated at low temperatures, gives about the same or a slightly higher limit of proportionality. Long-time (100 hrs.') treatment at 200° C. gives a still higher limit of proportionality (6·6 tons/in.^{2}). Treatment for 2 hrs. at 350° C. does not cause a lowering of the limit, as in the case of arsenical copper without silver. Treatment at 100° C. at least for 20 hrs. has only a small effect in raising the limit of proportionality.

(7) The limit of proportionality of similarly cold-worked copper containing 0·05–0·1 per cent. silver, in the absence of arsenic, is raised to above 3·5 tons/in.^{2} by low-temperature treatment, *i.e.* to a smaller extent than silver–arsenical copper or plain arsenical copper, but the raised limit is retained to a definitely higher temperature than in the case of arsenical copper.

(8) Tin–silicon–copper (1 per cent. tin + 0·02 per cent. silicon) cold-worked 5–10 per cent. gives on re-heating to 350° C. (2 hrs. or more) a limit of proportionality of 8–9·5 tons/in.^{2}, and retains a limit of about 7 tons/in.^{2} after treatment at 400° C. This material when heat-treated after 50 per cent. cold-work gives a high limit of proportionality (18–20 tons/in.^{2}), but at the expense of a much reduced percentage elongation. The tin–silicon–copper has also been found to possess a limit of proportionality of the order of 2·5 tons/in.^{2} even after annealing for ½ hr. at 750° C.

(9) The arsenical copper, silver–arsenical copper, and tin–silicon–copper referred to above, which have been treated to give them a raised limit of proportionality, all retain a fair proportion of that limit at 300° C., although it is probable that some of them will be superior to others at higher temperatures.

(10) Tensile tests have shown that silver–arsenical copper in the treated condition has a better resistance at room temperature to permanent deformation under stresses of from 5 to 9 tons/in.^{2} than similarly treated arsenical copper.

(11) Compression tests have shown :—

(*a*) In the annealed (soft) condition the relative resistance to deformation under a compressive stress of 3·5 tons/in.^{2} is in the order arsenical copper (least), silver–arsenical copper, tin–silicon–copper (greatest) at both 300° C. and 350° C.

(*b*) Under a compressive stress of 5 tons/in.^{2} applied for 1 hr. arsenical copper and silver–arsenical copper in the treated condition have the same resistance to deformation at 300° C. (0·01 per cent.). At 350° C. the deformations are 0·05 per cent. and 0·03 per cent. respectively.

(*c*) Under a compressive stress of 7·5 tons/in.^{2} the relative resistances to deformation of the treated materials are in the order arsenical (least), silver–arsenical, tin–silicon–copper (greatest) at both 300° and 350° C., the silver–arsenical copper being greatly superior to arsenical copper.

(12) The marked superiority of the properties which have been shown to be readily achieved by pre-treatment should warrant the attention of engineers and other users of copper where resistance to deformation under low stresses is of importance, as it is in so many applications.

The choice of the alloy will no doubt largely depend on economic and manufacturing questions, but the use of the low silver alloys may in many cases be preferred, despite the high cost of silver, in view of the persistence with which the silver content is retained throughout even large-scale melting operations.

Acknowledgments.

The authors desire to express their thanks to the Council of the British Non-Ferrous Metals Research Association for permission to publish this paper, and to the Director, Dr. R. S. Hutton, for his advice and encouragement in the work; to Messrs. Thos. Bolton and Sons, Ltd., and I.C.I. Metals, Ltd., for supply of material; to Professor D. Hanson, D.Sc., for the facilities placed at the authors' disposal for the work carried out in the Metallurgy Department of the University of Birmingham, and to Professor E. W. Burstall, for facilities for carrying out accurate measurements of compression test-pieces in the Engineering Department of the University of Birmingham. The authors' thanks are also due to Mr. H. J. W. Hipkins, B.Sc., for assistance in some of the mechanical testing, and to Mr. H. C. S. Read, A.R.C.S., B.Sc., for carrying out the chemical analyses.

THE PROPERTIES OF COPPER IN RELATION TO LOW STRESSES.*

THE EFFECT OF COLD-WORK, HEAT-TREATMENT, AND COMPOSITION.

PART II.—CREEP TESTS AT 300° C. AND 350° C. OF ARSENICAL COPPER AND SILVER-ARSENICAL COPPER.

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SYNOPSIS.

The paper deals with the results of creep tests on two copper alloys, the first containing 0·34 per cent. arsenic, and the second 0·31 per cent. arsenic together with 0·072 per cent. silver. Both alloys were tested in the soft condition, and also in the condition arising from 5 per cent. cold-work followed by heat-treatment at 300° C. and 350° C. respectively. It is shown that improvement in resistance to creep at 300° C. and 350° C. is effected by the special pre-treatment of the alloys, and that the alloys containing 0·072 per cent. silver aro superior to the silver-free alloys.

INTRODUCTION.

IN Part I of the paper ‡ the results of tests on four copper alloys to determine their resistance to tensile and compressive stresses, applied for a comparatively short time at moderate temperatures, are discussed in relation to the composition and pre-treatment of the alloys.

Part II deals with an investigation carried out on samples of two alloys of the type referred to in Part I, *viz.*, arsenical copper and silver-arsenical copper, soft and also cold-worked followed by moderate temperature heat-treatment, in order to determine their relative resistance to creep at 300° C. and 350° C. under prolonged loading conditions.

The work described herein was carried out at the National Physical Laboratory, at the request of the British Non-Ferrous Metals Research Association, under the authority of the Committee of the Department

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‡ Hudson and McKeown, *J.*, this volume, p. 69.

of Scientific and Industrial Research appointed to direct researches on the behaviour of materials at high temperatures.

PARTICULARS OF MATERIALS EXAMINED.

The materials used in the tests were supplied by the British Non-Ferrous Metals Research Association in the condition stated in Table I, which contains particulars of the sizes and compositions of the materials.

TABLE I.—*Particulars of Materials Tested.*

Material.	Mark.	Diameter of Bar. In.	Degree of Cold-Work. Per cent.	Heat-Treatment.	Composition.%
Arsenical copper, soft	I	$\frac{31}{32}$	nil	10 minutes at 650° C.	Arsenic 0·34 Oxygen 0·067
Arsenical copper, H.T.	II	$\frac{31}{32}$	5	2 hrs. at 300° C.	
Silver–arsenical copper, soft	III	$\frac{31}{32}$	nil	10 minutes at 650° C.	Silver 0·072 Arsenic 0·31 Oxygen 0·025
Silver–arsenical copper, H.T.	IV	$\frac{31}{32}$	5	2 hrs. at 350° C.	

CREEP TESTS.

The object of the tests was to determine the relative rates of creep of the four materials at temperatures of 300° C. and 350° C., and under prolonged stresses of the order of a few tons/in.^{2}. The temperatures of the tests are rather higher than might usually be encountered in service, but were chosen as being suitable for the purpose of indicating to what extent superiority in creep resistance, due to composition or pre-treatment or both, was retained at relatively high temperatures such as were adopted for the heat-treatments of the alloys which had received 5 per cent. cold-work.

Creep tests were carried out in testing machines which have been previously described,* and in which creep extension could be measured to 0·0001 in. on a 2-in. gauge length. The test-pieces used were approximately 0·564 in. in diameter.

Stresses ranging between 5 and 2 tons/in.^{2} were applied to specimens maintained within about ± 2° C. of the mean test temperature. From the strain–duration (creep) curves obtained from the tests the minimum rates of creep were determined, and the comparative resistance to creep of the four materials has been judged by the trend of the curves showing the relations between stress and log minimum rate of creep.

Table II summarizes the results of the creep tests.

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* *Dept. Sci. Indust. Research. Engineering Research Special Report* No. **1**, 1927. (London : H.M. Stationery Office.)

TABLE II.

Material.	Stress Applied. Tons/in.^{2}.	Approximate Initial Strain (including Elastic Strain). In. per in.	Approximate Minimum Rate of Strain. In. per in. per day.	Duration of Test. B = Broken. U = Unbroken Days.	Final Strain. Per cent.
		Temperature 300° C.			
Arsenical copper, soft (Marked 1)	5	0·031	0·0128	2B	8
	4	0·019	0·00238	7B	7
	3	0·007	0·00066	12U	1·7
	2	0·001	<0·000105	20U	0·4
Arsenical copper, heat-treated (Marked 2)	5	0·0019	0·00206	4B	2
	4	0·0016	0·00056	12B	2·5
	3	0·0006	0·00014	49B	0·5
Silver–arsenical copper, soft (Marked 3)	5	0·036	0·0078	3B	6·5
	4	0·0214	0·00139	12B	...
	3	0·0142	0·00026	40U	3·0
	2	0·0016	<0·000017	21U	0·37
Silver–arsenical copper, heat-treated (Marked 4)	5	0·0009	0·00037	7·5B	1·5
	4	0·0007	0·000091	26B	0·5
	3	0·0006	0·000020	42U	0·3
		Temperature 350° C.			
Arsenical copper, soft (Marked 1)	5	0·031	0·086	3½ hrs. B.	7·5
	4	0·017	Doubtful	<22 hrs. B.	12
	3	0·011	0·0045	3–4 B.	...
	2	0·001	0·00158	6B	2
Arsenical copper, heat-treated (Marked 2)	5	0·002	0·020	<1B	0·5
	4	0·001	0·0081	1B	0·5
	3	0·001	...	4–6B	2
	2	<0·001	0·00041	19U	1·3
Silver–arsenical copper, soft (Marked 3)	5	0·0345	0·138	5 hrs. B.	7
	4	0·0125	0·029	<22 hrs. B.	9
	3	0·006	0·0045	6B	17
	2	0·001	0·00036	23U	1·15
Silver–arsenical copper heat-treated (Marked 4)	5	...	...	About 1B.	...
	4	0·0038	0·0038	1B	4
	3	0·0025	0·00046	13–14B	...
	2	0·001	<0·00013	15U	0·4

The initial strains on loading (see col. 3, Table II) show that the soft alloys deform initially much more than the pre-treated alloys, and for that reason it appears very probable that the latter alloys possess higher limits of proportionality and higher " proof stresses " than the former at the test temperatures. The presence of silver in some of the samples does not appear to have a very marked effect on the initial deformation under tensile load (2–5 tons/in.^{2}), except that a reduction in initial deformation at 300° C. seems to be brought about by the presence of silver in the pre-treated alloy.

The results obtained for the initial strains on loading in general support the evidence obtained from the tensile and compression tests (3·5 to 5 tons/in.^{2}) on these alloys as quoted in the conclusions given in Part I of the paper.

The percentage elongations at fracture in the creep tests (Table II, col. 6) are somewhat low, and in some cases fracture occurred at gauge marks. As previously noted, the test temperatures were higher than the normal service temperatures of alloys of the type examined, and it would be inadvisable to assume that low elongation would be associated with failure under the prolonged application of load at service temperatures. In the case of certain metals submitted to examination it has been shown that, at comparatively low temperatures, failure by creep occurs as a result of deformation within the crystal grains and is associated with considerable ductility, but at comparatively high temperatures intercrystalline cracks develop by the separation of crystal grains from one another and failure is accompanied by little elongation. At intermediate temperatures both mechanisms of failure may be expected to operate to an extent depending on the temperature. An investigation into the nature of the failure of the copper alloys is being made.

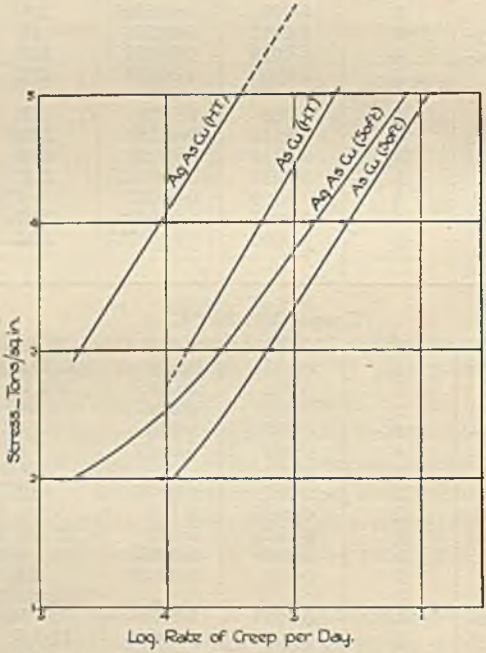

FIG. 1.—Relations between Stress–Log Rate of Creep at 300° C.

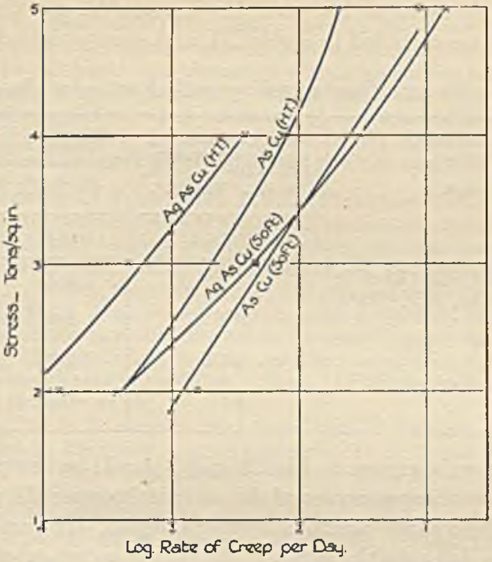

FIG. 2.—Relations between Stress–Log Rate of Creep at 350° C.

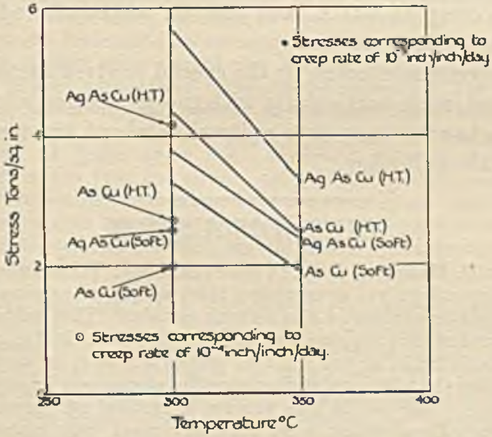

FIG. 3.—Stresses Corresponding with 10^{-3} and 10^{-4} in. per in. Strain Rate per Day at 300° C. and 350° C.

The relations between stress and log. minimum rate of creep for the soft and specially treated alloys at 300° C. and 350° C., respectively, are shown in Figs. 1 and 2.

From the curves of Figs. 1 and 2 the stresses corresponding with minimum creep rates of 10^{-3} and 10^{-4} in. per in. per day have been deduced, and are recorded in Table III, and shown plotted in Fig. 3.

TABLE III.—*Stresses Corresponding with Particular Rates of Creep.*

Material.	Stress Corresponding with Minimum Creep Rate of 10^{-4} in. per in. per day. Tons/in.^{2}.	Stresses Corresponding with Minimum Creep Rate of 10^{-3} in. per in. per day. Tons/in.^{2}.	
	300° C.	300° C.	350° C.
Arsenical copper, soft (Mark I)	2·0	3·3	1·9
Arsenical copper, H.T. (Mark II)	2·7	4·4	2·5
Silver–arsenical copper, soft (Mark III) . . .	2·55	3·8	2·4
Silver–arsenical copper, H.T. (Mark IV) . . .	4·1	5·7	3·3

Considering the curves in Figs. 1 and 2 it will be observed that the stress–log. rate of creep curves of the arsenical copper alloys are steeper than those of the silver–arsenical copper samples. The materials would not, therefore, fall into the same relative order as indicated by Table II for rates of strain of 10^{-5} in. per in. per day or less, and the materials containing silver appear likely to be still further superior in respect of resistance to creep at 300° C. and 350° C., to the silver-free materials at stresses less than 2 tons/in.^{2}.

The improvement effected by the special pre-treatment of the alloys is very marked, more particularly with the pre-treated alloy containing silver, which has its creep rate reduced to about one-tenth the value obtained for the soft alloy.

JOINT DISCUSSION.

PROFESSOR D. HANSON,* D.Sc. (Vice-President): What I should like to ask is: Have the members yet appreciated that we are witnessing the birth of a new type of heat-treatment of non-ferrous metals? This subject bids fair to be a very important one, because we have here had described to us a process for raising the elastic limit, or the limit of proportionality, of non-ferrous alloys without affecting the ultimate strength or the elongation in anything like the same proportion. We see in this process a method of converting many of the non-ferrous alloys which were formerly used into materials of much greater engineering utility than before. I think, therefore, that this is a subject which everybody should watch with the greatest care, and I hope many others will contribute to it in the course of the next few years.

I want to speak only on one small detail, and that is with reference to the influence of silver. The results in Messrs. Tapsell and Johnson's paper lead me to make these remarks in particular, because there a slight difference is pointed out which is attributed to the influence of silver. I would like to

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* Professor of Metallurgy, The University, Birmingham.

know if the authors have analyzed their samples for other impurities than those shown in the first part of the paper. I think that there might be iron, nickel, and various other things present that one should think about, which might vary in two different samples of an alloy; and if we are to attribute an effect to such a small amount of an impurity as 0·07 per cent. we ought to be assured that no other variations of that kind of order are present in the two types of sample. I see no reason to doubt the authors' conclusion, but I should rather like to ask them if they can give this additional information.

Dr. W. **Rosenhain**,* F.Inst.Met., F.R.S. (Past-President): These papers deal with a most interesting series of questions, and require more consideration than I have been able to give them; but there are two points I want to mention. One is the use, rather apologetically, by Dr. Hudson of the word "stiffness" as indicating the resistance of a metal or an alloy to slight plastic deformation. I think that it is desirable that we should find a different term, because stiffness in reality should be measured by the elastic modulus, and by nothing else—strictly speaking, by the modulus of rigidity; that is to say, the torsional elastic modulus. That, of course, does not come into this particular problem at all.

I noticed with a little surprise that the slopes of the lines drawn parallel to the elastic line in the paper are not quite uniform. It will be noticed, for instance, that *F* in Fig. 1 is appreciably steeper than the others. I believe that non-uniformity of slope must be due to some experimental error, because changes of modulus due to slight changes of composition are generally so small that they could not be shown on that scale. When I first read the paper I thought that "stiffness" referred to the angle of those curves. It is the meaning which would naturally be attributed to the word, but obviously that was not what was intended, and I think that resistance to plastic deformation should be expressed in some other way, because "stiffness" already has a very well-defined meaning in regard to metals.

The other point I should like to suggest to the authors is that if this work is carried further they should pay a little attention to some of the other alloys of copper which have been studied recently. For instance, the alloys containing antimony and arsenic at the same time, which have very interesting mechanical properties, may prove to be at least as good as those containing silver. I quite agree with Professor Hanson that it is very necessary to be certain that the silver, when added in these small amounts, is really the only variable. I presume that the authors are sure of that. The concentration of oxygen and other impurities in these alloys is a matter of very great importance, and certainly should be very clearly stated in regard to each material used.

Colonel N. T. **Belaiew**,† C.B. (Member): In studying some very old implements from the Sumerian period, I was confronted with a problem, the answer to which I thought I might get from these papers, and especially from the paper by Dr. Hudson and Dr. McKeown. The problem was as follows. The older implements were nearly always of bronze, but by 2500 B.C. the Sumerians were apparently unable to obtain any further supplies of bronze, and they had to manufacture copper implements. For instance, the implements which I was especially studying were bars which it is supposed were used as beams for steel-yards or balances. In that particular case it was very important to have mechanical qualities which would be those of bronze. The Sumerians were unable to obtain tin in sufficient quantities, and the analyses which have been published by several writers, and the analysis which I have here of one of the bars in the British Museum, show

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[*] London.

[†] Paris, France.

that the amount of tin was reduced to 0·22 per cent.—a very small amount. Then there were lead 0·36, iron 0·40, and nickel 0·67 per cent. There is another bar in the Constantinople Museum which apparently was also used as a beam, and that bar has not been analyzed. It is of exactly the same period, and the German professor who has examined it is of the opinion that it was very hard. He is quite sure that the elasticity of the bar, and all the mechanical properties, are not those of a copper, but of a bronze. Now I come to my point. The tin content in the first bar is much lower than the tin content which was cited by Drs. Hudson and McKeown. It is only 0·22 per cent. compared to 1 per cent. Our analysis does not show the presence of silicon, but I must say that we did not look for silicon. Such quantities as 0·02 per cent., if looked for, may be found. What I would like to ask is this: if the content of tin is only 0·22 per cent., and if some silicon was found, would the mechanical properties of that bar be sufficiently raised, taking into consideration also the amount of nickel and iron, more or less on the same lines which are mentioned here by the present authors? The examination of that bar shows that it was probably forged, and also very likely that some kind of heat-treatment was accidentally done which is not very far removed from the one which was mentioned here. What I have seen of the properties of the above-mentioned bar shows that the mechanical qualities were sufficiently raised to enable it to be used as a beam for very considerable loads.

The **President**: I endorse what Dr. Rosenhain has said—not perhaps only on this paper, but also on the paper that Dr. Hudson and his colleagues read at Düsseldorf, which directed attention to the effect of very small amounts of alloying material with copper. I do not know what Dr. Hudson and his colleagues have done lately, but I think that we may definitely say that, in the early experiments which were carried out with regard to the effect of small percentages of silver in copper, the copper was identical in every other respect except the addition of the very small percentage of silver.

One is delighted to feel that we are getting together a good deal of information, although perhaps on somewhat different lines from those on which investigators have worked in times past.

Dr. **McKeown** (*in reply*): I would like first to thank Sir Henry Fowler for the personal interest he has taken in this work all through. In reply to Professor Hanson, in Table I of Part I of the paper, the materials marked NA and NS are those which were tested for creep properties at the National Physical Laboratory. With regard to the other impurities, we have not got the figures here, but they are all very low, generally less than 0·01 per cent.

In reply to Dr. Rosenhain, I am personally responsible for the use of the word "stiffness," but I was rather at a loss as to what other word to use in this instance. We wanted to indicate that there was a difference in the character of the stress–strain curves. With reference to the changes of slope in Fig. 1, these are due to change in elastic modulus. There is some slight change in elastic modulus due to the heat-treatment, but such changes are so small that very accurate determination of elastic moduli would be necessary to indicate the relative values. I also thank Dr. Rosenhain for his suggestion about the other alloys containing antimony and arsenic.

I cannot answer Colonel Belaiew's question directly, except to say that it is quite probable, with the amounts of lead, iron, nickel, and tin present, that the material would have, in a heat-treated condition, a limit of proportionality approaching that of the tin–silicon copper of the present investigation.

Mr. **Tapsell** (*in reply*): There is nothing further that I need add to the remarks made by Dr. McKeown in reply to the discussion.

SOME BRONZE SPECIMENS FROM THE ROYAL GRAVES AT UR.*

By C. F. ELAM,† M.A., D.Sc., MEMBER.

SYNOPSIS.

A short account is given of the micro-structure of some bronze articles found by Mr. C. Leonard Woolley in the Royal Graves at Ur. The approximate composition has been determined and qualitative tests have been made of the corrosion products. Some of the objects had been cast; others showed signs of subsequent working and annealing.

THIS paper describes the microstructure and results of chemical analysis of some bronze objects found by Mr. C. Leonard Woolley during his excavations of the Royal Graves at Ur. Mr. W. E. Woodward, M.A., of the Cambridge University Engineering Laboratory, obtained them through his brother, Mr. A. M. Woodward, M.A., until lately Director of the British School at Athens. The author is indebted to Mr. W. E. Woodward for allowing her to carry out the investigation.

A considerable amount of work has already been done in examining similar objects by Professor C. H. Desch, F.R.S., under the auspices of the Committee appointed by the British Association for the Advancement of Science to investigate the supply of copper used by the Sumerians. A summary of results may be found in the British Association Reports of the meetings held at Glasgow, 1928, and at Bristol, 1930. These reports deal chiefly with the chemical composition of ores with a view to trace the copper supply from which the metals were manufactured. This is particularly interesting because of the presence of nickel in so many of the objects. No account has yet been given, however, of the general appearance and microstructure of any of these objects, and the members of this Institute may be interested to know what some of the copper and bronze articles were like which were made 3500–3000 B.C., and to see how they have corroded in the course of about 5000 years. No doubt a much fuller account will be forthcoming, as the articles here described are only a few out of a large number found. No attempt has been made to generalize upon

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* Manuscript received November 5, 1931. Presented at the Annual General Meeting, London, March 10, 1932.

† Cambridge.

the problems which naturally suggest themselves. Moreover, the investigation is incomplete, particularly with regard to the corrosion products. The author hopes that some of the experts in this field will carry it further.

The following objects were examined, and will be referred to by the numbers here assigned to them.

	Approximate Date.
1. Axe-head	3500–3200 B.C.
2. Probably part of a large axe-head	3500–3200 ,,
3. Blade of knife or spear	*ca.* 2700–2600 ,,
4. Square pin or nail	2700–2600 ,,
5. Round pin or nail, 1	2700–2600 ,,
6. Round pin or nail, 2	2700–2600 ,,
7. Small dish, of which no metal remained . . .	2700–2600 ,,

General Appearance.

Photographs of the specimens are shown in Figs. 3 and 4 (Plates I and II). A diagrammatic drawing of No. 1 in three positions and two sections is given in Fig. 1. All the objects were coated with a thick and, in some cases, an extremely hard layer of a bright green corrosion product. This layer was split and cracked in No. 1, and black in colour in the cracks. These cracks are to be seen in Fig. 3 (Plate I) and are shaded in the drawing (Fig. 1). When broken, a layer of red cuprous oxide was seen inside the green layer, and the innermost layer was black. With the exception of the small dish, all the other objects had a metal core. In some cases the green corrosion products broke off when the specimen was being sawn. The metal core was also very brittle. The axe-head No. 1 was so corroded that parts of it could be ground to a fine powder in a mortar. The powder was a dirty, dark brown colour. It was only when the surface was rubbed on emery cloth that its metallic nature became evident. On the other hand, there was a proportionately larger amount of uncorroded metal in the pins, and the square pin, No. 4, could be rolled into strip.

Embedding the whole specimen in some form of dental cement aided both cutting and grinding operations. The usual methods of polishing and etching were employed. The chief difficulty met with was the breaking away of the oxides and corrosion products, and even pieces of the metal, and the tendency for the oxides to be dissolved out by the etching reagents before the metal was attacked.

Analysis.

Owing to the extent of the oxidation and corrosion, no reliable or accurate analysis can be expected unless the proportion of oxides, basic acid radicles, &c., is also determined and due allowance made for

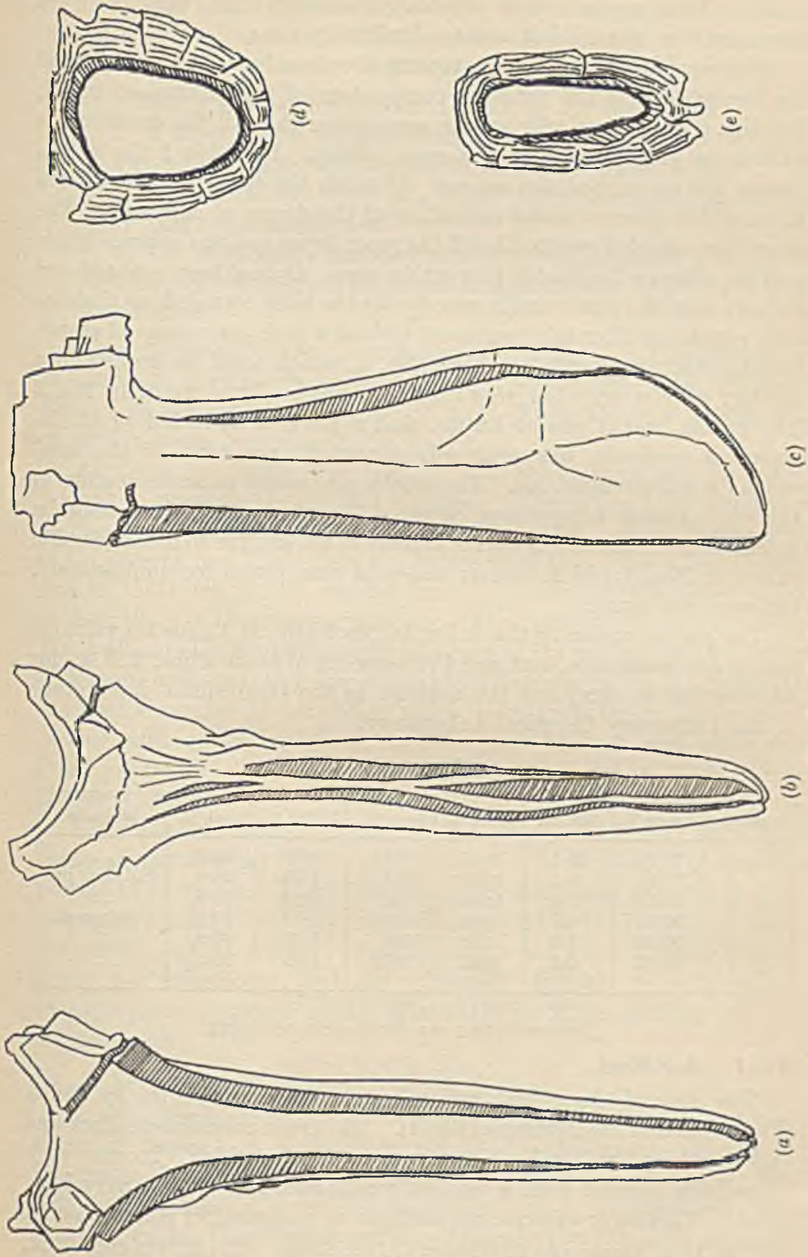

Fig. 1.—No. 1. Axe-head.

them. This requires very special knowledge and skill, as the literature * on the subject makes abundantly clear.

Professor C. H. Desch, in the reports already referred to, re-calculated his results to give the probable composition of the unoxidized metal, but this can be done only on the assumption that all the constituents oxidize or are corroded to the same extent. In Table I the actual figures are given, and the amount by which the total percentages fall short of 100 gives a useful indication of the degree of corrosion. The procedure adopted was to file off the green layer and the cuprous oxide and to analyze the metal plus oxide core. It has been pointed out already that the pins or nails were by far the least corroded, so that the core remaining after this treatment yielded a high percentage of metal. On the other hand, the axe-head, No. 1, which could be ground in a mortar, gave a very low result. There was so little metal in No. 3 (the blade), and it was so brittle, that a piece of it, including all the corrosion products, was analyzed. About 25 per cent. of the total weight is unaccounted for. The results are useful as an indication of the approximate composition of the different objects, but cannot be regarded as complete. Nickel is present in all, and tin to a considerable extent in Nos. 1 and 2. Silver and gold were tested for qualitatively, but were not found.

The author wishes to thank Dr. D. Stockdale, M.A., for his valuable advice and assistance, and also Professor Sir William Pope, F.R.S., for allowing her to carry out the analyses in the Goldsmiths' Laboratory of the University Chemical Laboratory.

TABLE I.

Specimen.	Copper, %.	Tin, %.	Lead, %.	Iron, %.	Nickel, %.	Total, %.	Remarks
No. 1	70·24	11·1	0·43	0·15	0·59	$82{\cdot}5_1$	...
,, 2	79·46	8·1	trace	0·15	1·29	$88{\cdot}0_0$	Sulphur pr.
,, 3	72·10	2·4	trace	pr.	0·12	$74{\cdot}6_2$	...
,, 4	94·41	nil	trace	0·03	1·77	$96{\cdot}2_1$	Sulphur pr.
,, 5	92·89	1·0	nil	0·5	1·45	$95{\cdot}8_4$	,,
,, 6	92·95	0·1	0·04	0·02	1·43	$94{\cdot}5_4$	...

DESCRIPTION OF MICROSTRUCTURES.

No. 1. *Axe-Head.*

The general shape and external appearance are shown in Fig. 3 (Plate I) and in the diagrams (Fig. 1). The green corrosion product was very hard and mineralized, and up to 4 mm. thick. It was very beautifully banded with a whitish constituent and took a very high polish. This layer was cracked and split in a number of places running

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* W. H. J. Vernon and L. Whitby, *J. Inst. Metals*, 1929, **42**, 182–202; 1930, **44**, 389–408.

right through to the cuprous oxide layer, and these cracks were black. Remains of a wooden handle adhered to the corrosion products and were saturated with them. A polished section showed four layers:

1. The green banded corrosion product, 3–4 mm. thick.
2. A layer of red cuprous oxide somewhat coarsely crystalline, 2 mm. thick. This layer appeared blue with reflected light.
3. A much thinner layer of a nearly black substance, appearing grey under the microscope.
4. The very much corroded core of metal, together with small amounts of red cuprous oxide and a large amount of the dark grey constituent.

These layers are shown diagrammatically in Fig. 1. The differences of colour are very poorly brought out in a photograph, although quite distinct in the actual specimens. Fig. 11 (Plate IV) is a photograph of similar layers occurring in No. 3.

Although the metal was riddled with oxide, there was sufficient present to preserve the original structure. The rather large dendrites of Figs. 5 and 6 (Plate III) are typical of a casting. From the amount of tin present (see Table I) it can be assumed that some δ constituent was in the cores of the original casting. Corrosion has taken place preferentially in these areas, resulting in their almost complete removal. Fig. 6 (Plate III) is a photograph of a part of the casting which has not undergone such extensive corrosion as that depicted in Fig. 5 (Plate III). It shows a number of blowholes which were probably in the original casting, although it is difficult to distinguish between such holes and those produced by the falling out of pieces of metal or oxide during cutting and grinding.

Some cuprous oxide occurred in the metal. This may have been partly in the original copper and partly due to deposition during the process of corrosion. The predominating constituent was a dark grey substance similar to the layer immediately next to the metal and inside the cuprite layer. These two constituents are easily distinguishable under the microscope, but are extremely difficult to differentiate photographically (see Fig. 11 (Plate IV)). Their identity will be discussed later.

No. 2. Probably Part of an Axe-Head.

A photograph of this specimen is seen in Fig. 4 (Plate II). A considerable amount of wood fibre remained adhering to the inside. The green layer was neither so hard nor so thick as in No. 1. The only metal remaining occurred where the section was thickest. The thinner sections were entirely oxide. The metal was coarsely dendritic (Fig. 7 (Plate III)). The total amount of oxidation was less than in

No. 1, in spite of flaws and blowholes, and the δ tin constituent remained, together with much of the original oxide. That this was original oxide was deduced from its appearance in the dendrites and the shape of the particles. Most of the corrosion product was the dark grey constituent referred to already.

No. 3. *Blade.*

This is illustrated in Fig. 4 (Plate II). The green corrosion product was very hard, botryoidal, and laminated. There was a ridge down one side of the blade, which was repeated through the oxide layers to the metal core. Inside the red cuprite layer was a very complete layer of the dark grey constituent (Fig. 11 (Plate IV)). Very little of the metal remained. The section is illustrated diagrammatically in Fig. 2. There was no dendritic structure, and the regular polymorphic crystals suggested working and annealing. (Fig. 8 (Plate III).) Corrosion followed the crystal boundaries. Small pieces of flattened-out cuprous oxide and a general fibrous structure produced by the corrosion indicate a considerable degree of distortion. In this respect, No. 3 differs from either of the previous specimens.

Various attempts were made to bring up twin boundaries in the crystals. All etching reagents attacked the oxide in preference to the metal, and, although with a light polish attack, slight differences of level were noticeable under the microscope, all attempts to obtain convincing photographs failed.

Fig. 2.—No. 3. Section of Blade.

No. 4. *Square Pin or Nail.*

The general appearance can be seen in Fig. 3 (Plate I). This specimen was the least corroded of any. The corrosion products, consisting of a green layer and a layer of cuprous oxide, were neither hard nor firmly attached. The black layer was absent, and the metal was penetrated by cuprous oxide. It has been mentioned already that the metal was sufficiently ductile to be rolled into strip. Reference to Table I shows that less than 4 per cent. has to be accounted for in the form of oxides, &c. The chief constituent other than copper is nickel. The microstructure is shown in Fig. 9 (Plate III). The fine twinned crystals indicate working and annealing: the remains of coring indicate insufficient annealing after casting. The small particles of cuprous oxide scattered about were probably in the original metal.

Round Pins, Nos. 5 *and* 6.

These were very similar to the square pin, in that the corrosion products were not very firmly attached and readily crumbled away. No. 6 is interesting because of the pattern on the surface (Plate I). It is suggested that this is due to a piece of material in contact with the original metal, the fibres having become saturated with the copper salts and the pattern reproducing the cloth.

An almost perfect metal core remained in the centre of the thickest parts. Cuprous oxide had penetrated to a considerable extent, and the thinner parts were completely oxidized. Fig. 10 (Plate III) is a photograph of the microstructure of No. 5. Remains of coring are clearly marked, but evidently the metal has been worked and annealed to produce the twin crystals. Small, scattered cuprous oxide inclusions can also be seen. Both round pins were very similar in structure and composition, so that a photograph of No. 1 only is given. The coring in all three pins may be attributed to the presence of nickel.

The specimens fall into two classes: (1) simple castings, (2) castings that have been worked and annealed.* The amount of corrosion is noticeably different in the two cases. Assuming that they are all of the same age and have been subjected to similar conditions of environment, the castings have corroded to a much greater extent in the time (with the exception of the blade, which had a much thinner section to begin with). This is to be expected from the greater porosity and inhomogeneity of the castings.

THE CORROSION PRODUCTS.

These specimens all came from diggings above the Flood level, and have probably been in an exceptionally dry atmosphere † for many centuries, but nothing can be said with any certainty about the conditions under which corrosion has gone on. No quantitative analyses were made of the corrosion products, but a few qualitative tests were made, and the following general observations may be of interest.

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* T. A. Rickard (*J. Inst. Metals*, 1930, 43, 297–365) has suggested that the earliest articles were fashioned direct from native copper. This cannot have been so in the case of Nos. 1 and 2, and it is impossible to say anything of the others with certainty.

† Since writing the above, Mr. Woolley has informed the author that the soil in which the objects were found was distinctly damp. Also that it is "salty and full of acids," and selenite (gypsum) crystals readily form in it. The moisture is, no doubt, due to the rising up of liquids from below, due to capillary action of the fine sand and débris. The liquid would contain salts in solution, such as chlorides, sulphates, &c., and these would be left behind when the moisture evaporated from the surface. Concentration may become great in this way, and it is not surprising that gypsum crystals separate in the soil. It would also be expected that the concentration would be greatest nearer the surface; exactly the opposite to the effect produced by rain.

The hard green layers very much resembled malachite, and effervesced in acids with the liberation of carbon dioxide. Sulphates were present, but not chlorides.

The layer of cuprite between the metal and the salts is probably of secondary origin, due to the further oxidation of cuprous salts to cupric, such as is described in the Fifth Report to the Corrosion Committee of the Institute of Metals.*

The underlying black layer, and what appears to be the same constituent penetrating Nos. 1, 2, and 3, is more difficult to identify. It is too thin to remove for analysis, and no method could be discovered of separating it from the metal and from the layer of cuprite. Two attempts were made to obtain X-ray photographs. In the first instance, the outer layers were carefully filed away until the black layer was reached. A powder photograph obtained by reflection from the surface gave lines which could be identified only as belonging to the cuprous oxide lattice. In the second instance, a piece of No. 1 was ground up in a mortar, the larger particles were discarded, and a photograph was taken through the dirty, brownish powder that remained. On this occasion lines were obtained belonging both (1) to the cuprous oxide lattice, and (2) to the α bronze lattice.

Dr. G. D. Bengough and Dr. W. H. J. Vernon, of the Chemical Research Laboratory, Teddington, very kindly examined the specimens and confirmed the observation that this material differed in appearance from normal cuprous oxide, and Dr. H. Fisher, of the Royal School of Mines, examined them with reflected polarized light, and confirmed the presence of two constituents, one of which was identified as unmistakable cuprous oxide. The exact nature of this constituent is still uncertain, but it is suggested that it consists chiefly of cuprous oxide contaminated with both tin and nickel oxides, which cause the discoloration. It is certainly present to a greater extent in those specimens containing tin, although it is well developed in No. 3, which has only a small percentage of tin and still less of nickel.

ACKNOWLEDGMENTS.

The author wishes to express her thanks to Mr. W. E. Woodward, M.A., for giving her the specimens to examine; to Dr. D. Stockdale, M.A., for assistance with the analyses; and to Professor C. E. Inglis, F.R.S., for facilities for working in the Cambridge University Engineering Laboratories.

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* G. D. Bengough, R. M. Jones, R. Pirret, *J. Inst. Metals*, 1920, 23, 65.

PLATE I.

No. 7.

No. 6. No. 4. No. 1.

FIG. 3.—Natural Size.

[*To face p.* 104.

PLATE II.

No. 3. No. 2.

FIG. 4.—Natural Size.

FIG. 5.—Axe-head, No. 1. × 100.

FIG. 6.—Axe-head, No. 1. × 100.

FIG. 7.—Axe-head. No. 2. × 100.

FIG. 8.—Blade. × 100.

FIG. 9.—Square pin, No. 4. × 200.

FIG. 10.—Round pin, No. 5. × 200.

FIG. 11.
× 60.

DISCUSSION.

Dr. T. A. Rickard,* A.R.S.M. (Member): I am ashamed to say that I have not yet read this paper, but I am looking forward keenly to reading it, because the subject interests me greatly. I am glad to see here Dr. C. H. Desch, who has done so much good work in bringing together archæologists and metallurgists. It had been my hope, as a mining engineer, to be a *liaison* officer between mining and metallurgical engineers on the one hand and archæologists and prehistorians on the other, and this Institute, more than any other body, is fitted to assist the archæologists, because you are research metallurgists, whereas my friends in the Institution of Mining and Metallurgy are industrial metallurgists.

Only yesterday I was in the Coins and Medals Department of the British Museum, talking to Mr. Mattingly, after having seen a Roman *aes signatum* in a case just outside that department; it was a plaster cast of a piece of currency —I will not call it money or coin—of 5 lb. weight, and it had been faked so well that where it had been scratched one could see the glint of copper, not bronze. When I asked Mr. Mattingly to explain why it was labelled bronze, he told me it was only a cast, and not the original; and he then showed me the original, which exhibited the unmistakable patination of bronze. In other words, the artist who had reproduced this piece of early Roman metal had been so little assisted by metallurgical knowledge that he had coloured the places supposed to have been abraded so that they looked unmistakably coppery. I venture to say to you that a large proportion of the specimens in museums labelled " bronze " are copper of various kinds. Any given specimen may not be pure native copper, but it may be copper containing accidental impurities, and therefore not entitled to be called " bronze." I was once walking with my friend Professor Myres across the campus of the University of California, where I live, and he suddenly turned to me and said, quizzically, " What is bronze ? " I replied, " Bronze is an alloy of copper with tin, purposefully made." I submit that we have to have some such idea, of intention, because the presence of tin in copper may be, and frequently is, accidental, and in some cases tin and copper are present in the same ore, both in the northern and southern hemispheres. In South America, copper and tin occur with silver; so that it is quite understandable that with copper there would be inadvertent inclusions of tin.

I hope that we shall cause our archæological friends to drop their Bronze Age. It is most bewildering to follow an archæologist who talks about the Early Bronze Age when he is really referring to the beginning of the use of copper. If we can get our friends to be more precise in these matters, and if we take a greater interest in their subject and they in ours, there will be a gain all round.†

Colonel N. T. Belaiew,‡ C.B. (Member): The archæologist is beginning now to take a keen interest in the help which is forthcoming from the metallurgist, and, as Dr. Rickard has just said, this Institute is especially fitted to tender its assistance.

I should like to refer, before passing to more special points, to one matter of general interest, where the help of the metallurgist was of great value to the archæologist. I refer to the presence of nickel in all these Sumerian bronzes and Sumerian coppers. Nickel is present in all the specimens analyzed by

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† See also remarks on p. 108.

‡ Paris, France.

Dr. Elam (see Table I). The percentage of nickel ranges from 0·12 in specimen No. 3 to 1·77 in specimen No. 4. As a rule, in Sumerian coppers we find 0·5, 0·6, or 0·7 per cent. nickel, and the same thing in bronze. As is made clear from Dr. Desch's report to the British Association, the presence of nickel enabled the metallurgist to trace the source of supply of the ores which were used by the Sumerians to a land which is called Magana, which is mentioned in the inscriptions of Sargon. Recently the metallurgist was able to analyze some samples of ores coming from Magana, and incidentally was able to settle two questions. The first was that the Sumerian copper and ore supplies actually came from that land, and the second that this " land which is called Magana " in the inscriptions is actually the region of the same name archæologically identified by Professor Langdon in Arabia. That is a very important point. There are still some who are somewhat doubtful of it, because there are a few other sources of supply of nickel ores in India and Sinai, but now the consensus of opinion is that these ores come from Arabia, from Oman, and that Magana is a little corner of Oman. A village was found the name of which even now is rather like Magana. That shows how two people—the archæological expert deciphering an inscription of the time of Sargon, 2700 B.C., and the metallurgist, examining samples or ores sent to him by the prospecting engineer—are able to co-operate, and it is only by their co-operation that such questions can be settled. For a very long time people were looking for Magana in Ethiopia, Egypt, and so on, but when it was found that no trace of nickel was present in the Egyptian samples, the matter became clearer; Egypt could be ruled out.

I would mention another sample, a very interesting one from the British Museum, which was kindly given to me by Mr. Sidney Smith. The analysis of it is :

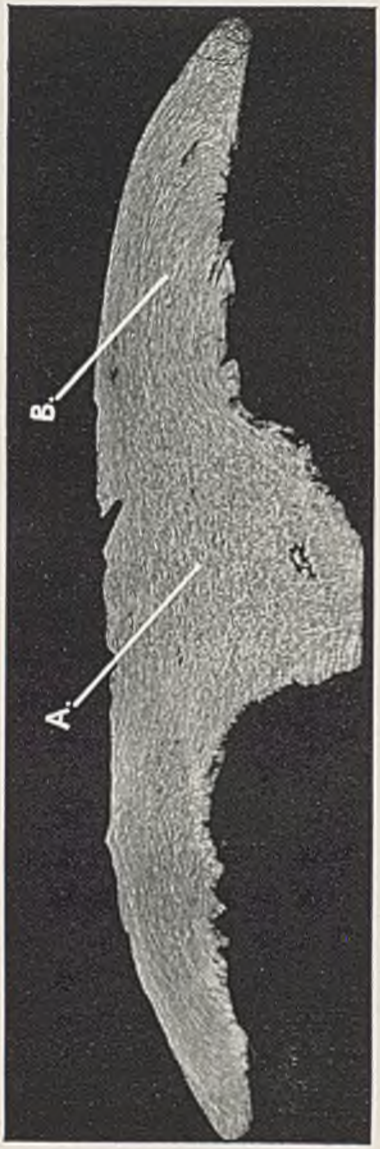
	Per cent.
Copper	95·22
Tin	0·22
Lead	0·36
Iron	0·40
Nickel	0·67

The interesting point about that sample is that there is an inscription on it, and it can thus be dated, and the date of the inscription would appear to take us back to 2500 B.C., the date of the second Sumerian revival. The fact that the percentage of tin in it is very small shows that, from the metallurgical point of view, it was made at a period when the Sumerians were deprived of their tin ores, and we know that all the samples of coppers of that type belong to the period 3000–2500 B.C. Here, on the other hand, we have an inscription which allows us to say quite definitely that by that period the Sumerians, whilst using ores which still contained nickel, were unable to have such a balance of tin ores as to use bronze, and in that particular instance in Sumera we have a Bronze Age which was followed by a Copper Age.

From the point of view of corrosion, that particular sample which has been identified as a steelyard beam shows quite distinct signs of the old inscription. That means that the layer of corrosion products are only about 2 mm. deep, as otherwise the inscription could not have been read, and it shows that some of the samples, in spite of their great age, are corroded on the surface to only a small extent. The amount of oxygen is a little more than 3 per cent., but, in spite of that corrosion, some of the surface was so lightly corroded that part of the inscription is quite readable.

The inspection of the corrosion products which was made by Dr. Plenderleith and myself shows that the sequence of layers is exactly the same as that

PLATE V.



5. FIG. A.—Section through Bolt-Head, showing Forging. × 5.

[*To face p.* 106.

6. *A.* × 250.

FIG. B.

7. *B.* × 250.

FIG. C.

Copper Bolt-Head. Ur. (Longitudinal.)

mentioned by Dr. Elam. We have here a layer of cuprous oxide and a greenish product which is malachite, and that enhances the importance of the work presented to this Institute, and shows us that in the near future no important archæological research dealing with arts and crafts can be conducted without the aid of the metallurgists, and in particular without the aid of this Institute.

Dr. C. H. Desch,* F.R.S. (Member of Council): I have naturally been greatly interested in this paper, and I feel much indebted to Dr. Elam for the work she has done on these specimens. Actually we have in recent years carried out a number of examinations not only of the microstructure of the specimens, but also of the patination product, but it so happens that none of the photographs has been shown to any metallurgical gathering, but only to the Anthropological Section of the British Association. In 1929 some photographs were exhibited there showing these structures.

Fig. A (Plate V) shows a bolt-head taken from the first graves at Ur, 3500 B.C. It consists of copper, and is strongly cold-worked.

Figs. B and C (Plate VI) show the undistorted and cold-worked structures respectively.

The twinned structure shows that the metal has been annealed after its first production, and cold-work has been superimposed on it.

As regards the patination, we have made the same observations as Dr. Elam—that essentially one has this fine blackish layer, very thin, then the cuprite, and then the malachite, and I agree with her interpretation that the cuprite is a secondary product, and that the original hydrated carbonate gradually mineralizes, becoming malachite, but by secondary reaction with copper in the early stages, when much moisture is present, cuprite is formed. The substances are highly crystalline, and what is curious is that sometimes one finds an alternation of cuprite and malachite layers in the same specimen.

We are now engaged on a study of the patination and the formation of these minerals by microchemical methods. In particular, we find that the methods developed by Professor Chamot are of considerable help, and we hope before long to have some results to communicate on the process of formation of the corrosion products.

Dr. Elam (*in reply*): With regard to the use of the term "bronze" by archæologists when they do not always mean a tin–copper alloy, they are not the only culprits, because metallurgists often talk about "bronze" when they mean "brass."

I have heard that Mr. Bertram Thomas found some nickel-bearing ores in part of Arabia, and it would be very interesting if this were confirmed. I would suggest to archæologists that they should not confine themselves to looking for metal specimens, but also for slag heaps and old furnace workings, where much useful information might be obtained.

With regard to Colonel Belaiew's reference to the inscription appearing under the corrosion products, I do not think that that necessarily means that there was not much corrosion. On reference to the photograph of the blade (Fig. 4) which had a ridge on one side it will be seen that the ridge is represented again in the corrosion product, and I think that any markings on the surface are quite frequently also marked in the corrosion products themselves.

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CORRESPONDENCE.

Dr. Elam (*in further reply to the discussion at the meeting*): I should like to thank both Colonel Belaiew and Dr. Desch for the further information they have given with regard to specimens they have examined and for confirming my observations on the corrosion products. In my opinion, it is essential that the largest possible number of specimens be examined and described before any generalizations are made with regard to the supply of ores and methods of manufacture. One is apt to forget that long periods may have elapsed between the manufacture of some of these objects. Those described in this paper represent a possible period of a thousand years, and enormous changes can take place in that time. Even assuming that during the whole of that period the supply of ores was from the same locality, considerable variation would be expected in the composition. Moreover, as all the workings were probably confined to small outcrops at the ground surface, the local variations would also be great. These considerations may account for the variable nickel content.

The presence of tin is a different problem. Dr. Rickard suggests that this was also added inadvertently. The first discovery of the effects of tin may have been accidental, as most discoveries are. But it must have become a well-known fact amongst ancient metallurgists. Otherwise, why did a "bronze" age universally supersede a "copper" age? It cannot possibly have been that after a certain date all the copper ores smelted also contained tin ores. Traces of tin might have been inadvertent, but scarcely as much as 11 per cent. (No. 1).

The absence of bronze at a later period of Sumerian civilization may be due to the cutting off of the supply of tin ores or to the loss of the art of smelting bronzes, owing to the lack of knowledge of the use of tin ores. In my opinion, credit should be given to the early metallurgist for adding tin—in whatever form—with intention and knowledge of what he wanted to produce.

Dr. T. A. Rickard, A.R.S.M. (Member) (*continuing the remarks made at the meeting*): In reply to Dr. Elam's query, I would say that the objects numbered 3 to 6 are unlikely to have been made of hammered native copper, because the high tin content of Nos. 1 and 2 proves that the art of smelting was already known. The diminished proportion of tin in the objects of later date, in the Sargonid period, might indicate a lack of tin or of tin ore, for making bronze, but it may warrant an inference even more interesting—namely, that the presence of tin in these coppery objects was inadvertent, meaning thereby that the tin was an accidental constituent of the ore that was smelted. The smelting, presumably, was not done at Ur, in a fluviatile region devoid of mineral resources, but the metal probably came from the upper country in the Caucasus highlands. The presence of 2·4 per cent. of tin in No. 3, of 1 per cent. in No. 5, and of nil in No. 4 suggests a variability so great as to indicate inadvertency.

The nickel content, characteristic of all the objects, may suggest a common origin for the ores smelted. Nickel is an associate of copper in many mining districts, notably Sudbury, in Ontario, whence we derive most of the nickel used to-day in alloy manufacture. Recently I happened upon a mention of nickel in a coppery object found in Central Europe. On p. 106 of "Die Kupferzeit in Europa," by Matthaeus Much, published in 1886, the author describes a prehistoric copper mine discovered near Salzburg (close to the Austro-German border) in 1879. There were no iron tools, nor any signs that any such had been used. The period was believed to be that of the Swiss lake-dwellers. A copper tool unearthed in the workings assayed copper 97·78, nickel 0·88, lead 0·05, sulphur 0·24, and slag 0·07 per cent.

Dr. Elam (*in reply*): I wish to thank Dr. Rickard for his further communication. Most of the points he raised have now been discussed in my written reply to the discussion at the meeting.

THE RELATIVE CORRODIBILITIES OF FERROUS AND NON-FERROUS METALS AND ALLOYS. PART III.—FINAL REPORT.* THE RESULTS OF THREE YEARS' EXPOSURE AT SOUTHAMPTON DOCKS.†

By J. NEWTON FRIEND,‡ D.Sc., Ph.D., F.I.C., MEMBER.

SYNOPSIS.

Nearly one hundred bars of ferrous and non-ferrous metals were exposed to sea action in Southampton Docks for three years, and an account is given of seventy-two of these. The metals examined included lead, zinc, tin, aluminium, copper, nickel, and various alloys containing iron, chromium, nickel, copper, and zinc. The effect of grain-size on the corrodibility of brass has been studied. The results appear to indicate that small grain is preferable to coarse. Nickel–copper alloys, particularly the 70 : 28 alloy, offered great resistance to corrosion. High-grade zinc and tin were slightly more attacked than the less pure metals. The effect of arsenic in copper is discussed. Tension, riveting, and cold-working did not appreciably affect the corrosion of nickel–chromium alloy steels, but in every case cracks appeared at welds. Shell fauna did not appear to affect the corrosion of the metals appreciably while living. Dead shelly fauna stimulated localized corrosion in alloy steels, nickel, and nickel alloys not rich in copper. The alloy steels resisted corrosion well, but previous results showing that alloy steels are subject to serious localized corrosion are confirmed.

THE metals employed in this research were, except where otherwise stated, in the form of round bars 60 cm. (2 ft.) in length and 2·87 cm. (1⅛ in.) in diameter. After weighing they were fixed in eight stout rectangular oak frames similar to, but smaller than, that already figured. [See Plate XVII (facing p. 112), *J. Inst. Metals*, 1928, **39**.] The number of bars in each frame varied from eight to thirteen (see Fig. 1, Plate VII). The ends of the bars were supported in holes in the frames 2½ in. apart from centre to centre, and plugged with felt saturated either with tar or with vaseline thickened with paraffin wax. In the previous research (*loc. cit.*) putty was used, but this proved unsatisfactory with ferrous

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* For Parts I and II see *J. Inst. Metals*, 1928, **39**, 111, and 1929, **42**, 149, respectively.

† Manuscript received September 8, 1931. Presented at the Annual General Meeting, London, March 9, 1932.

‡ Head, Department of Chemistry, The Technical College, Birmingham.

bars and aluminium, severe localized corrosion taking place at the ends. The new method gave good service, the ends of all the bars on dismantling being found in good condition. The frames were fixed under a jetty at Southampton Docks at approximately half-tide level by Mr. F. E. Wentworth Sheilds, to whom the author desires to express his great indebtedness. After 3 years (1928–1931) the frames were dismantled.

Owing to the thick accumulation of mud and shelly fauna, it was not possible to gauge the extent of corrosion from visual inspection *in situ*. This was unfortunate, for, on dismantling, it was found that corrosion had not proceeded so far as had been expected, and the results are not so conclusive as the author had wished. The oil from the ships assisted in the formation of a more or less protective layer of mud round the bars, which was not scoured off by the slowly moving waters, as would have been the case at Weston-super-Mare, where the tidal currents are very rapid. The present results, therefore, are not exactly comparable with those previously obtained. It was observed that the shelly fauna did not collect in any appreciable numbers on the copper or copper-rich alloys, although all the other bars were covered, even the lead (Fig. 2, Plate VII) and zinc bars.

The shell fauna did not appear to affect the corrosion of the metals appreciably while living. Dead shell fauna stimulated local corrosion in alloy steels, nickel, and in nickel alloys not rich in copper, leaving more or less circular patches (Figs. 3 and 4, Plate VII).

The methods of clearing and examining the bars were the same as in the previous research, save that tensile tests were not applied, as corrosion had not proceeded sufficiently far to justify them.

CONSIDERATION OF THE RESULTS.

Wrought Iron and Mild Steel.—These bars were included in the tests to serve as standards of comparison with the results obtained at Weston (*loc. cit.*). The two wrought irons were very uniformly attacked, the fibrous structure appearing at various places; they lost less in weight than the steels. The mild steels had also been uniformly attacked, particularly the copper steels. As in the Weston tests, the addition of 0·15 per cent. copper proved slightly beneficial (Table I).

Alloys of Nickel and Chromium.—The addition of chromium up to 20 per cent. to nickel does not appear, on the whole, to have greatly enhanced the resistance of the nickel to corrosion. The loss in weight was slightly less with 4·79 per cent. chromium, but slight pinholing occurred, and also slight localized corrosion where dead fauna had remained (Table I).

TABLE I.—*Bars containing Iron, Chromium, and Nickel.*

Frame.	Metal.	Identity Mark.	Ni.	Cr.	Fe.	Mn.	Cu.	C.	Si.	S.	P.	Loss in Weight. Grms.	Mean Loss.	Remarks.
E	Wrought iron	EB1 EB2	...	...	99·36	0·10	0·06	0·06	0·12	0·03	0·27	39·0 41·9	40·5	Uniformly corroded. Fibrous structure revealed.
E	Mild steel	WM1 WM2	...	...	99·09	0·55	...	0·13	0·12	0·06	0·044	47·6 55·3	51·5	Uniform corrosion.
E	Copper-steel	HCU1 HCU2	...	...	99·21	0·44	0·15	0·13	0·01	0·025	0·036	48·4 48·5	48·5	Extremely uniform corrosion.
B C	Nickel	M1B M1C	99·60	...	0·16	...	0·06	...	...	...	...	0·1 0·4	0·25	Perfect except where shell-fish caused slight local attack.
B C	Nickel–chrome	M8B M8C	93·71	4·71	...	...	...	...	...	...	...	0·0 0·1	0·05	Perfect except slight pinholing and localized attack by shelly fauna.
B C		M7B M7C	79·63	19·44	...	...	...	...	...	...	...	0·2 0·2	0·20	
B	Nickel–iron	M11B M11C	78·10	...	21·04	...	...	...	...	...	...	0·2 0·7	0·45	Widespread incipient pitting and very shallow shell fauna attack.
B C	Nickel–chromium –iron alloys	M9B M9C	36·67	...	62·31	...	...	...	...	...	...	4·3 5·0	4·65	Ditto, but more pronounced. Fig. 5.
B C		M10B M10C	34·81	3·19	60·30	1·23	...	0·223	0·23	0·009	...	1·9 2·5	2·20	All in excellent condition except where locally attacked.
A		R1937	10·8	15·7	72·66	0·44	...	0·12	0·28	...	...	...	0·7	
A A		R2033 R2033A	10·6	17·2	71·60	0·12	...	0·16	0·32	...	...	0·7 0·7	0·7	
B		FST	7·9	18·2	73·10	0·30	...	0·15	...	0·35	...	...	0·6	
A		R1630	2·61	20·6	76·00	0·29	...	0·21	0·28	...	...	...	1·2	
A		R1498	0·10	20·4	78·80	0·10	...	0·10	0·31	...	...	...	0·6	
A	Ditto, twisted and stretched	R1702	10·5	15·7	72·99	0·25	...	0·11	0·45	...	...	...	<0·1	Cold-working does not appear to have affected corrodibility. Figs. 6 and 4.
A		R1746	2·15	17·0	79·93	0·28	...	0·08	0·16	...	...	...	0·4	
A	Ditto, riveted and welded	R1708	10·7	15·7	71·33	0·24	...	0·15	0·38	...	...	...	1·5	
A		R1733	2·08	17·8	77·42	0·32	...	0·09	0·39	...	...	...	1·9	

Alloys of Nickel, Chromium, and Iron.—All these alloys resisted general corrosion exceedingly well, but all were subject to localized corrosion, even the nickel bars, M1, yielding to the attack of shell fauna. The addition of iron to nickel (bars M11 and M9) has increased the corrodibility (Fig. 5, Plate VIII), but this is partly countered in bar M10 of "Dull ray" by addition of 3 per cent. chromium. The remaining bars containing 16–20 per cent. chromium retained their high polish, and, apart from localized corrosion, were in excellent condition (Table I).

Effect of Cold-Working on Alloy Steels.—The nickel–chromium steels R1702 and R1746 had been stretched at *A* (Fig. 6, Plate VIII) and very heavily cold-worked at *B*, the surfaces of the bars being indented at several of the bends. There was no special corrosion at these places, however, apart from localized attack due to dead shell fauna. Where riveted, bars R1708 and R1733 were in as perfect condition as the main body of the bar, as seen at *RR* in Fig. 4, Plate VII; the round patch *F* shows localized attack by fauna. In every case, however, the welds had cracked in the frame (Fig. 4). One rivet of bar R1733 had snapped in the frame, and the two parts were nearly lost (Table I).

Nickel–Copper Alloys.—Both nickel and copper resisted sea-water corrosion exceedingly well. As at Weston, the nickel lost considerably less in weight than the copper (Table II), but was somewhat less uni-

TABLE II.—*Bars containing Nickel and Copper.*

Frame.	Metal.	Identity Mark.	Ni.	Cu.	Fe.	Mn.	As.	Pb.	Loss in Weight. Grms.	Mean Loss.	Remarks.
B C	Nickel	M1B M1C	99·60	0·06	0·16	...	...	...	0·1 0·4	0·25	Perfect except slight shell fauna attack.
B C	"Corronil"	M5B M5C	70·27	28·03	0·67	0·80	...	...	0·0 0·0	0·00	Slightly stained locally. Traces of shell fauna attack.
B C	"Silveroid"	M4B M4C	44·21	54·47	0·90	0·33	...	...	0·0 0·4	0·20	" "
B C	80 : 20 copper-nickel	M3B M3C	20·08	79·72	0·11	0·07	...	...	1·3 1·2	1·25	Brick red corrosion product. Uniform attack.
B C	90 : 10 copper-nickel	M2B M2C	9·55	90·11	0·26	0·10	...	...	2·6 2·1	2·35	No obvious shell-fish attack.
F G		NC2F NC2G	1·93	98·00	0·04	...	nil	nil	4·0 3·8	3·9	
D	Copper (arsenic free)	E	...	99·92	trace	...	0·01	0·02	3·5	3·5	
F G	Copper (with arsenic)	CO1 CO2	0·07	99·70	"	...	0·11	0·02	4·0 3·9	3·9	Perfect.
D	" "	G	...	99·38	...	...	0·25	0·05	3·4	3·4	"
F G	" " " "	AC1 AC2	0·03	99·42	trace	...	0·39	0·03	5·0 5·1	5·05	" "
D	" "	B	...	99·32	...	...	0·43	0·05	2·9	2·9	"

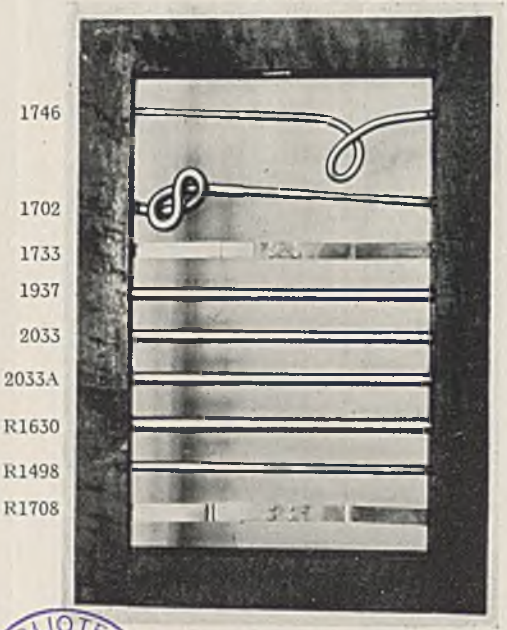

FIG. 1.—A Typical Frame. Frame A.

FIG. 2.—Lead Bar covered with Mud and Shells.

FIG. 3.—Nickel-Chromium Steel Bar FST.

FIG. 4.—Nickel-Chromium Steel Bar R1708.

[*To face p.* 112.

PLATE VIII.

FIG. 5.—Nickel-Iron Bar M9B.

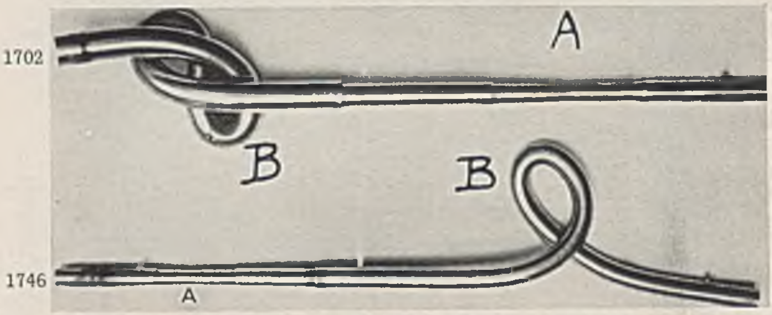

FIG. 6.—Bars 1702 and 1746 of Cold-worked Nickel-Chromium-Iron Alloys.

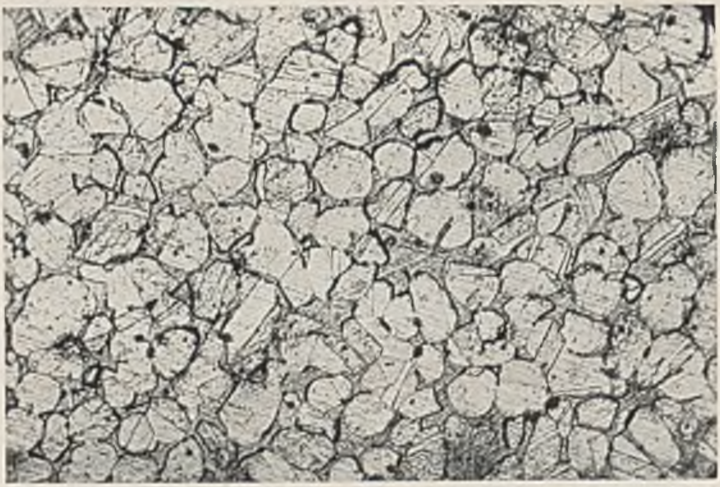

FIG. 7.—Coarse Muntz Metal, MM3. × 200.

FIG. 8.—Fine Muntz Metal, MM1. × 200.

formly attacked. There were no marks on the copper similar to those on the nickel and high nickel alloys caused by shell fauna. These latter do not appear to have attached themselves to any appreciable extent to the copper and high copper alloys. Bars M5 of "Corronil" lost least in weight and were in excellent condition. Bars M4 of "Silveroid" were closely similar. Further increase in copper content resulted in an increased loss in weight, but corrosion was very uniform. The presence of 1·93 per cent. nickel (bars NC) had no appreciable effect on the resistance of the copper.

Copper.—The copper bars resisted corrosion well and uniformly. Vernon found in his aerial tests that the presence of 0·45 per cent. of arsenic greatly enhanced the resistance of his copper specimens to corrosion,* and in the present author's tests at Weston-super-Mare † arsenic was found to retard slightly the corrosion of copper exposed to alternate wet and dry sea-action. Bar B (Table II) supports this conclusion for sea-action. Smaller quantities of arsenic appear to give varying results (Bars CO, G, and AC).

Copper–Zinc Alloys.—The influence of grain-size on the rate of corrosion of brass has frequently been discussed. The general opinion appears to be that the grain-size should not be large ‡; some regard the effect as not important within normal limits,§ whilst Brühl ‖ concludes that a small crystalline structure is conducive to most rapid corrosion. Bars of screw metal and Muntz metal were prepared, three of each of almost identical chemical composition, but differing in their grain-size. The results obtained with these are given in Table III. The greatest resistance to corrosion was offered by the bars of smallest grain-size in the case of screw and Muntz metal. Figs. 7 and 8 (Plate VIII) show the relative grain-sizes of the coarse and fine Muntz metals, MM3 and MM1, respectively. These results are suggestive, but are not in themselves conclusive, for other factors besides grain-size may be at work.¶

The *ordinary zinc bars*, OZ1 and 2, were made of the usual commercial metal such as is supplied to the Admiralty, shipbuilders, and shipping companies for anti-corrosive purposes. The greatest impurity was lead. The bars contained approximately 98·82 per cent. zinc, 1·12 per cent. lead, 0·05 per cent. each of iron and cadmium, together with

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* Vernon, *Trans. Faraday Soc.*, 1927, **23**, 178. Also Friend, *J. Inst. Metals*, 1929, **42**, 149.

† Friend, *J. Inst. Metals*, 1928, **39**, 127.

‡ Anderson and Enos, *Amer. Inst. Min. Met. Eng.*, **1924**; abstract, this *J.*, 1924, **31**, 431.

§ Anderson and Brooks, *Mech. Eng.*, 1925, **47**, 643.

‖ Brühl, *J. Inst. Metals*, 1911, **6**, 285.

¶ See Donovan and Perks, *J. Soc. Chem. Ind.*, 1924, **43**, 72T.

TABLE III.—*Copper–Zinc Alloys. Effect of Grain-Size.*

Metal.	Identity Mark.	Grain.	Cu.	Zn.	Pb.	As.	Tin.	Loss in Weight. Grms.		
								Frame F.	Frame G.	Mean
Screw metal	SM3	coarse	59·55	38·77	1·37	trace	0·22	3·8	4·5	4·2
	SM2	medium*	59·91	38·51	1·24	,,	0·25	3·8	3·8	3·8
	SM1	fine	59·97	38·35	1·32	0·09	0·25	3·8	3·0	3·4
Muntz metal	MM3	coarse	61·22	37·83	0·74	trace	0·12	4·0	3·3	3·65
	MM2	medium	61·18	37·93	0·68	,,	0·11	3·5	2·5	3·0
	MM1	fine	61·36	37·68	0·74	0·01	0·12	2·4	1·4	1·9

* Nickel 0·11%.

a trace of arsenic and aluminium. The bars complied with the Admiralty specification for rolled zinc for anti-corrosive purposes—namely, that they had been rolled from castings three times the finished thickness. Bars PZ1 and 2 were prepared in a similar manner from high-grade spelter containing 99·9 per cent. of zinc. It is interesting to note that, as with tin (below), the ordinary metal has proved more resistant to corrosion than the commercially pure spelter (Table IV) which latter suffered somewhat severe pitting near its ends. Two pits measured on bar PZ2 were 1·3 and 1·35 mm. deep, respectively. Shallow pits occurred at numerous other places. The ordinary zinc bars were in very good condition, such pitting as occurred being very

TABLE IV.—*Bars of Miscellaneous Metals.*

(For Analyses see Text.)

Frame.	Metal.	Identity Mark.	Loss in Weight. Grms.	Mean Loss.
G	Common lead	LC13	4·0	4·75
G	,, ,,	LC13	4·5	
C	,, ,,	LP12	6·0	
D	,, ,,	LP12	4·5	
F	Antimonial lead (1·6% Sb)	LA13	4·2	...
D	High-grade 99·9% pure zinc	PZ1	15·6	15·4*
D		PZ2	15·2	
D	Ordinary 98·8% zinc	OZ1	13·9	14·35
D		OZ2	14·8	
D	High grade 99·75% pure tin	SR1	1·0	0·95
D		SR2	0·9	
D	English common ingot 99·2% tin	SC1	0·7	0·55
D		SC2	0·4	
H	Aluminium	AL1	0·2	0·15
H		AL2	0·1	

* Both bars were pitted near their ends, especially PZ2, the depths of two pits in which were 1·3 and 1·35 mm.

shallow. These results are in harmony with those recently obtained* with plain and amalgamated zincs in electric batteries containing either dilute sulphuric acid or ammonium chloride solution. It appears, therefore, that the presence of about 1·1 per cent. of lead in zinc exerts a beneficial action on its resistance towards corrosion.

The tin bars, which were specially cast for this research, had undergone no further mechanical or heat-treatment. They were not subject to analysis, as the general composition of the English common ingot tin was known, namely:

	Per cent.		Per cent.
Antimony . . .	0·300	Lead	0·398
Arsenic . . .	0·017	Copper . . .	0·060

with traces of bismuth, iron, silver, and sulphur. In the high-grade pure tin the guaranteed percentage of tin is 99·75; the impurities consist of the above in proportionately smaller amounts. The bars, after cleaning, were found to be in excellent condition. The pure tin lost slightly more weight than the common metal, as in the Weston tests. In all cases there were very slight indications of incipient pitting (Table IV).

The *aluminium bars* had been rolled down rapidly or broken down from rods 2·5 in. square to 2 in. square in rod mills at a commencing temperature of 460° C., which fell to 390° C. during the process. They were then cold-drawn from 2 in. square to round bars 1¾ in. in diameter by $\frac{1}{16}$ in. reductions.

Analysis showed the bars to contain 0·32 per cent. iron and 0·25 per cent. silicon.

On cleaning, the bars were seen to be in excellent condition, having suffered a negligible loss in weight (Table IV). A similar bar exposed at Weston-super-Mare in the author's previous research was practically destroyed by pitting; one pit, 5·81 mm. deep, had penetrated through more than one-fifth of the diameter of the bar. The conditions of exposure in the two cases, however, were different. At Weston the rushing of the tide scoured the metal, whereas at Southampton the layer of oily mud adhered tenaciously to the aluminium, and thus tended to preserve its outer skin unbroken.

These results support the conclusion previously arrived at—namely, that the pitting was due, in the Weston tests, to discontinuities in the protective skin, and that if this pitting could be stopped aluminium might be very serviceable for marine work.

The *lead bars* were prepared by extrusion from a solid block of metal.

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* Friend, *J. Inst. Metals*, 1929, **41**, 92.

The antimonial lead was prepared by melting down antimony and lead in the requisite proportions and casting into a block for extrusion. The compositions of the bars were as follows :

	Lead LC. %.	Lead LP. %.	Antimonial Lead. %.
Lead	99·968	99·922	98·391
Antimony	trace	0·003	1·600

Traces of copper, bismuth, silver, iron, zinc, and tin were also present.

The bars of ordinary lead LC and LP had sagged in the frames, and two of them almost fell out. The antimonial lead bar remained straight and rigid throughout the test. To what extent the observed losses in weight (Table IV) were caused by mechanical action it is difficult to decide, but all the bars were in excellent condition when cleaned, apart from points of obviously mechanical local injury. From these results and those obtained at Weston there can be no doubt that the addition of 1·6 per cent. of antimony appreciably enhances the resistance of lead to sea action.

In conclusion, the author desires to express his thanks to the various firms who presented him with the bars for this research, particularly those who have assisted him to defray the cost of the research ; also to the Royal Society for a grant which enabled the micrographic study to be carried out.

THE TECHNICAL COLLEGE,
BIRMINGHAM.
August 31, 1931.

DISCUSSION.

DR. W. H. J. VERNON * (Member) : In the absence of Dr. Friend, I prefer to communicate in writing anything in the nature of a contribution to the discussion on this paper. There is, however, one aspect of the work which should not pass without comment. I understand that this paper is the last of the long series of reports in which Dr. Friend has communicated the results of his various field tests : some of these have been conducted in the sea, some in the open air, and altogether they have extended over many years. I think, therefore, that the moment is opportune for us to express our appreciation of this long record of corrosion investigation; and particularly should we bear in mind the pioneer character of much of Dr. Friend's work in this country.

Professor T. TURNER,† M.Sc., A.R.S.M., F.Inst.Met. (Past-President) : I should like to re-echo what Dr. Vernon has said as to our thanks to Dr.

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* Chemical Research Laboratory, Department of Scientific and Industrial Research, Teddington.

† Professor Emeritus, The University of Birmingham.

Friend for the work that he has done extending over so many years. There are only two points to which I wish to refer. The first is as to the question of the corrosion of large grain-size as compared with small grain-size, which is referred to on p. 113. Dr. Friend refers to the work done by Brühl. This work was done in my laboratory more than twenty years ago, and his paper was the first contribution to the subject of corrosion which was communicated to this Institute, and which has, of course, in other hands developed so much during the interval. Now, Brühl did not make a very definite statement on the matter, as might be supposed from the reference by Dr. Friend. Brühl proceeded by taking a cold-rolled 70 : 30 brass plate. Two specimens were annealed at the same temperature, but for different times, the result being that one developed a much larger grain structure than the other. They were then placed in synthetic sea-water, and the rate of corrosion was observed for a period of fifteen weeks. On immersion, the small grain lost approximately 5 per cent. more weight than the coarse grain, but at the end of twelve weeks the reverse effect was observed. On account of the length of the University term, the work had to be cut short at the end of fifteen weeks, but the trials showed that the rate of corrosion was gradually altering, and that in all probability the curves would have crossed each other had the experiment been conducted for a few weeks longer; and Brühl says, "It would be interesting to ascertain the reason for such a change." It would therefore not be correct to suggest that Brühl concluded that a small crystalline structure is conducive to most rapid corrosion—except in the initial stage. In the initial stage the small grain may corrode most rapidly. The experiments of Brühl are scarcely comparable with those of Dr. Friend, because Dr. Friend used practically a 60 : 40 alloy, whilst Brühl was using a 70 : 30, and thus would have quite different rates of corrosion in sea-water. We still require further information as to why in some cases small grain may corrode more quickly than large grain, and why in other cases—and the more usual cases—the large grain corrodes more quickly than the small grain.

Dr. Friend has also referred to the fact that zinc, and particularly tin, in corrosion are less affected when less pure; that is, that the pure materials do not resist corrosion so well as those that contain a small quantity of impurity. That raises a very wide field of inquiry—first, as to which of the particular impurities present was responsible for the good effect; and, secondly, how much of the impurity would be beneficial. It has been observed that varieties of commercial tin are in some cases distinctly more resistant to the effects of corrosion than the extremely pure kinds which have been tested side by side. On the other hand, some impure tins are worse. So that obviously there is some suitable proportion of an element that is commonly present which will give beneficial results.

The **President**: As Dr. Vernon has said, this is the concluding paper of a series of reports which have been very interesting, but I do not think for a moment that it is the end of the subject. I look at this question perhaps from rather a different point of view. At present I am doing some work on the subject, and what I want to know, and what I cannot find any information on, is what the shelly substances shown in Fig. 2 leave behind them?

CORRESPONDENCE.

Dr. Friend (*in reply to the discussion at the meeting*): I greatly appreciate the kind remarks of Dr. Vernon and Professor Turner on the corrosion studies which have engaged my attention for nearly thirty years. I thank Professor Turner for very correctly pointing out the differences between Brühl's research and my own. Our knowledge of the influence of grain-size on corrodibility is still far from satisfactory. From the numerical data given, Dr. Vernon does not think that there is sufficient justification for attributing any beneficial effect to the addition of 0·15 per cent. of copper to steel. If Dr. Vernon could have seen the bars and personally noted the smooth even appearance of the copper-steels, I think that he would have agreed with everything I say about them. The results with copper containing arsenic were very disappointing. Although this is my final report, the President is right in believing that it is not the end of the subject. I can assure him that a few odds and ends still remain to be cleared up ! The above are some of them.

Mr. K. G. Lewis,[*] M.Sc. : I am very interested in Dr. Friend's paper, and would like to ask if microscopic examination of the different materials was made. I cannot tell whether flat bars were used for the riveting tests and two such bars riveted together, or whether the rivets were "snapped" over in one bar (flat or round). It is with regard to the riveted bars of R1708 and R1733 that I ask if microscopical examination has been made. I imagine that bar R1708 was in the austenitic state, otherwise riveting would have been a matter of very great difficulty. Similarly, after riveting, the areas of the bar which are in the region of the rivet would become martensitic, due to cold-working. I cannot imagine some type of corrosion not taking place where there would be a change of structure in adjacent parts of the material, at any rate, after three years' exposure.

With regard to the plain (*i.e.*, not worked in any manner) steels of the nickel-chrome type, I was very interested to note Dr. Friend's remarks on the high corrosion resistance, as I have obtained the same result on similar material in sheet form which has been subjected to exposure in a marine atmosphere and showing, also, no loss in tensile strength.

It is fairly well known now that steels of the "acid-resisting" type, in sheet form at any rate, do sometimes undergo intercrystalline attack, which, of course, can only be observed microscopically.

Dr. W. H. J. Vernon[†] (Member) (*in continuation of remarks at the meeting*): The present paper raises issues that must be associated with the inherent difficulties of investigations of this kind. The conditions of Dr. Friend's tests are obviously extremely complex; and when one considers the various factors which enter into the process—chemical, physical, and mechanical—the number of possible permutations and combinations must be very great indeed. Any definite result or definite conclusion which can be obtained from such conditions is greatly to be welcomed. To this end, however, it is highly desirable that some information should be forthcoming as to the relation between corrosion and time, on which the real comparison of the behaviour of the various materials so largely depends. In view, moreover, of the difficulty of attaching any significance to results from isolated, or sometimes even duplicated specimens under such complex conditions, it may well become necessary to base conclusions only on results that have been confirmed by tests conducted in multiple.

It is for reasons such as these that I would urge the exercise of considerable care in interpreting the experimental results. For example, from the data given in Table I, there appears to be no justification for attributing a slightly beneficial effect to the addition of 0·15 per cent. of copper to steel. The results are given in duplicate for the plain steel and copper steel respectively;

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[†] Chemical Research Laboratory, Department of Scientific and Industrial Research, Teddington.

but the difference between one pair of duplicates exceeds the difference between the means; therefore one cannot say that the results bring out any appreciable difference in behaviour between the materials.

In connection with the results for the copper specimens, Dr. Friend has been good enough to refer to my aerial tests. Considering the evidence, however, this cannot be said to bring out any correlation between the two groups of results. The actual (loss of weight) figures in the atmospheric tests were as follows :—

High-conductivity copper .	1·768	Arsenical copper . .	0·786
„ „ „ .	1·788	„ „ . .	0·782

On the other hand, the figures in the present paper do not show any marked restraining effect due to arsenic; the unduplicated value for copper containing 0·43 per cent. arsenic is certainly lower than that for the unduplicated value for the arsenic-free material; but since the duplicated values for 0·39 per cent. arsenic are appreciably higher, one is scarcely justified in reaching any definite conclusion as to the effect of arsenic. After all, the difference between the atmospheric and sea-water results is not surprising, because there can be no doubt that we are dealing with entirely different mechanisms. In ordinary atmospheric corrosion the attack is definitely associated with the presence of sulphur dioxide in the atmosphere; this is oxidized at the metal surface with formation of sulphate. There is good reason to believe that the action of arsenic is directed specifically towards restraining this process; but, of course, it does not necessarily follow that any comparable restraining effect will take place during complete immersion in sea-water. Most probably a similar state of affairs holds good in the case of copper in steel, which would explain why marked protection has been recorded for copper–steels in the atmosphere, particularly in industrial atmospheres, whilst little or no protection is afforded against sub-aqueous corrosion.

Dr. Friend's results with the cold-worked nickel–chromium–iron alloys are of interest as showing that a considerable amount of strain has set up no appreciably greater corrosion in these materials, notwithstanding that the air-formed film might be expected to undergo cracking on account of the stresses in the underlying metal.

Finally, I should like to refer to the interesting observations which Dr. Friend makes about the accumulation of shelly fauna. The aversion which these fauna show towards copper is striking, and affords another illustration of the toxic effect of copper towards the lower organisms, as illustrated in the manufacture of certain anti-fouling preparations. It is interesting also, although of course not surprising, that the organisms are more harmful dead than alive; incidentally, the rather greater effect on the alloys containing nickel is no doubt due to the presence of sulphur in the decaying organic matter. There are other cases in which organisms are more harmful to metals when alive than when dead, as, for example, the death-watch beetle, which will bore through lead sheet as well as wood, but in these cases the evil they do lives after them !

Dr. Friend (*in reply*) : In reply to Mr. Lewis, I would say that flat bars were used for the riveting tests, the rivets being prepared from small round bars. No microscopic examination of the actual bars was made. Undoubtedly specimen R1708 was austenitic, as Mr. Lewis concludes. It would be difficult, if not impossible, to put it in any other condition except by drastic cold-work ; as far as heat-treatment was concerned, it was a stable, austenitic steel. After riveting, which was done in the cold, the severely deformed parts of the rivets would presumably contain some martensite, as they were slightly magnetic. It is unlikely, however, that even in these parts the structure would be entirely or even preponderatingly martensitic. The adjacent parts of the bar would be practically entirely austenitic in character.

Truth is stranger than fiction. Mr. Lewis cannot imagine some type of corrosion not taking place where there would be a change of structure in adjacent parts of the material. Neither can I; but the fact remains that there was no sign of corrosion either in the severely deformed rivet heads or on the adjacent unaltered austenitic bar, even after an exposure of three years. Actually the riveted bars had been exposed for a longer total period than this; they had previously been exposed for two years to the much more rigorous action of a stormy sea at Weston-super-Mare.

Bar R1733 would consist of ferrite grains through which fine particles of carbide were dispersed more or less uniformly. Cold-work would distort the ferrite grains more or less severely, but cause no phase charge.

It is well known, of course, that intergranular attack is sometimes produced in the austenitic nickel–chromium stainless steels; this type of attack, however, appears to be only produced in these materials when, owing to faulty heat-treatment, they contain free carbide as membranes round the austenitic grains. This structural condition, as also the intergranular attack, may be produced in bars, forgings, castings or any other form in addition to sheets. It is gratifying to note that Mr. Lewis obtains confirmation of some of my results.

THE "FOGGING" OF NICKEL.*

By W. H. J. VERNON,† D.Sc., Ph.D., D.I.C., MEMBER.

SYNOPSIS.

A study has been made of the characteristic filming or "fogging" that occurs under suitable conditions on polished nickel surfaces. The effect is attributed mainly to the catalytic oxidation of small amounts of atmospheric sulphur dioxide; suspended sulphates play a minor part. There is a critical relative humidity, below which the metal may be exposed, apparently indefinitely, without action taking place, and above which fogging readily occurs. The process is affected by light, film formation being approximately halved when light is completely excluded. In the early stages the film contains nickel sulphate with free sulphuric acid; later, it passes into basic nickel sulphate. The formation of the primary film may be largely suppressed by pre-exposure of the metal to an atmosphere containing traces of hydrogen sulphide, which appears to act as an anticatalyst. Fogging may also be inhibited by alloying the nickel with chromium, or by covering the surface with a film of lanoline.

THE brilliant lustre and high degree of whiteness that characterize the surface of polished nickel constitute an important factor in the wide application of this metal as a protective and decorative coating. An offset to this, however, is the readiness with which the metal assumes, under many conditions of exposure, a dull creamy film, whereby the initially high reflectivity is rapidly obscured; this phenomenon may conveniently be described as "fogging." Considering the practical problems to which it gives rise, the phenomenon is doubtless of considerable economic importance; yet, judged by the published literature, it is one to which surprisingly little systematic investigation has been devoted. Some tests by the present author on the fogging of nickel and nickel–copper alloys were described in the First Report to the Atmospheric Corrosion Committee of the British Non-Ferrous Metals Research Association;‡ and at a later date a few additional results were communicated privately to the Association.§ The object of the present paper is to give a connected statement of the subject as a whole and to record the results of certain experiments which have been conducted quite recently.

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† Chemical Research Laboratory, Department of Scientific and Industrial Research, Teddington.

‡ *Trans. Faraday Soc.*, 1924, 19, 880.

§ *Bull. British N.-F. Metals Res. Assoc.*, 1927, (21), 16.

PREVIOUS RESULTS.

The earlier observations * may be summarized as follows. In an indoor atmosphere maintained sufficiently above the dew-point, a polished nickel surface remains bright apparently indefinitely. If, however, the minimum temperature approaches near to the dew-point temperature, then the characteristic "filming" or "fogging" of the surface occurs. In the early stages the film can be removed quite readily, merely by wiping with a cloth, leaving the brightness of the underlying metal apparently undiminished. Very soon, however, more vigorous treatment is needed in order to dislodge the film, and at a later stage it cannot be removed completely without abrading the metal. Evidently an initial physical condensation is followed by chemical reaction between the deposited film and the underlying metal. The minimum relative humidity necessary for fogging was not systematically worked out; but from the recorded values it appeared to be in the neighbourhood of 70 per cent.

In contrast with the fogging of nickel, the tarnishing of copper and silver appears to proceed entirely by way of a metal-gas reaction. Thus, tarnishing is actually impeded at high humidities, but proceeds readily at low humidities; fogging, on the other hand, is facilitated by high humidities and ceases at low humidities. The distinction between tarnishing and fogging is well brought out by the behaviour of nickel-copper alloys. Here the tendency for tarnishing increases with the copper content, whilst the tendency for fogging increases with the nickel content. Various alloys containing copper and nickel were exposed, together with specimens of the metals themselves, to atmospheres favouring respectively fogging and tarnishing. In the "fogging" atmosphere the attack commenced on the pure nickel specimen and proceeded through the series of alloys with an intensity proportional (so far as could be judged by visual examination) to the nickel content, the specimen of pure copper being practically unaffected. In the "tarnishing atmosphere" the exact converse obtained, the attack proceeding from the copper and copper-rich end of the series, whilst the nickel specimen remained unaffected.

Information was obtained on the composition of "fog films" after prolonged exposure.† A specimen of heavily fogged nickel (99 per cent. nickel) after exposure in an indoor atmosphere for a period of four years, was treated for the removal of film by rubbing with cotton wool moistened with alcohol. The surface of the underlying metal was definitely etched, and all trace of the original lustre had dis-

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* 1924 Communication (*loc. cit.*). † 1927 Communication (*loc. cit.*).

appeared. The weight of film removed was 82·6 mg. (area of specimen was 100 cm.^{2}). The material was insoluble in water; and an analysis gave Ni 27·9 per cent., SO_4'' 21·7 per cent., showing that it consisted essentially of basic nickel sulphate. This result provides another point of contrast between the fogging of nickel and the tarnishing of copper; for the sulphur in a tarnish film, although usually accompanied by oxide, is present entirely as sulphide. In the tests which J. C. Hudson * conducted in Stevenson screens, the corrosion product on nickel specimens also consisted essentially of basic sulphate; the extent of corrosion was greatest in the most polluted atmosphere, and in this atmosphere nickel suffered much more severe attack than other non-ferrous metals. It would appear that the conditions of a Stevenson screen, in which the specimen is subjected to high humidities although screened from rain, are such as to exaggerate greatly the incidence of fogging; the severe corrosion which ensues under such conditions may be regarded, indeed, as an advanced stage of "fogging," intensified by the hygroscopicity of the corrosion product itself. Hudson has also shown that on free exposure to the open air, whereas the corrosion of other common non-ferrous metals and alloys is increased, that of nickel and nickel alloys is actually reduced, owing to the fact that nickel is then free from the peculiar disability which distinguishes it under screened conditions.

As already noted, copper, when alloyed with nickel, is neutral in respect to its influence on fogging. Chromium, on the other hand, has a marked inhibitory effect. Specimens of chromium–nickel alloys, prepared in exactly the same way as the ordinary nickel specimens, remained quite bright in an atmosphere in which the nickel specimens fogged heavily. Although the lowest content of chromium employed was 15 per cent., the result was sufficiently striking to suggest that favourable results might still be obtained from the addition of chromium in smaller proportions. An interesting corollary to this result is again provided by the work of Hudson, who found that chromium greatly reduced the attack on nickel under Stevenson screen conditions; so much so that a chromium–nickel alloy was one of the most resistant of the various materials examined.

Thin films of grease afford efficient protection against fogging; their drawback, of course, is the way in which they detract from the appearance of a polished surface. Tests in which as much as possible of the grease was removed by wiping with a cloth showed that lanoline is much more effective than vaseline when the thinnest films are con-

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* Third Report to Atmospheric Corrosion Research Committee, *Trans. Faraday Soc.*, 1929, 25, 200.

cerned. If the protection is required only for a limited period, as during storage, the film can be removed at any time by means of any of the usual solvents and the original brightness at once restored. The lanoline may conveniently be applied in the form of a solution in an organic reagent. Protection may also be obtained by the use of transparent lacquers, subject to the usual disadvantages inherent to artificially applied coatings. It is of interest to note that certain lacquers have a tendency to exhibit a species of fogging on their own account (technically known as "blooming" or "blushing"), especially if exposed to humid conditions before the lacquer has thoroughly set.

New Experimental Work.

Some of the experiments to be described were suggested by a practical example of fogging, which, when it came to the notice of the author, appeared to have interesting implications. In a shop window employed for the display of cameras (the conditions of a shop window, it may be noted, are usually particularly favourable for fogging), nickel fittings on the most exposed parts were subject to the most severe fogging, whilst those in sheltered positions, as for example in the shadow thrown by the bellows, were comparatively immune. The observed effects were such as to suggest that the process was influenced by light. Accordingly, experiments were started to test this possibility. Preliminary tests, in which polished nickel specimens were exposed in glass vessels with and without the exclusion of light, soon revealed a difficulty. For whether the air remained stagnant or whether it was drawn through the vessels, the rate of fogging was enormously reduced as compared with that of a freely exposed specimen. In several experiments, although no change was visible on the "dark" specimen, the extent of fogging on the "light" specimen was so slight as to preclude any very definite conclusions being reached. The experiments were therefore repeated under more drastic conditions, the apparatus being set up on the roof of the Chemical Research Laboratory, with the vessels freely exposed to the weather, the length of the glass tube leading into each vessel being reduced to the minimum.

The type of vessel used in the experiments is illustrated in Fig. 1. The delivery tubes pass through the ground-on cap, which fits on to the lower cylindrical part; the specimen is suspended by a glass hook from the upper delivery tube. Two such vessels were rendered opaque, partly by wrapping with black paper and partly by coating with black varnish; two identical vessels were left free from covering of any kind. The whole set of four tubes, each containing a specimen prepared as described below, was supported on a stand as shown in the photograph (Fig. 2); the stand faced due south. Provision was made for aspirating air at a uniform rate through the vessels by means of a filter pump, the rate of flow through each being shown by a "bubbler" placed on the exit side of the air stream.

The nickel sheet, from which the specimens were cut, was in the fully annealed condition; from the point of view of "fogging," however, this was probably of no significance, because previous observations had failed to show any difference in behaviour between the hard and the soft material. The sheet was 1 mm. in thickness and each specimen measured 8·3 × 2·3 cm. (these dimensions were employed for convenience in fitting into the holder used in the reflectivity determinations). The specimens were polished to a bright "mirror" finish under works conditions. Before use they were freed from traces of polishing material by immersion in pure carbon tetrachloride, aided

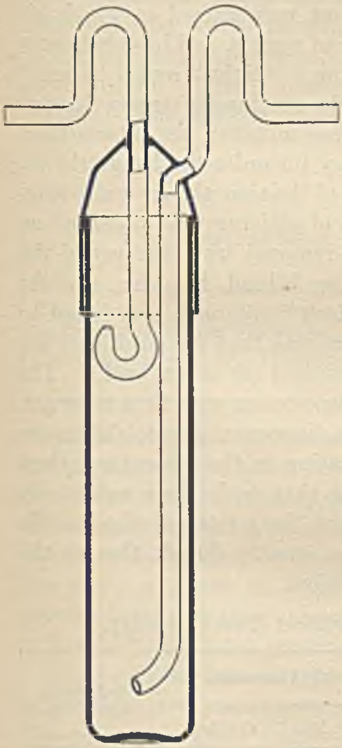

FIG. 1.
(½ Full size.)

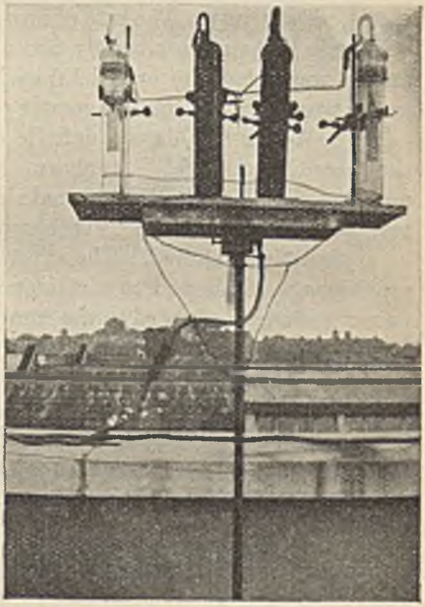

FIG. 2.

by gentle rubbing with cotton wool. This procedure was necessary on account of subsequent weighings; but it had already been found to have no apparent effect on the fogging of the metal. In certain of the experiments, the specimen, besides being carefully weighed, was submitted to a measurement of its surface reflectivity.*

Influence of Light.

On January 19th, 1931, an experiment was started in which air was drawn continuously through one pair of vessels, and intermittently through another pair, each pair comprising a "light" and a "dark" vessel, respectively. The rate of flow of the continuous stream through each vessel was approximately 250 c.c. per minute; the intermittent stream was passed for only ½ hr. each day (in order to change the air in the vessel), so that for the greater part of the time the air was "stagnant." Within two days a definite film of moisture was observed on the "continuous light" specimen. On removal from the vessel the moisture film quickly disappeared, leaving behind, however, a slight permanent fog film; the "continuous dark" specimen was found to be apparently unaltered. The experiment was then resumed, and the specimens were allowed to remain undisturbed for seven weeks. The pair of specimens exposed to the continuous stream were then removed. Both had fogged, the "light" specimen, however, appreciably more than the "dark." After vacuum desiccation in the laboratory, their weight increments were determined, together with their reflectivity losses. The results (Table I) showed that the weight of film on the specimen exposed to the light was almost exactly double that on the specimen from which light had been excluded.

TABLE I.—"*Continuous*" *Experiment* (*Seven Weeks*).

	Weight Increments.		Reflectivity Losses. %.
	Actual. Mg.	Mg./dm.^{2}.	
"Dark" specimen . . .	0·73	1·9	55
"Light" specimen . . .	1·47	3·8	95

Influence of Light and of Previous Exposure.

The "intermittent" experiment was continued for 15 weeks. Neither the "light" nor the "dark" specimen then showed any sign of fogging. For a further period of 3 weeks the specimens were allowed

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* By means of a reflection photometer at the Paint Research Station, Teddington (through courtesy of Dr. L. A. Jordan and co-operation of Mr. R. F. Hanstock). The method is normally used for the measurement of the gloss of flat (painted) panels. Unfortunately the nickel specimens were not sufficiently flat; only in a few instances, therefore, could reproducible values be obtained.

to remain in their respective vessels with the air stream completely stopped. Passage of air was then resumed as a *continuous* stream; and at the same time two new specimens were exposed in the other pair of vessels, the air stream being maintained through the whole at an approximately equal rate. This was continued for 16 weeks, when all specimens were removed. The striking result then emerged that those specimens which had been previously exposed to "stagnant" conditions (34 weeks in all) had fogged very much less than those which had been exposed only to the continuous stream. In each case, however, the "light" specimen had fogged definitely more than the "dark." The weights of the respective films are given in Table II, together with the corresponding reflectivity losses. Thus, just as in the previous experiment, the weight of the film produced under light conditions is approximately double that produced in the dark; furthermore, the weight of film on specimens exposed only to the continuous stream is approximately four times that on corresponding specimens previously exposed to stagnant air. Maximum differences (to the extent of 1 : 8) are thus exhibited between previously exposed specimens in the dark and more recently exposed specimens in the light.

Table II.

Conditions of Air Supply.		Weight Increments.		Reflectivity Losses. %.
		Actual. Mg.	Mg./dm.².	
"Stagnant" (18 weeks) followed by continuous stream (16 weeks)	Dark	0·379	0·99	
	Light	0·812	2·12	22
Continuous stream only (16 weeks)	Dark	1·696	4·45	
	Light	3·243	8·50	97

It is evident from the preceding results that the fogging of nickel necessitates the continuous replenishment of air near the specimen. The protective effect induced by previous exposure to stagnant conditions at once suggests an analogy with earlier results with copper, in which it was shown that inhibition from tarnishing could be obtained either by previous exposure of the specimen to relatively pure air,* or, alternatively, by previous confinement in a limited volume of the very same air, which, in larger quantity and allowing free diffusion, was responsible for the tarnishing from which immunity was sought.† In the case of copper, protection was attributed to the formation, during the preliminary period, of an invisible film of oxide, atmospheric

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* *J. Chem. Soc.*, 1926, 128, 2273.

† Second Report to Atmospheric Corrosion Research Committee, *Trans. Faraday Soc.*, 1927, 23, 183.

impurity being present in too low a concentration to interfere with the continuity of the film. It was found, in fact, that the effect could be reproduced by heating the specimen in air for 1 hr. at temperatures between 75° and 100°. At higher temperatures the film becomes thick enough to display interference colours; at lower temperatures protection ceases, probably because the thickness of the film has not reached that of the unit space lattice of cuprous oxide. In order to ascertain whether the presence of oxide films might be associated in a similar way with the protection of nickel against fogging, the following tests were carried out.

Influence of Previously Heating Specimen in Air.

A series of specimens was heated in air for 1 hr. at (respectively) 225°, 250° (no visible change), 275° (very faint yellow), 300°, 325°, and 350° C. (faint yellow). On subsequent exposure to a fogging atmosphere for 32 days, the weight-increment of a blank specimen (due to fogging) was 0·33 mg., whilst the weight-increments of heat-treated specimens ranged from 0·31 to 0·36 mg.; no protective influence due to the previous oxidation could be detected. Although these results were definitely unfavourable to the oxide-film hypothesis as applied to protection against fogging, some attempt was made to account for the apparent difference in behaviour between oxide films produced at the higher and lower temperatures. The influence of humidity was examined by heating specimens in atmospheres the humidity of which had been artificially raised. Experiments were also carried out in which any cracking of the film was minimized by very slow cooling, extending up to several days. In no case, however, was any superiority in behaviour observed on subsequent exposure to a fogging atmosphere; indeed, slowly-cooled specimens fogged to a rather greater extent than specimens cooled in the normal manner. Yet another alternative explanation might be sought in possible differences in structure between oxide films produced at the lower and higher temperatures. Nevertheless, experiments with synthetic atmospheres (to be described under a later heading) have shown that it is possible to explain the protection induced by previous exposure to ordinary air at ordinary temperatures quite independently of the formation of oxide films.

Influence of Filtering and Screening the Air.

Previous work has shown * that the rusting of iron above the dew-point may be entirely prevented either by filtering the air or by the

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* Vernon, "Second Report to the Atmospheric Corrosion Research Committee" (1927), *loc. cit.*, p. 159.

simple expedient of screening the specimens behind a single thickness of muslin. A specimen of iron suspended within a muslin "cage" will remain bright indefinitely, whilst a similar specimen outside the cage may rust heavily; moreover, on subsequent (normal) exposure the pre-exposed specimen displays marked resistance to further rusting. In order to examine the effect of filtering the air on the fogging of nickel, four vessels, as used in previous experiments (Fig. 1), were employed. Light was not excluded from any of the vessels, but to the entry tube of two of them a Jena glass air-filter (mean diameter of pores, 20–30 microns) was attached; in each vessel a polished nickel specimen was suspended. The whole apparatus was set up on the roof of the Chemical Research Laboratory. The rate of flow of air was approximately 250 c.c. per minute at the start, slowing down to approximately 80 c.c. per minute at the end of 2 weeks, owing to the choking of the filters. The rates of flow of the unfiltered streams were adjusted so as to keep approximately equal to those of the filtered streams. The effect of filtering the air was to reduce, but not to eliminate, the fogging of the specimens. After 2 weeks the weight of film on the specimens exposed to filtered and unfiltered air, respectively, was 1·25 and 3·17 mg.

In addition to the foregoing, an experiment with a muslin "cage" similar to that used in the iron experiments has been conducted in an indoor atmosphere (relative humidity varying between 65 and 75 per cent.). Two specimens of polished nickel were suspended inside the "cage" and two immediately outside. The four specimens were set in line, parallel with and at a distance of 9 in. from the wall of the room, which was an outer wall of the building. After 2 weeks' exposure the specimens outside the cage had fogged appreciably; the weight-increments were 0·19 and 0·16 mg. There was very little to choose between the fronts and the backs of these specimens, the estimated reflectivity loss being 15 per cent. The weight-increments of the specimens inside the cage were 0·12 and 0·11 mg.; these specimens, however, showed a marked difference between front and back, the fronts being practically unaltered (estimated reflectivity loss, *less than* 1 per cent.), whilst the backs were approximately equal in appearance to specimens outside (estimated reflectivity loss, 15 per cent.). Whereas, therefore, observation of the surfaces which faced the room would suggest that screening had a pronounced effect, the appearance of surfaces which faced the wall would lead to a negative conclusion. There is evidently a chilling effect due to the wall, which would be expected to favour fogging. It is striking, however, that this is apparent only within the muslin cage where the influence of suspended particles is negligible. The conclusion to be reached from the foregoing results is that fogging is due partly to suspended matter and partly to gaseous matter; furthermore, the latter component appears to be the more readily affected by relative humidity.

In order to obtain information bearing on the nature of the suspended matter, the residue on a glass air-filter (already described) has been examined after prolonged passage of air both outside the building and in a room indoors. The presence of combined ammonia was found, together with excess of sulphuric acid. The ratio of $NH_3 : H_2SO_4$ was 1 : 10·3 in the open air and 1 : 2·0 in the laboratory. Clearly, ammonium sulphate is a constituent of the intercepted matter; but possibly other alkali sulphates are also present.* The condensation of these substances when the air is sufficiently humid is not difficult to understand.

Production of "Fog Films" in Synthetic Atmospheres.

Recent work on copper exposed to synthetic atmospheres † has shown that the oxidation of sulphur dioxide is catalyzed at the metal surface with the formation of copper sulphate; this is accompanied either by excess of copper hydroxide or by excess of sulphuric acid according as the concentration of sulphur dioxide in the atmosphere falls below or exceeds 0·85 per cent. An enormous acceleration in the rate of film formation (especially within the region in which free sulphuric acid is formed) takes place when a certain critical humidity (in the neighbourhood of 70 per cent. relative humidity) is exceeded. The much greater catalytic activity of nickel suggests that with this metal the deposition of a film of sulphuric acid should take place at very much lower concentrations of sulphur dioxide. Experiments have been carried out in which nickel specimens have been exposed to various synthetic atmospheres. The appropriate technique has been described in connection with the previous work; it involves the preparation of the atmospheres in bell-jars, usually of 10-litre capacity, which are themselves contained in an air-thermostat at 25° C. In these experiments it has been found that all the phenomena of fogging may be reproduced in an atmosphere containing 0·003 per cent. sulphur dioxide. Provided this concentration is not exceeded, the metal remains bright for weeks at a relative humidity of 50 per cent.; at 75 per cent. relative humidity, however, fogging occurs fairly rapidly,

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* In this connection it is interesting to note that Dr. G. F. New, of the Paint Research Station, Teddington, found in 1928 that many paint and varnish surfaces, and also certain other surfaces, acquire from suitable atmospheres a crystalline deposit of ammonium sulphate. (Private communication.)

† W. H. J. Vernon, *Trans. Faraday Soc.*, 1931, 27, 255, 582.

the surface being slightly filmed after 1 day's exposure. The resulting film appears to be identical in properties with that produced on normal exposure. It may be removed readily in the early stages merely by wiping with a cloth, leaving the brightness of the underlying metal apparently undiminished; subsequently, however, it cannot be removed without abrasion of metal. Analyses of films removed in the early stages from specimens normally exposed and from those in the synthetic atmosphere have shown that the composition is similar; in each case the film contains nickel sulphate with free sulphuric acid. The similarity between films produced in the synthetic atmospheres and those produced by normal exposure has also been confirmed by microscopic examination.

Suppression of Fogging by "Poisoning" the Nickel Surface.

The conclusion to be reached from the foregoing results is that fogging is due mainly to the catalytic activity of nickel in bringing about the oxidation of sulphur dioxide at the metal surface. According to this mechanism, the process should be capable of suppression by previously exposing the metallic surface to conditions such that the catalyst is poisoned. In order to test this, the effect of traces of hydrogen sulphide has been examined. In a first series of experiments, four specimens were exposed respectively to the following atmospheres (concentration of H_2S and period of exposure stated in each case; relative humidity was 75 per cent. throughout); 0·0001 per cent. (1 day); 0·00002 per cent. (1 day); 0·00002 per cent. (3 hrs.); "Blank" (no H_2S) (5 days). Following this preliminary exposure (and immediate vacuum desiccation on its conclusion) the specimens were weighed and then exposed to an atmosphere containing 0·005 per cent. sulphur dioxide (relative humidity, 75 per cent.). After 1 day appreciable fogging had occurred; but the specimen which had been previously exposed to the lower concentration of hydrogen sulphide for the shorter time had undergone much less change than any of the other specimens. The weight-increments (Table III) confirmed the impression gained from visual examination. A second series of three specimens was then exposed to an atmosphere containing only the lower concentration of hydrogen sulphide (0·00002 per cent.) for shorter times, namely, 2 hrs., 1 hr., and ½ hr., respectively. None of the specimens was visibly affected by the treatment. After vacuum desiccation and weighing they were then exposed (together with a "blank" specimen that had not been previously exposed at all) to the same fogging atmosphere as before. After 1 day an interesting state of affairs was revealed. The blank specimen had fogged definitely more than any of the pre-exposed specimens. Of these the degree of fogging increased with time of previous exposure (thus confirming the previous results), that specimen which had been previously treated for the shortest time being relatively

TABLE III.

Series.	Preliminary Exposure.		Subsequent Exposure.	
	Atmosphere.	Period.	(Atmosphere containing 0·005% SO_2, 75% Relative Humidity, 1 Day's Exposure.) Weight Increments.	
			Actual. Mg.	Mg./dm.^{2}.
I	0·0001% H_2S, 75% R.H.	1 day	1·65	4·3
	0·00002% H_2S ,,	1 ,,	1·17	3·25
	,, ,,	3 hrs.	0·68	1·77
	No H_2S ,,	5 days	1·18	3·35
II	0·00002% H_2S, 75% R.H.	2 hrs.	0·537	1·40
	,, ,,	1 hr.	0·413	1·08
	,, ,,	½ ,,	0·373	0·97
	Not previously exposed (" blank ")	...	0·817	2·13

bright. The visual observations were again borne out by the weight-increments (Table III). Hence, whilst previous exposure to the atmosphere containing hydrogen sulphide has afforded definite protection, the best result is exhibited by the specimen on which the gas has had the least time to act. Atmospheres containing lower concentration of hydrogen sulphide than that used in the second series of experiments (one volume of H_2S in 5 million volumes of air) are inconvenient to prepare synthetically. It is reasonable to assume, however, that protection would continue to be obtained by previous exposure to still lower concentrations of hydrogen sulphide for longer periods. Previous tests have shown * that the concentration of hydrogen sulphide normally present in town air reaches a maximum in winter-time of something in the order of one volume of H_2S in 36 million volumes of air; these concentrations are sufficient to produce quite marked effects on suitable metal surfaces.

The foregoing results appear to accord quite well with a catalytic mechanism of fogging. It would be expected that the concentration of hydrogen sulphide necessary to poison the active centres on a given surface would be extremely low, certainly much lower than that necessary to produce a film in the ordinary sense of the word. They appear,

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* Vernon, "Second Report to the Atmospheric Corrosion Research Committee" (1927), *loc. cit.*, p. 122.

moreover, to have an important bearing on the results recorded in an earlier part of the paper, in which it was shown that prolonged exposure to ordinary stagnant air affords marked protection on subsequent exposure to fogging conditions. In the light of the present results it seems most probable that this protection is due to a slow poisoning of the metal surface by traces of hydrogen sulphide or possibly some other anticatalyst. This would readily account for the fact that the protection cannot be reproduced by short-period oxidation at higher temperatures.

ADDENDUM.

Influence of Traces of Hydrogen Sulphide.—In the concluding section of the paper it was shown that a considerable degree of immunity from fogging could be obtained by pre-exposure of the specimen to purified air to which very small amounts of hydrogen sulphide had been added. The results strongly suggested that the protection induced by pre-exposure to ordinary air was also due to the presence of traces of this gas. This conclusion has since been put to a further test by examining the effect of ordinary air from which traces of hydrogen sulphide have been *removed*. In this experiment four specimens were suspended, each in the same type of vessel previously employed (Fig. 1). The air in each vessel was changed daily by aspirating air at a uniform (slow) rate for ½ hr.; the conditions thus corresponded with those of the original "intermittent" experiment (p. 126), except that light was not excluded from any of the vessels, and that the air entering two of them was first led through a tube packed with granulated silver. The interception of any hydrogen sulphide was thus ensured without risk of introducing any complicating factor. After exposure in the vessels for 39 days (without visible change), the specimens were transferred, together with two freshly polished "blanks," to a synthetic atmosphere containing 0·003 per cent. sulphur dioxide at a relative humidity of 70

TABLE IV.

Conditions of Previous Exposure. (39 days.)	Weight Increments on Exposure to Synthetic Atmosphere (0·003% SO_2, 75% relative humidity) for 2 days.	
	Actual, Mg.	Mg./dm.^{2}.
Ordinary air	0·02	0·05
" "	0·02	0·05
Purified air	0·178	0·46
" "	0·188	0·49
Not previously exposed (" blank ") .	0·149	0·39
" " " " .	0·153	0·40

per cent. Within 2 days the two specimens that had been previously exposed to the ordinary unpurified air showed very slight fogging at the edges only; on the other hand, the two specimens that had been exposed to the purified air had fogged appreciably all over, actually to a rather greater extent than the "blank" specimens. The respective behaviour of the specimens is well brought out by the weight-increments (Table IV). The result of this experiment, employing the "analytic" method, thus amply confirms the conclusions previously reached from the "synthetic" method as to the part played by traces of hydrogen sulphide during pre-exposure of the specimen to ordinary air.

Composition of "Fog Films."—The similarity between the composition of films produced in normal and synthetic atmospheres in the early stages of exposure was referred to on p. 131. Further experiments have shown that in each case there is a progressive increase in basicity. This is illustrated by the formulæ given in Table V, calculated from analyses of the films after 21 days' and 88 days' exposure.

TABLE V.

Period.	"Normal" Atmosphere.	Synthetic Atmosphere.
21 days	$NiSO_4.0{\cdot}26H_2SO_4$	$NiSO_4.2{\cdot}15H_2SO_4$
88 days	$NiSO_4.0{\cdot}33Ni(OH)_2$	$NiSO_4.0{\cdot}15H_2SO_4$

The method followed was to dissolve the film in dilute acetic acid ($0{\cdot}5N$; this was without action on the metal under the conditions of the test). Nickel was estimated colorimetrically by dimethylglyoxime; sulphate was precipitated as barium sulphate and estimated by comparison of the resulting opalescence with that produced in a standard solution. Ammonia, which was definitely present (as ammonium sulphate) in the "natural" product (but not of course in the synthetic product), was estimated by Nessler reagent.

The presence of ammonium sulphate in the films produced on normal exposure to the air is of special interest, as confirming the conclusions reached from the "filtering experiment" described in the text. It is significant, moreover, that the proportion of this substance increases greatly with time. At 21 days there was not sufficient to estimate by the Nessler reagent; at 88 days it was present in appreciable quantity, and an appropriate correction was made in calculating the relative proportion of other radicals. It would seem that the accumulation of ammonium sulphate in the product does not become appreciable until the surface of the metal has become covered with a primary film through the oxidation of sulphur dioxide.

SUMMARY AND CONCLUSIONS.

The "fogging" of nickel consists in the formation of a creamy-white film on the polished surface of the metal. In the early stages the film contains nickel sulphate with associated sulphuric acid; it can then be removed readily by wiping with a cloth; subsequently its removal is effected with greater difficulty, and finally it cannot be dislodged without abrasion of metal. In this condition the film consists of basic nickel sulphate. Copper, when alloyed with nickel, is neutral in respect to its influence on fogging, the tendency to fogging of copper–nickel alloys being approximately proportional to the nickel content. Chromium, on the other hand, has a marked inhibitory effect. Thin films of grease effectively prevent fogging; lanoline is superior to vaseline for this purpose when the thinnest films are concerned.

For the initial condensation to take place, the relative humidity of the atmosphere must exceed a certain critical value in the neighbourhood of 70 per cent.; at lower relative humidities the metal remains bright indefinitely. Fogging is due partly to the presence of suspended sulphates in the air, and partly (probably mainly) to the presence of small amounts of sulphur dioxide, which are catalytically oxidized at the metal surface when the critical humidity is exceeded. The fogging process is affected by light, film formation being approximately halved when light is completely excluded. Prolonged exposure of polished nickel to stagnant air at ordinary temperatures induces a large measure of immunity to fogging on subsequent free exposure. This effect, which cannot be reproduced by short periods of exposure at higher temperatures, is probably due to the poisoning of the nickel surface by traces of an anticatalyst. A similar effect has been induced artificially by traces of hydrogen sulphide.

ACKNOWLEDGMENTS.

The author wishes to acknowledge the valuable part taken in the experimental work by Mr. E. G. Stroud; he is indebted also to Mr. W. H. Sullivan for much assistance. Acknowledgment is due to Messrs. Henry Wiggin & Co., who kindly supplied the nickel sheet used in the experiments; to Mr. W. R. Barclay, O.B.E., for his interest in this connection; to the Council of the British Non-Ferrous Metals Research Association for permission to incorporate certain of the earlier results; and particularly to Dr. R. S. Hutton, by whom the attention of the author was first directed to the phenomenon of fogging. The more recent work has been carried out for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research; and the thanks of the author are due to the Chairman,

Professor Sir Harold Carpenter, Kt., F.R.S., and to Professor G. T. Morgan, O.B.E., F.R.S., Director of Chemical Research, for facilities afforded and for permission to publish.

DISCUSSION.

Mr. U. R. Evans,* M.A. (Member): Dr. Vernon's skilful investigation is very much to be welcomed. His care and accuracy always invite confidence, and the interpretation which he has given can be accepted in every essential respect.

The idea that traces of sulphur dioxide in the air are oxidized catalytically affords a satisfactory explanation of three important facts: (1) It explains why nickel, with its high catalytic activity, is more susceptible to this type of attack than any other metal known; (2) it explains why motion in the air is needed; the amount of sulphur dioxide in ordinary air is very small, and only if the air is constantly renewed will the nickel surface pick up a sufficient amount; and (3) it explains why fogging does not occur when the nickel is actually exposed to rain, which would wash away the sulphur compounds and prevent them from accumulating to the required concentration; moreover, a film of rainwater is much thicker than a film of condensed moisture, and it would take much longer to reach a dangerous concentration in a rain-film than in a dew-film.

Dr. Vernon is right in describing the effect of hygroscopic dust as a minor one. If dust played a main part, there would be no reason why other metals with low catalytic activity should not be as susceptible as nickel. Probably the rôle played by hygroscopic matter is simply to collect moisture; the sulphur dioxide can then dissolve in that mixture, and since a solution of sulphurous acid is more prone to oxidation than anhydrous sulphur dioxide, the sulphuric acid will be produced more quickly.

My confidence in the view that the unique susceptibility of nickel to sulphur dioxide is connected with catalytic oxidation is increased by a recollection of some qualitative observations made ten years ago.† I exposed a large number of dry metals and alloys in the upper parts of vessels containing, in their lower parts, certain volatile acids or alkalis, such as sulphurous acid, hydrochloric acid, ammonia, and others. In some cases the materials suffered no serious change; in others corrosion occurred, and sometimes the corrosion product became perceptibly damp or moist; and it was in those cases, in which the corrosion product picked up liquid from the *unsaturated* atmosphere, that the corrosion was most rapid. In three cases out of more than one hundred combinations tried, the metal became not only damp, but running wet, and here the corrosion was very rapid indeed. In the first, zinc placed over hydrochloric acid started to "weep tears" of a syrupy liquid, and was eaten through within a few weeks; for zinc chloride, the corrosion product, a very hygroscopic substance, picked up moisture so that, in the place of slow dry corrosion, rapid wet corrosion set in. Secondly, copper placed over ammonia began to shed tears of a purple liquid containing a complex nitrite; this shows that ammonia on the surface of copper may be catalytically oxidized by air to a nitrite. Thirdly, nickel placed over saturated sulphur dioxide solution gave out a pale green liquid containing nickel sulphate, and here the hygroscopic substance which succeeded in absorbing moisture from an unsaturated atmosphere can only have been sulphuric acid; presumably the reason why the nickel became thoroughly

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* Cambridge University.

† *Trans. Faraday Soc.*, 1923, **19**, 201.

wet, whilst the other metals remained dry or merely moist, was because the nickel was catalytically far more active for this particular oxidation than any of the other metals tested.

Regarding the effect of pre-exposure to stagnant air in preventing fogging, I think Dr. Vernon's explanation is the right one. There *is* an oxide film formed on nickel by exposure to air at ordinary temperatures; it has in fact been detected optically by Dr. Tronstad,* but he also showed the film to be soluble in sulphuric acid, and therefore it is not surprising that, in the case of nickel, pre-oxidation has very little action in preventing fogging, although in protecting copper from a tarnishing atmosphere, as Dr. Vernon showed some years ago, an oxide film is of very great importance indeed.

Dr. J. S. OWENS †: Dr. Vernon has referred in his paper to particulate matter and to some crystals which Dr. New discovered at the Paint Research Station, Teddington. Through Dr. Vernon's kindness I had an opportunity to compare these crystals, which Dr. New identified as ammonium sulphate, with crystals which I found deposited out of fog while the wind was blowing from London over my house in Cheam. These crystals appeared identical with the ones I discovered, and I have no reasonable doubt that they also were ammonium sulphate.

In this connection I should like to emphasize, for those who are interested in corrosion, the extraordinary distance which sulphur will travel from its source. We are producing in London some hundreds of tons of sulphuric acid per day, and it has to go somewhere; it does not simply disappear. I have no doubt that a good deal of it is deposited in the form of sulphates, and fortunately we have strong winds and some is blown out over the sea.

Dr. Vernon refers to an experiment on the protective effect of muslin; a piece of steel hung inside it was protected, and the inference was that it was particulate matter which was kept out. If the muslin is able to keep out particulate matter, then the size of the hole must have some bearing on the matter. If the hole is too large it will not keep out this matter, whereas if it is small it will. The size of the particles is approximately 0·5 or 1 micron, and the hole in the gauze is of the order of 500 microns. If you picture a mouse travelling along a country road and coming across a railway bridge and finding it impossible to get through that railway bridge, that is the sort of condition these particles are up against when they meet the holes in the gauze. It does not seem reasonable that the mouse cannot walk underneath the railway bridge; but you must go a step further, and imagine that the mouse had been at a dinner, say, of the Institute of Metals, and was staggering about the road. Then imagine that the sides of the railway bridge were coated with birdlime, so that if he struck the side he would stick there, and the chances are that he will strike the side before he gets through. I think that that must be what is happening in this case. There is a hole through a comparatively thick plate and a little particle trying to get through is subject to the Browning oscillation and it strikes the side before it gets through.

If that is so, there will be a critical size of hole, and I have been trying to find what that is. To do that I exposed some slides which were made in the following way. First an ordinary microscopic slide, on that a cover glass, and on the cover glass a cell 0·5 mm. deep, on the top of the cell wire gauze of varying mesh, and on the top of that a piece of indiarubber plaster fixing all to the slide. The wire gauze was about 0·1–1·0 mm. mesh. The slides were exposed for 48 hrs., and after that a deposit of dust was found under the gauze on each cover glass. Five slides with gauze of varying mesh were exposed and a control without a gauze cover was exposed beside them.

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* *Z. physikal. Chem.*, 1929, [A], **142**, 241.

† Superintendent of Observations on Atmospheric Pollution, London.

The first experiment made produced very remarkable results. It is the first, and requires checking, but the results were these. Roughly, the deposit of dust on the control was 77,000 particles per cm.^{2}. The deposit on the other slides taking the unsheltered area only, and deducting the area which was covered by the wire, was: using gauze with the hole 1·09 mm. 73,000; with a 0·48 mm. hole 69,000; with a 0·27 mm. hole 51,000; with a 0·15 mm. hole 39,000, and with a 0·09 mm. hole it was 30,000. If there was no such effect as I have indicated, then all these figures should be the same; there should be as much dust on the unsheltered area under the gauze as on the control, but such was not the case. It is interesting to note that the hole 1 mm. in diameter had practically no effect.

Mr. W. R. **Barclay**,* O.B.E. (Vice-President): I feel that those of us who are in the nickel industry must be grateful to Dr. Vernon for this paper, and on behalf of myself and a number of colleagues in that industry I should like to tender him our thanks. There are only one or two things that I desire to contribute to this discussion. I wish particularly to refer to Dr. Vernon's intimation on p. 123 that he confirms the property of chromium additions in inhibiting this "fogging" of nickel. It may be useful to mention that some 4 or 5 years ago I was very much interested in the properties of pure nickel or relatively pure nickel to which small percentages of such elements as aluminium, silicon, manganese, copper, cobalt, chromium, &c., had been added. Some work was carried out by the Mond Nickel Company's Research Department on these lines to ascertain the effect of small additions of such elements to ordinary malleable nickel. At the time we were concerned mainly with physical and mechanical properties, but were naturally also interested in corrosion effects, and some of these specimens, including one containing slightly less than 3 per cent. of chromium, were exposed to the atmosphere of Birmingham (which I suppose is fairly typical) for several months. We discovered that while no other element we tried had any apparent effect on the rate of fogging of nickel, the chromium-containing alloy was quite distinctive; with a small percentage of chromium (2·5 per cent. to be exact), the contrast was quite striking in regard to fogging under ordinary conditions of exposure to the atmosphere.

We were naturally interested in this, and followed it up by trying further additions of chromium of about 5 per cent., 6 per cent., and up to 9 per cent. Whilst we were not able at the time to investigate the subject so accurately and systematically as Dr. Vernon has done, we felt quite satisfied that a chromium content of about 6 per cent. would almost completely inhibit fogging. We found, indeed, that the 6 per cent. containing alloy was really very little inferior to one containing 9 per cent., and my own opinion is that a chromium content of the order of 5–6 per cent. will, for practical purposes at any rate, effectively inhibit the fogging of nickel.

We confirmed the observation Dr. Vernon has made (p. 129) that the filtering of air did not eliminate fogging in any of our specimens.

Dr. R. S. **Hutton** † (Vice-President): Dr. Vernon's reference to the work he did on this subject for the British Non-Ferrous Metals Research Association makes me rather ashamed of the way in which the Association has failed to utilize that work, because it seems that we have been cognisant of the main results and of the implications thereof for many years, and I cannot help thinking that something has been amiss with the drive and push we have given to their practical application.

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

The association of the "fogging" of nickel with its catalytic properties some of us have had in mind for a considerable time in connection with this research; and I think that a solution of the problem can perhaps be found much more readily than by adding 6 per cent. of chromium, which Mr. Barclay says is sufficient to stop this fogging.

The great amount of work done on nickel catalysts has shown the inhibition caused by a fraction of 1 per cent. of arsenic and some other elements and one cannot help feeling that their addition to nickel and its alloys for the prevention of its tendency to "fog" may have great practical importance. The first firm that brings out a non-fogging nickel or nickel alloy would immediately brighten up our shop fronts and other fittings and lead to a wide extension in the uses of nickel. That idea has been available to the industry at least since the year 1924. I do not know that anything very much has yet been done with it, but perhaps this paper will revive interest in the subject and lead to some definite practical results.

Professor T. TURNER,* M.Sc., A.R.S.M., F.Inst.Met. (Past-President): It has been shown that if nickel be exposed to the ordinary atmosphere and left unpolished, the surface effect increases steadily and at a much more rapid rate than might be anticipated as compared with a metal like tin. If a sheet of nickel and a sheet of tin are exposed, it will be found that the nickel goes on corroding on the surface, although uniformly, at a rate which is greater than that of the tin.

It is obvious, therefore, that the protection of nickel surfaces by removal of this fogging is important. That brings in a question which was raised in discussing a previous paper, as to the adhesion of films, say to magnesium or magnesium alloys, and how we are to measure the strength or amount of adhesion. It will be found that some films can be much more easily removed than others, and obviously what we want to do is to remove the film without abrading the metal which is underneath. To do that it is necessary to have a material which is harder than the film but not so hard as the metal. It is merely a question of selecting a suitable material. The whole of the film may be removed, and no metal, provided that the right material is employed.

I have made experiments in connection with certain films and noted the difference, for example, between rubbing with cotton wool, with woven cotton, with soft linen, with linen which had been ironed and was hard, and so forth. One can go through the gamut, and there are many other soft materials, such as a loofah and indiarubbers of varying degrees of hardness, and these may be followed by various polishing powders. In that way for the soft films it is possible to get a scale of hardness on the same principle as the Moh scale for the hardness of metals, and say definitely that a particular film can be removed by a particular rubbing material, which will remove the film, but which will not affect the metal that is underneath it.

Those who use ordinary nickel should take care that it is kept clean and that it is rubbed by a suitable material which is not too hard, but which is sufficiently hard to remove the surface film, and then, as Dr. Vernon mentions, a very slight film of lanoline or some other oily matter will help very much in preserving the nickel and saving it from deterioration.

Dr. VERNON (*in reply*): I greatly appreciate Mr. Evans' agreement on essential points concerning the interpretation of results recorded in the paper. With regard to the hygroscopicity of the product, this is no doubt a very important factor; I believe, however, that it comes into operation at a secondary stage, subsequent to the formation of the "fog" film. With high concentrations of sulphur dioxide at high relative humidities, fogging, as

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* Emeritus Professor of Metallurgy, Birmingham University.

understood in the paper, is no longer observed; the secondary process described by Mr. Evans then predominates from the outset. This leads, of course, to more serious corrosion owing to the fact, as Mr. Evans has said, that the surface becomes definitely moist.

Dr. Owens' contribution is particularly welcome, not only because of its immediate bearing on the present paper, but also because of its wider issue. The linking up of two apparently independent groups of phenomena represented by Dr. Owens' work on fogs and Dr. New's results on the "blooming" of paints is of the greatest interest, and I feel that I myself have acted as a catalyst by bringing together these two "reactants." I very greatly welcome Dr. Owens' experiments in connection with the "muslin cage effect" because that is just the sort of work that I had been hoping would be done, and there is no one whom I would rather see take up the matter than Dr. Owens. It is gratifying that he has brought his great skill to bear on this subject. I appreciate his analogy of the mouse and the bridge. As applied to the muslin screen, there is only one thing I would add; and that is that we should regard the bridge, perhaps, as an ancient one, from which there are many appendages. This would correspond with the fact that in the muslin screen the hole is not clean-cut, but is partly obscured by small "branch" fibres which, coupled with the Brownian movement of the particle, might be expected to play some part in its interception. Nevertheless, this does not affect the principle underlying Dr. Owens' experiments; and it is greatly to be hoped he will carry them to a still further stage.

I am much indebted to Mr. Barclay for his encouraging and corroborative remarks. It was due to his co-operation that we were able to show the influence of the larger amounts of chromium, and it is particularly interesting to know that he has found that much smaller amounts are equally efficacious.

Dr. Hutton's contribution is especially welcome at this stage in view of the fact that the early tests on fogging were carried out at his instigation. Recent work has made it clear that catalysis must play some part in the phenomenon. Arising from this, certain additional tests are already in hand which bear on some of the points that Dr. Hutton has raised; possibly something may emerge from this work, but it is too early to say yet.

Finally, I would like to thank Professor Turner for his interesting remarks and for the novel suggestion he has made for classifying the adhesiveness of surface films such as those on fogged nickel.

CORRESPONDENCE.

The Author (*in further reply to discussion at meeting*): Dr. Owens' interesting analogy of the mouse and the bridge tempts me to suggest a further slight extension. At the meeting I mentioned that a dilapidated bridge, with many appendages, would probably more nearly represent the hole in the gauze. In a similar way, as the particle intercepted by the gauze is likely to be of a fibrous (sooty) character rather than granular (or siliceous), so perhaps a spider would afford a sounder analogy than a mouse. It would, of course, have to be correspondingly large—something in the nature of a giant tarantula! The possibility of a specific (electrical) attraction between the particle and the gauze should also, presumably, be taken into account.

Dr. J. Newton Friend * (Member): Dr. Vernon's results are of great interest and importance in that they deal with a branch of corrosion in which reliable data are very scanty. The close proximity of nickel to copper in the Periodic Classification of the elements would lead one to expect a close

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* Head, Chemistry Department, Central Technical College, Birmingham.

similarity in their corrosion effects, and the marked contrasts observed by Dr. Vernon serve to illustrate Davy's pithy remark that "analogy is the fruitful parent of error." The stimulating action of light on "fogging" was an observation of interest. I showed in 1911 that diffused daylight markedly assists the corrosion of iron completely immersed in water under conditions which negatived the suggestion that it could be due to a purely thermal effect. I also carried out numerous experiments in glass vessels of varying colour in order to ascertain which kinds of wave-length are most active, but unfortunately the results were inconclusive. If Dr. Vernon can see his way clear to study tarnishing and fogging under the influence of selected stimulating rays, results of very considerable interest and importance may be obtained.

Dr. J. C. HUDSON,* D.I.C., A.R.S.M. (Member): There is no doubt that under certain conditions nickel is particularly susceptible to a peculiar type of corrosion which Dr. Vernon has designated as "fogging," and the present paper is a very important contribution to our knowledge of this phenomenon. I am in entire agreement with Dr. Vernon as to the importance of the relative humidity in determining whether this type of corrosion occurs or not, and I further agree with him in fixing the critical humidity at round about 70 per cent.

Dr. Vernon's explanation of the immunity produced by long exposure to air as being due to anticatalysis is interesting, and agrees with the experimental evidence. It might be of value to endeavour to incorporate the anticatalyst in the metal itself, say by alloying the nickel with a fraction of 1 per cent. of arsenical copper, thus yielding an alloy with a very low arsenic content—provided, of course, that there were no metallurgical objection.

The experimental results obtained in opaque and transparent vessels afford very clear evidence as to the influence of light on the fogging of nickel. It would be of interest to ascertain whether the effect is due to the direct suppression of the actinic rays or indirectly to differences in the internal temperature and humidity of screened and unscreened vessels respectively. The point could be settled by a few comparable temperature determinations in each type of vessel, and it would be of value to have such determinations even if, as appears probable, the results were negative.

Dr. C. H. M. JENKINS † (Member): Dr. Vernon's paper forms a further advance in the study of corrosion, and it is hoped that the author will widen the scope of his work to include other forms of nickel than rolled sheet, as electrodeposited metal has been perhaps more exposed, particularly in the past years, to atmospheric corrosion than any other form. The sulphate solutions from which the nickel has been deposited are liable to be entrapped in the deposited metal. Although the microscopic examination of polished specimens frequently fails to indicate the presence of any included non-metallic material, the presence of a fairly considerable quantity of included material can be shown by examination of specimens annealed *in vacuo* or in a neutral atmosphere. It would be of considerable interest to the problem if the author would give us information on the degree of fogging in nickel-plated articles as compared with rolled sheet nickel, as the former may contain sulphate-bearing material which possibly possesses an accelerating effect on the fogging action now described. If such fogging action is perchance accelerated in electrodeposited nickel coatings, it may assist in a fuller under-

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† Senior Assistant, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

standing of the mechanism of peeling in these deposits, and thus supplement the information that has been accumulated by empirical means.

Dr. A. R. Martin [*]: It is possible to explain both Dr. Vernon's present results with nickel and his previous ones with copper by the hypothesis that sulphur dioxide dissolved in a layer of water on the surface of the metal is oxidized by aerial oxygen to sulphuric acid, which attacks the metal.

In his reply to the discussion on his copper paper [†] Dr. Vernon states that an aqueous solution of sulphur dioxide is not oxidized to sulphuric acid on exposure to air. I have verified the incorrectness of this statement both experimentally and by reference to the literature.[‡] Contrary to Dr. Vernon's statement, copper is attacked slowly by dilute sulphuric acid in the presence of air.[§] I have exposed small quantities (about 0·5 grm.) of the powdered chlorides of potassium, barium, and copper, and of the carbonates of nickel and copper to moist, but not saturated, atmospheres containing about 2 per cent. of sulphur dioxide for about 2 days. On dissolving the salts and testing for sulphates, none was detected in the cases of the chlorides of potassium and barium, but with the nickel and copper salts appreciable quantities were found. In the case of the copper salts the facts can be explained, without making any new hypothesis, by the known accelerating influence of the copper ion (homogeneous catalysis) on the oxidation of solutions of sulphurous acid and sulphites.[||] The influence of the nickel ion on this oxidation is unknown, but, in view of the general chemical similarity of copper and nickel, it is probably the same as that of the copper ion. It is uncertain whether the oxidation is accelerated by traces of copper and nickel ions dissolved in a superficial layer of water, or by the ions occurring in the crystal lattice and in contact with the sulphurous acid solution. However, in the light of modern knowledge of the nature of solutions and solids, the difference is unimportant. I think that in the case of the metals the process which occurs is similar to that which takes place with its salts. It is different from the heterogeneous catalysis at a few active centres followed by a reaction such as:

$$2SO_3 + O_2 + 2Cu = 2CuSO_4$$

postulated by Dr. Vernon in his paper on copper [¶] and presumably believed by him to occur also with nickel, although here he has not made his position so clear. The copper hydroxide which occurred at low concentrations of sulphur dioxide was probably formed by the hydrolysis of copper sulphate.

Heat-treatment would cause sintering and destruction of active centres, which in any case one would not expect to find on *polished* nickel, and hence on Dr. Vernon's hypothesis protection from fogging. No such protection was observed.

The reduction of fogging by previous exposure to hydrogen sulphide may be explained without resort to the *ad-hoc* hypothesis of poisoning by supposing that adsorbed hydrogen sulphide (which would not be removed by vacuum desiccation) reacts with sulphur dioxide according to the well-known equation:

$$2H_2S + SO_2 = 2H_2O + 3S$$

[*] Aberdeen.

[†] *Trans. Faraday Soc.*, 1931, 27, 590.

[‡] See, for example, Lowry, *Inorganic Chemistry*, 1931, p. 377; Mellor, *Comprehensive Treatise on Inorganic Chemistry*, Vol. X, p. 207.

[§] Lowry, *loc. cit.*, p. 854.

[||] See Mellor, *loc. cit.* F. Binnecker, "Über verschiedene Metallsalze als Sauerstoffübertrager an schweflige säure," Wetzlar, 1887, and L. Meyer, *Ber.*, 1887, 50, 219, found that nickel ions accelerate the oxidation of sulphurous acid solutions.

[¶] *Trans. Faraday Soc.*, 1931, 27, 266.

The oxidation of sulphites may proceed both thermally and photochemically,* the two reactions being completely similar. It seems likely, on general grounds, that sulphurous acid would resemble sulphites in this respect, and therefore it is not surprising that Dr. Vernon finds that the fogging of nickel is influenced by light. However, in Dr. Vernon's experiments the conditions of heating and cooling by radiation, and consequently for deposition of a film of moisture, were not the same for the two specimens, and hence it is desirable to repeat this work at constant temperature in order to *prove* that light influences the fogging of nickel.

Tin ions retard the oxidation of sulphites,† and therefore nickel–tin alloys might fog less readily than pure nickel.

The Author (*in reply*): Dr. Friend's interesting quotation of Davy comes opportunely, for probably in no other field is there a greater temptation to reason by analogy than in corrosion, and certainly not one in which there is greater danger of its leading to false conclusions. In the case of nickel and copper, it is interesting to note that the similarity between the metals is maintained even in respect to fogging, although in greatly different orders of magnitude, so long as the external conditions are suitably chosen; it so happens that the conditions which most commonly obtain are favourable for fogging in the case of nickel, but not in the case of copper. With regard to the influence of light, further work on the effects of selected stimulating rays, as suggested by Dr. Friend, would no doubt lead to results of definite interest.

Dr. Hudson has also commented helpfully on the "light experiments." The question that he has raised about the possibility of slight temperature differences in screened and unscreened vessels is a perfectly sound one. As Dr. Hudson mentions, the point could be settled by careful temperature determinations in each vessel; for the results to be conclusive, however, some sort of recording arrangement would have to be employed. Whilst freely admitting the desirability of this procedure, I believe that thermal effects were not responsible for the results reported in the text. One would expect that any such effect would vary from experiment to experiment according to the prevailing external conditions; whereas in three separate experiments the same difference (between results from transparent and opaque vessels) was observed in *practically identical numerical ratio*.

The confirmation of certain points discussed in the paper, which Dr. Hudson is able to supply from his own experience, is particularly welcome. Incidentally, I should like to take the opportunity to make clear that the term "fogging" is actually due to Dr. R. S. Hutton, by whom I first heard the term used in the present connection. The very aptness of the term makes one use it almost instinctively; and for this reason I much regret the omission if, as seems probable, this acknowledgment should have been made in the text. The influence of arsenic (among other possible anticatalysts) on electrodeposited nickel is now being investigated, with the co-operation of Messrs. D. J. Macnaughtan and A. W. Hothersall (Research Department, Woolwich); but Dr. Hudson has suggested a convenient means of introducing arsenic into rolled nickel which may well prove to be helpful.

I am much indebted to Dr. Jenkins for the interesting and important point that he has raised concerning the comparative behaviour of rolled and electrodeposited nickel. A qualitative observation made some years ago left me with the impression that there was little to choose. Following Dr. Jenkin's inquiry, however, I have recently conducted tests with remarkable results; the electrodeposited coating (actually from two independent sources) has proved

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* Backstrom, *J. Amer. Chem. Soc.*, 1927, 49, 1460.

† Titoff, *Z. physikal. Chem.*, 1903, 45, 641.

to be definitely superior to the rolled metal. Two alternative explanations suggest themselves to account for the superiority of the electrodeposited nickel —namely, differences in composition due to occluded hydrogen in the deposit on the one hand, or metallic additions in the rolled metal on the other. Each of these possibilities is now being investigated, the latter through the co-operation of Mr. W. R. Barclay. It is interesting to note in this connection that Bowden and Rideal* found that the catalytic activity of nickel with respect to the discharge of hydrogen ions was much less for an electrodeposited surface than for the rolled or polished metal.

On a previous occasion Dr. Martin disagreed with a catalytic interpretation of allied phenomena involving the oxidation of sulphur dioxide at the metal surface. He now tacitly admits that the mechanism is essentially catalytic in character, for he prefers to regard it as an example of homogeneous catalysis rather than the heterogeneous type postulated in this and in a preceding paper. My own feeling is that the evidence is definitely in favour of heterogeneous catalysis so far as the primary mechanism is concerned,† although homogeneous catalysis may play an important contributory part. In any case, it is regrettable that Dr. Martin should seek to support his views by misquoting statements that I have made in support of my own. On the previous occasion, in reply to Dr. Martin, I stated that "whereas solutions of sulphurous acid undergo negligible oxidation on exposure to air (low results in titration being due almost entirely to evaporation of SO_2), sulphite solutions, on the other hand, readily undergo oxidation." This particular passage was taken practically verbatim from a recently published work;‡ it compares the respective behaviour of sulphurous acid and sulphite solutions and, with the context, provides a possible basis for the homogeneous catalysis viewpoint. Dr. Martin now represents me as having stated simply that "an aqueous solution of sulphur dioxide is *not* oxidized to sulphuric acid on exposure to air," and he further supplies the information that he has verified the incorrectness of this statement by reference to the literature! A more flagrant misrepresentation follows when Dr. Martin writes that "contrary to Dr. Vernon's statement, copper is attacked slowly by dilute sulphuric acid in the presence of air." It is, of course, absurd to suggest that I have ever disputed this well-known fact. What I actually stated was that "the action of dilute sulphuric acid on copper is far too slow to account for the quantities of sulphate produced in the experiments." This remains perfectly true, and provides, indeed, the crux of the question which Dr. Martin has evaded.

The present paper deals with a specific problem; it makes no attempt to investigate a wide range of sulphur dioxide concentrations, as was the case with the previous work on copper. Here a critical concentration of sulphur dioxide was recognized below which copper sulphate is accompanied by copper hydroxide and above which free sulphuric acid appears. It seems highly probable that a similar state of affairs obtains for nickel, except that the critical concentration is depressed to a very much lower value; thus, concentrations of sulphur dioxide that occur normally in the atmosphere, although far too low to produce free sulphuric acid on the surface of copper, are amply

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* *Proc. Roy. Soc.*, 1928, [A], **120**, 80.

† The mechanism cannot consist primarily in the solution of sulphur dioxide in an adsorbed film of water, as postulated by Dr. Martin, because the sorption of water vapour on nickel is practically negligible. (See McBain's *Sorption of Gases and Vapours by Solids*, 1932, p. 316.) Moreover, on glass, where the sorption of wates is relatively enormous, no sulphuric acid is formed under conditions such that large amounts would be formed on copper (Vernon, *Trans. Faraday Soc.*, 1931, **27**, 591) and, as the present work shows, still larger amounts on nickel.

‡ Vallance, Twiss, and Russell, *Inorganic Chemistry*. Edited by J. Newton Friend, 1931, p. 130.

sufficient to do so on the surface of nickel. Dr. Martin's remarks on the effect of heat-treatment of the nickel appear to ignore the fact that the heating was conducted in air, with consequent production of a film of oxide which, however, in most of the experiments, was not sufficiently thick to be visible; his confidence, moreover, in the absence of active centres on a polished surface is scarcely compatible with the experimental facts.*

Dr. Martin's alternative explanation of the influence of traces of hydrogen sulphide is discounted by results obtained since the issue of the advance copy of the paper, and now incorporated in the Addendum. It is not to be expected that any free hydrogen sulphide could be associated with a specimen that has been exposed merely to " ordinary air " drawn into the vessel from the open. Moreover, in the case of the atmospheres to which traces of hydrogen sulphide were added, on Dr. Martin's view the inhibiting effect should increase with the time for which the specimen was exposed; but the exact converse was the case.

In the experiments in which the influence of light was investigated the vessels were in close proximity (Fig. 2), so that any differences in thermal conditions (apart from any that might be introduced by the provision to exclude light—a *reasonable* point that was, in fact, raised by Dr. Hudson) must cancel out after a long period of exposure. That this is actually the case is obvious, to anyone but a captious critic, from an inspection of the results themselves.

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* See, for example, the work of Bowden and Rideal, *loc. cit.*

MAGNESIUM ALLOY PROTECTION BY SELENIUM AND OTHER COATING PROCESSES.*

By G. D. BENGOUGH,† M.A., D.Sc., Member, and L. WHITBY,† M.Sc., Member.

Synopsis.

A process has been developed for the production of films of selenium on several light magnesium alloys. These films confer considerable resistance to the corrosive action of sea-water spray. They are normally produced by immersion for a few minutes in a bath containing selenious acid at laboratory temperature, but may also be produced by rubbing the alloy with porous material dipped in the bath.

The film has the property of self-healing to a limited extent, especially when immersed in stagnant sea-water. It is only a few thousandths of a millimetre thick, and its production does not cause any appreciable dimensional change in the alloys treated. It forms a satisfactory base for certain types of paint, and further work on this property is proceeding.

The special object of this research was to find a process for the protection of magnesium-rich alloys, particularly those used in aircraft construction, against corrosion by the atmosphere and chloride solutions, especially sea-water spray.

The action of some kinds of atmosphere is quite slow; Hiege ‡ points out that the metal may become covered with a protective coating of magnesium carbonate. In Berlin, bus wheels of Elektron have been in use for some years, and serious attack has been recorded only when salt was used for melting snow in the streets. At Teddington, vertically suspended specimens of alloys AZM, Z3, and 66 (see Table I) have been exposed to the weather in a field for nearly a year; on AZM specimens a patchy film showing interference colours has formed; on Z3 a small amount of greyish-white deposit has formed, and alloy 66 has turned dull grey, but there is no serious corrosion on any.

In addition to these bare specimens, others were similarly exposed after treatment in the twelve baths recorded in Table II. Altogether

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* Manuscript received December 12, 1931. Presented at the Annual General Meeting, London, March 10, 1932.

† Chemical Research Laboratory, Department of Scientific and Industrial Research, Teddington.

‡ *Metallwirtschaft*, 1930, 9, 361.

162 specimens have been exposed to the weather in the suburban conditions of Teddington for about a year, but not one has seriously corroded. Harvey * claims that more than 2½ years' protection against the weather has been conferred on magnesium-base alloys by priming with thermoprene resin and finishing with spar varnish, both being pigmented with aluminium powder.

Some specimens of alloy 66 exposed to an indoor atmosphere liable to be contaminated with products of combustion gave much worse results, and at the end of 12 months were covered with a loose white deposit; even in this case, however, serious pitting was absent.

Nevertheless, the main problem for aircraft consists in securing adequate protection against chloride solutions. Sutton and Le Brocq † have recently reviewed the possibilities as regards alloying, protection by means of simple chemical immersion treatments, coating with other metals, and anodic oxidation. The present authors agree with their conclusion that chemical immersion is the most hopeful line of investigation; the field is wide owing to the ease with which films can be produced on such reactive material as magnesium-rich alloys. Coatings have been produced on alloy D.T.D. 120 (Air Ministry specification) in sheet form, containing 5 per cent. aluminium and 0·75 per cent. manganese from more than 500 different solutions or mixtures of the following substances: aluminium, cadmium, cobalt, copper, lead, nickel, and zinc salts (selected from their chlorides, sulphates, and nitrates), and sodium or potassium aluminate, arsenate, arsenite, borate, borofluoride, chromate, dichromate, fluoride, meta-

TABLE I.—*Composition of Alloys Investigated.*

Alloy.	Air Ministry Specification. D.T.D.	Aluminium.	Zinc.	Silicon.	Manganese.	Magnesium.
British Maximum 66 (sheet) . .	120	5	...	...	0·75	94·25
Elektron Z3 (sheet).	...	0–0·2	3·0	0–0·3	...	97·0
Elektron AZM (sheet) . .	125	6·15–6·45	0·8–1·2	0–0·2	0·2–0·5	92·5
Elektron AM503 (sheet) . .	118	...	...	0–0·3	1·3–1·7	98·0
Elektron VI (extruded rod) .	129	9·5–11·5	0–0·6	0–0·3	0·2–0·5	88·0

Note.—Compositions are those given by the makers.

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* *Trans. Amer. Electrochem. Soc.*, 1929, **56**, 57.

† *J. Inst. Metals*, 1931, **46**, 53.

phosphate, molybdate, nitrate, oleate, oxalate, perborate, persulphate, orthophosphate, phosphotungstate, pyrophosphate, selenate, selenite, silicate, silicofluoride, stearate, sulphate, and tungstate. Some synthetic resins and several organic acids and salts, mainly easily obtainable dyestuff intermediates, have also been tried.

The coatings obtained have usually been remarkably adherent, reasonably smooth, and easily produced. For exploratory corrosion testing, specimens 5 cm. square were suspended vertically in the laboratory by glass hooks and sprayed with sea-water twice daily for 20 days. The corrosion products were removed by solution in chromic acid, as described elsewhere * by one of us, and the loss of weight was determined. The great majority of the coatings failed quickly under this preliminary test, and were not further investigated. About a dozen methods were selected, which resulted in weight losses between 1/5th and 1/30th of that of the untreated alloy. Most of these were based on the use of chromic acid or bichromate, and a new set of specimens was submitted to the following corrosion test, which was used for the rest of this research.

The specimens were suspended vertically, by gutta-percha covered wires, in a field adjoining the laboratory at Teddington, and sprayed three times daily with sea-water collected 3 miles outside Plymouth breakwater, and supplied by the Marine Biological Association. The water was brought to Teddington and stored in glass carboys, and the spray itself was made of glass. Pressure was supplied from the laboratory service and kept approximately constant by means of a water column 48 in. high. Tests were carried out for 4 weeks on alloys AZM, Z3, and 66, and results for twelve different treatments are recorded in Table II. As a reference standard the sulphate-bichromate process developed by Sutton and Le Brocq was used; this process is described on p. 150. The results for alloys 66 and Z3 sometimes show wide variations between duplicates. This is probably due to heterogeneity of the alloys themselves, the production of which had not reached its present stage when these tests were started. On the whole the best results were obtained with the tungstate–chromic–nitric acid bath and the selenite bath, particularly for the AZM alloy.

Since the selenite bath was the simpler, it was decided to begin intensive investigation on it, using the AZM, AM503, and VI alloys, which appear at this stage to be most useful alloys technically. The film formed on AZM has been investigated, and found to consist mainly of selenium, which is precipitated either in the red or the grey form

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* *J. Soc. Chem. Ind.*, 1931, **50**, 83T.

according to the experimental conditions. It is possible that a layer of magnesium selenide is formed next to the metal, but if so it is too thin for detection by a 4-mm. Zeiss objective. This film would be hydrolyzed by water, and the resulting hydrogen selenide decomposed in presence of oxygen, resulting in deposition of selenium—a reaction

TABLE II.

Bath (aqueous solution).	Time of Treatment.	Temp. (° C.).	Coating.	Alloy.	Loss of Weight. Grm.
1% Sodium tungstate + 1% chromic anhydride + 8 c.c. 2*N*-nitric acid/l.	30 mins.	90	Dirty yellowish-grey; smooth after brushing.	GG	0·60; 0·62
			Dark greyish-brown.	Z3	0·17; 0·25
			Smooth dirty grey.	AZM	0·05; 0·07
2% Chromic anhydride + 0·1% magnesium chloride.	1 hr.	80	Matt greyish-brown.	GG	1·01; 1·38
			" " "	Z3	0·37; 0·59
			Smooth dark brownish-grey.	AZM	0·06; 0·10
2% Chromic anhydride + 0·1% magnesium chloride.	2 hrs.	80	Smooth greyish-brown.	GG	0·86; 0·79
			Smooth brown.	Z3	0·28; 0·26
			Smooth and dark brownish-grey.	AZM	0·07; 0·07
2% Chromic anhydride + 5% sodium dichromate + 0·1% ammonium chloride.	25 mins.	80	Dark brown smooth coating after brushing.	GG	0·87; 0·93
			" " " "	Z3	0·16; 0·18
			" " " "	AZM	0·07; 0·07
1% Potassium chlorochromate.	15 mins.	80	Dark brown, matt coating, after brushing.	GG	1·26; 1·20
			" " " "	Z3	0·61; 0·19
			" " " "	AZM	0·13; 0·11
1·5% Potassium dichromate + 1·5% sodium sulphate 10 aq. (sulphate–bichromate process).	6 hrs.	95	Black film with bright specks.	GG	0·50; 0·53
			Deep brown shiny film.	Z3	0·14; 0·65
			Black, uniform film.	AZM	0·08; 0·08
5% Sodium dichromate + 1% sodium persulphate.	6 hrs.	80	Smooth black with yellow spots.	GG	1·03; 0·73
			Smooth shiny black.	Z3	0·36; 0·23
			As GG.	AZM	0·37; 0·35
1% Sodium dichromate + 0·5% sodium persulphate + 2 c.c. 2*N*-nitric acid/l.	3 hrs.	80	Dark steely blue film.	GG	1·05; 1·02
			Deep shiny brown film.	Z3	0·16; 0·17
			Greyish-black, bright spots.	AZM	0·29; 0·23
2% Chromic anhydride + 1% ferric sulphate.	5 mins.	80	Dark grey etched coating.	GG	1·02; 1·04
			Dark brown etched coating.	Z3	1·19; 1·53
			" " " "	AZM	0·97; 0·63
2% Chromic anhydride + 1% ferrous sulphate.	30 mins.	80	Coating like smooth rust-covered iron (after brushing off loose powder).	GG	0·57; 0·60
				Z3	1·34; 1·38
				AZM	0·09; 0·09
2% Sodium perborate + 1% chromic anhydride + 25 c.c. 2*N*-nitric acid/l.	2 hrs.	80	Dark brown smooth coating.	GG	0·41; 0·38
			Brown shiny film.	Z3	0·35; 0·47
			Black shiny film.	AZM	0·10; 0·09
1% Sodium selenite + 20 c.c. 2*N*-hydrochloric acid/l.	1·5 hrs.	80	Dark reddish-brown; rough before brushing.	GG	0·34; 0·19
			" " " "	Z3	0·31; 0·52
			Shiny black after brushing.	AZM	0·06; 0·06
Blanks—emeried and pickled in 10% nitric acid.				GG	1·65; 1·55
				Z3	0·90; 0·88
				AZM	0·25; 0·23

which would explain not only the slight hepatic smell which is produced when large numbers of specimens are stored in a confined space, but also some phenomena described later.

The main part of the film is strongly adherent, and usually about 2 μ (0·002 mm.) thick, as estimated by weighing the metal before and after removal of the film by warm 66 per cent. caustic potash solution. On top of the coherent film powdery selenium is sometimes formed, which is easily brushed off. This loose layer is rarely more than 0·00025 mm. thick.

The loss of thickness of magnesium in the coating bath from all the alloys mentioned above is usually of the same order as the thickness of the deposited film, so that the dimensional change of the specimen is slight.

Sodium selenite solution itself does not deposit selenium on the alloys tested, but a great variety of additions to the bath enables it to do so. Amongst those tried were: nitric, sulphuric, hydrochloric, phosphoric, acetic, and oxalic acids; sodium chloride, sulphate and phosphate, and sodium selenite–selenious acid mixtures with and without the addition of sodium chloride; each was tried at laboratory temperatures, 50°, 75°, and 100° C. The coatings produced by the addition of acids to sodium selenite do not give satisfactory protection alone, but have not yet been tested as bases for paint films. Sodium selenite–selenious acid mixtures, with the addition of sodium chloride, gave excellent protection, but were abandoned in favour of a simple selenious acid bath, owing to the longer life of the latter and to the much shorter time of immersion necessary for the formation of a satisfactory film.

To obtain the optimum conditions for any one type of bath it is necessary to test the effects of concentration, temperature, and time of immersion, as well as slight variations of composition. As a result of intensive investigation of selenite baths, the following compositions and conditions were selected for use on the AZM alloy:

1. 8 per cent. solution of sodium selenite + 3·2 per cent. selenious acid + 0·1 per cent. sodium chloride used at 80°–90° C.; time of immersion 3 hrs.
2. 10 per cent. solution of selenious acid in water, + 0·1–0·5 per cent. sodium chloride, used at atmospheric temperature; time of immersion 5–10 minutes.

Most of the work was done with the second bath, which is only slowly exhausted. For instance, forty specimens were treated successively in 500 c.c. of 5 per cent. selenious acid. After 8 weeks' testing by the salt spray, no difference could be detected between the first and last specimen, and many more could probably have been treated.

Although the best films have been produced by dipping the specimens into the bath, this procedure is not absolutely necessary. Protective films have been obtained by merely rubbing specimens with cotton wool saturated with No. 2 solution, given above. This procedure affords an easy method of repairing the film if it should be locally damaged, and would be a great advantage in industrial use. Plane surfaces may be protected in this way, as exemplified in Fig. 14 (Plate XI).

The behaviour of AZM sheet treated in the selenious acid bath has been compared with similar sheet treated by the following processes:

1. The I.G. process, which consists of immersion in a bath containing 20 per cent. nitric acid and 15 per cent. potassium bichromate.
2. The Jirotka process (see English Patent No. 328,485).
3. The alum–bichromate process.
4. The sulphate–bichromate process.

} Developed at the Royal Aircraft Establishment, South Farnborough.

TABLE III.—*Alloy AZM* (8 *Weeks' Exposure*).

Composition of Bath: Selenious Acid at Laboratory Temperature.

Losses of Weight, Grm.

Time of Treatment.	0·5%.	2·0%.	5%.	10%.
1 min.	1·47; 1·87	0·55; 0·41	0·21; 0·20	0·07; 0·20
5 mins.	0·20; 0·49	0·19; 0·13	0·11; 0·11	0·09; 0·11
15 ,,	0·30; 0·26	0·18; 0·13	0·17; 0·11	0·14; 0·17
30 ,,	1·02; 0·32	0·22; 0·26	0·16; 0·30	0·28; 0·18
3 hrs.	0·65; 0·87	0·39; 0·40	0·51; 0·81	1·13; 0·93
Untreated	*Blanks.* 3·92; 3·86			
6 hrs. (95° C.)	*Sulphate–bichromate process.* 2·08; 1·74			

Note.—The experiments with the selenium treatment were repeated at 50°, 75°, and 100° C., but the laboratory temperature gave the best results. The general result of increase of temperature was similar to that illustrated in Table IV.

The first specimen of each pair was brushed after treatment, but before being submitted to the corrosion test.

The Jirotka specimens were treated by Messrs. Protective Coatings, Ltd., the others were prepared in the laboratory after a preliminary cleaning of the alloy sheet by immersion for about 30 seconds in 10 per cent. nitric acid. Processes (3) and (4) were conducted according to the directions of Sutton and Le Brocq. All the specimens were sub-

PLATE IX.

AZM Alloy

FIG. 1.—Untreated Metal. 8 weeks' exposure.

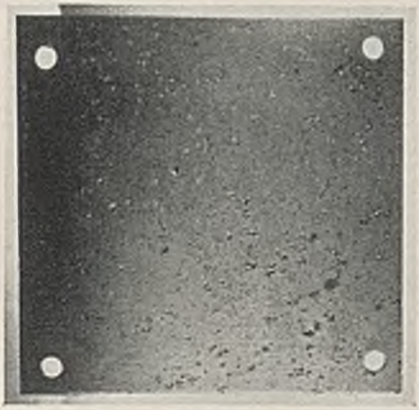

FIG. 2.—Selenium Process. 14 weeks' exposure.

FIG. 3.—Sulphate-dichromate Process. 14 weeks' exposure.

FIG. 4.—Alum-dichromate Process. 14 weeks' exposure.

FIG. 5.—Jirotka Process. 8 weeks' exposure.

FIG. 6.—I.G. Process. 4 weeks' exposure. (Corrosion-product not removed.)

[*To face p.* 152.

PLATE X.

V1T Alloy.

FIG. 7.—Untreated Metal. 8 weeks' exposure.

FIG. 8.—Alum-dichromate Process. 8 weeks' exposure.

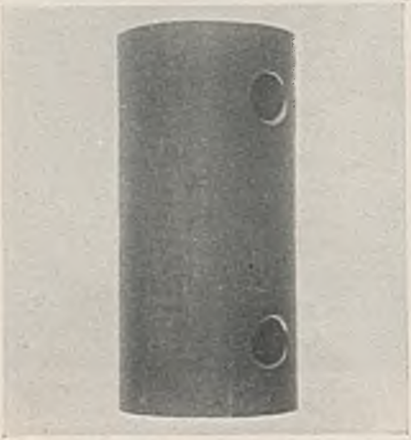

FIG. 9.—Selenium Process. 8 weeks' exposure.

AM503 Alloy.

FIG. 10.—Untreated Metal. 12 weeks' exposure.

FIG. 11.—I.G. Process. 2 weeks' exposure.

FIG. 12.—Selenium Process. 12 weeks' exposure.

PLATE XI.

Alloy AZM.

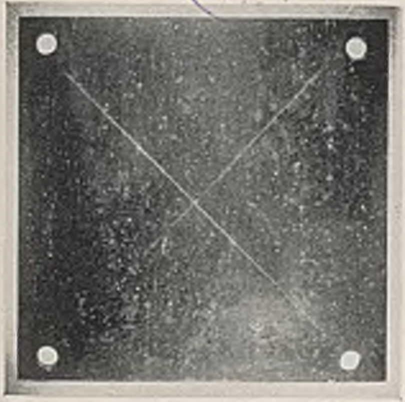

FIG. 13.—Selenium Process—Film Scratched. (Note lack of preferential attack along scratches, and partial covering of scratch in bottom left-hand corner.) 9 weeks' exposure.

FIG. 14.—Selenium Process. Film Produced by Rubbing. 9 weeks' exposure.

FIG. 15.—Selenium Deposition on Paint Surface. 12 weeks' exposure.

FIG. 16.—As Fig. 15, but Paint Removed—no Attack Visible. 12 weeks' exposure.

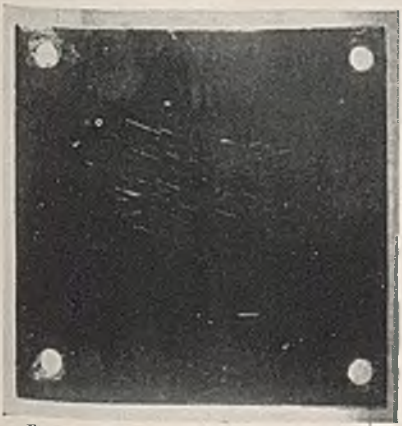

FIG. 17.—Thermoprene Resin over Selenium. 16 weeks' exposure.

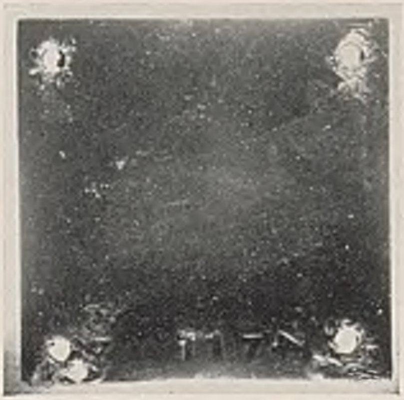

FIG. 18.—Thermoprene Resin on Untreated Metal. 3 weeks' exposure.

mitted to the spray test, after which the corrosion products were removed by the chromic acid method and the losses of weight determined. The results are given in Tables III and IIIA, and some of them are illustrated in Plate IX. The blank specimens and those coated by the Jirotka process gave very poor results; the alum-bichromate, the sulphate-bichromate, and the I.G. process gave considerably better, but the selenious acid bath gave the best.

In considering the results it should be remembered that the Jirotka, the sulphate- and alum-bichromate, and the I.G. processes are used to best advantage as undercoats for paints, and not alone. Moreover, a film that gives the best results alone does not necessarily give the best results with a top-coat of paint. Although subject to these limitations, the results in Tables III and IIIA suggest that selenium films may give useful protection to AZM alloy when used in mildly corrosive conditions, and would be especially valuable when rapidity of treatment and accuracy of dimensions are necessary. In severe conditions some reinforcement of the very thin film would probably be desirable, and a few preliminary tests on top-coats of paints, &c., are described later.

TABLE IIIA.—*Alloy AZM* (14 *Weeks' Exposure*).

Composition of Bath: Selenious Acid at Laboratory Temperature.

Loss of Weight, Grm.

Time of Treatment.	5%.	5% + 0·1% NaCl.	10%.	10% + 0·1% NaCl.	10% + 0·5% NaCl.
5 mins.	2·00; 1·67	0·20; 0·18	0·37; 0·15	0·15; 0·16	0·13; 0·22
10 ,,	... ...	... ...	0·25; 0·34	0·20; 0·15	0·19; 0·17
Untreated	*Blanks.* 2·77; 3·11				
	Jirotka process (8 *weeks' exposure only*). 3·17; 2·41				
6 hrs. (90° C.)	*Sulphate–bichromate process.* 0·51; 0·96				
6 hrs. (90° C.)	*Alum–bichromate process.* 0·80; 0·93				
	I.G. process (8 *weeks' exposure only*). 0·19; 0·11				

Table IV gives results for alloy AM503. The best coating conditions were obtained at laboratory temperatures, with 5 per cent. acid and very short times of immersion. In spite of the fact that the selenium

film is patchy, this alloy is the easiest to protect of all those tested, and Table IV shows that the sulphate–bichromate process gave results as good as, or better than, those given by the selenium process. When comparing the selenium-coated specimens with others, it should be remembered that the loss-of-weight figures for the longer periods of

Table IV.—*Alloy AM*503 (12 *Weeks' Exposure*).

Loss of Weight, Grm.

Time of Treatment.	5% Selenious Acid.	10% Selenious Acid.
Laboratory Temperature.		
5 mins.	0·09; 0·08	0·10; 0·11
10 ,,	0·09; 0·11	0·13; 0·16
15 ,,	0·10; 0·13	0·14; 0·16
Temperature 50° C.		
2 secs.	... ...	0·07; 0·08
5 ,,	0·07; 0·07	0·09; 0·11
10 ,,	... ...	0·08; 0·11
1 min.	0·08; 0·07	0·08; 0·08
5 mins.	0·09; 0·11	0·12; 0·14
10 ,,	... ...	0·14; 0·20
15 ,,	... ...	... ...
Temperature 75° C.		
2 secs.	... ...	0·12; 0·10
5 ,,	0·09; 0·10	0·12; 0·13
10 ,,	... ...	0·10; 0·11
1 min.	0·11; 0·11	0·10; 0·11
5 mins.	0·13; 0·18	0·19; 0·19
Temperature 100° C.		
2 secs.	... ...	0·10; 0·12
5 ,,	0·12; 0·15	0·13; 0·14
10 ,,	... ...	0·12; 0·13
1 min.	0·16; 0·18	0·17; 0·16
5 mins.	0·17; 0·25	0·26; 0·16
10 ,,	0·22; 0·30	... ...
I.G. process (2 *weeks' exposure only*).		
5 mins.	0·07; 0·08	
Sulphate–bichromate process.		
6 hrs.	0·06; 0·04	
Blanks.		
Untreated	0·68; 0·73	

Note.—The first specimen of each pair was brushed before the corrosion test.

immersion should be decreased by about 0·03 grm. to allow for selenium removed by the chromic-acid bath.

Occasionally specimens of alloy AM503 showed intense local pitting, which is probably due to local segregation of manganese-rich materials, which are liable to occur unless special care is taken in the preparation of the alloy. None of the protection processes prevents this type of pitting, but the effect of paints has not yet been sufficiently tested.

TABLE V.—*Alloy VI* (8 *Weeks' Exposure*).

Losses of Weight, Grm.

Time of Treatment.	5% SeO_2.	5% SeO_2 + 0·1% NaCl.	5% SeO_2 + 0·5% NaCl.	10% SeO_2.	10% SeO_2 + 0·1% NaCl.	10% SeO_2 + 0·5% NaCl.
Laboratory Temperature.						
5 mins.	0·05; 0·06	0·64; 0·09	0·09; 0·09	1·16; 1·07	0·51; 0·52	0·11; 0·11
10 ,,	1·46; 0·04	0·55; 0·09	0·11; 0·13	0·06; 0·97	0·10; 0·80	0·09; 0·11
15 ,,	0·04; 1·61	0·10; 0·14	0·52; 0·12	0·05; 0·09	0·78; 0·12	0·53; 0·12
Temperature 50° C.						
5 mins.	2·44; 0·09	0·12; 0·13	0·11; 0·45	0·45; 0·13	0·13; 0·45	0·13; 0·17
10 ,,	0·09; 0·59	0·14; 0·13	0·12; 0·16	0·15; 0·14	0·14; 0·70	0·44; 0·14
15 ,,	1·37; 0·10	0·16; 0·14	0·16; 0·15	0·31; 0·16	0·12; 0·13	0·13; 0·85
Temperature 75° C.						
5 mins.	0·07; 2·48			0·11; 0·31		
10 ,,	0·10; 0·16			0·14; 1·74		
15 ,,	0·09; 0·16			0·14; 0·23		
Temperature 100° C.						
1 min.	1·60; 0·10			0·12; 0·25		
5 mins.	0·42; 0·16			0·14; 0·69		
Blanks.						
Untreated	2·70; 2·95					
Alum–dichromate process.						
6 hrs.	4·72; 0·42					
Sulphate–dichromate process.						
6 ,,	0·70; 2·70					
I.G. process.						
5 mins.	0·48; 0·04					

Note.—The first specimen of each pair was brushed before the corrosion test.

Alloy VI was tested in the form of cylinders 2·4 cm. in diameter and 5 cm. long, turned down from extruded rod, 2·5 cm. in diameter. Holes about 0·8 cm. in diameter were drilled near the ends for suspension vertically by gutta-percha covered wire. The results are shown in Table V. Considerable variation is shown between duplicates, which again seems to be due to local variations in composition. However, the bulk of the specimens stood up extremely well, as exemplified in Fig. 9 (Plate X). On the whole, the 10 per cent. selenious acid bath used at room temperature for 15 minutes seems to be the most hopeful.

The behaviour of most of the selenium-coated specimens of AZM, VI, and AM503 alloys was peculiar. After spraying, corrosion started at a few scattered centres, with deposition of specks of white product; but instead of proceeding rapidly, as is usual with magnesium alloys, it stopped, and the appearance of specimens was similar after several weeks under test to that after a few days. Probably corrosion was stopped by self-healing of the films due to deposition from hydrogen selenide released by decomposition of magnesium selenide at pores. To test this a selenium-coated specimen of AZM alloy was scratched and immersed in sea-water. Obvious deposition of selenium took place at the scratches, which became covered with a reddish-brown film. A similar phenomenon could occasionally be seen to take place at scratches in films exposed to the spray tests. No preferential attack occurred at scratches, even when no deposition of selenium could be observed. The partial covering and the lack of preferential attack along the scratch are illustrated in Fig. 13 (Plate XI).

The selenium protection process is covered by provisional patents Nos. 14724/31 and 1350/32.

TESTS ON PAINTED SPECIMENS.

A large number of different paints was applied to the untreated alloy 66, but none was satisfactory under the spray test. Intense corrosion occurred after only 10 days' exposure, and usually started from the holes or edges; blistering and stripping of the paint were frequent. Mediums tested included bitumen, tung oil, tung oil–glyptal resin, linseed oil, sulphur-treated oil, spar varnish, thermoprene resin, chlorinated rubber, and cellulose nitrate. Pigments tried included aluminium, ferric oxide, red lead, and titanium white. Several proprietary paints and lanoline were also tested. As a result of these tests it was decided to discontinue paint investigations on the bare alloys.

The effect of paints on selenium-coated specimens of AZM was very different. Several specimens have been exposed to the spray test for more than 16 weeks, and blistering and stripping have not yet occurred. The value of the selenium film is illustrated in Figs. 17 and 18 (Plate XI). The paint coat is still intact after 16 weeks on the treated specimens, whereas it failed at the holes after a comparatively short time on the untreated alloy.

Coats that have stood up reasonably well on selenium-treated AZM alloy are thermoprene resin and sprayed lanoline solution pigmented with aluminium powder. Thermoprene resin appears to harden to a much greater extent after application over a selenium film than after application to the bare metal; it is possible that an action analogous to vulcanization takes place.

A peculiar phenomenon was observed with an aluminium pigmented tung oil–glyptal resin medium. A large number of small red spots appeared on the surface of the paint in the early stages of the test, and increased in number with time. This phenomenon, inexplicable at first sight, is thought to be due to deposition of selenium at and round the pores in the paint film, owing to formation of a trace of hydrogen selenide, which is decomposed by the water and oxygen surrounding the pore. The function of the selenium is to close the pores in the paint. Fig. 15 (Plate XI) illustrates a specimen after 3 months' exposure, showing a mass of these small red blisters. It appears to be severely attacked, whereas after removal of the paint film each red blister was found to correspond only with a light and thinned patch in the selenium coating as shown by Fig. 16 (Plate XI). No pitting was visible at any of the light patches, and the loss of weight of the specimen was but 20 mgms. The same phenomenon has been noticed at the edges of a specimen with a top coating of spar varnish, where, although the varnish has actually cracked, corrosion has been stopped at these parts.

Cellulose enamels, although useful as top coats for other paints, appear of little use by themselves, whether on bare or on selenium-coated metal. This is thought to be due to their lack of elasticity, a disadvantage when dealing with a metal such as magnesium which has a high coefficient of thermal expansion. A comprehensive investigation is at present in progress on the effect of both pigment and medium on selenium-coated metal.

ACKNOWLEDGMENTS.

The authors wish to acknowledge the assistance they have received in the later part of the experimental work from Mr. J. B. Ditcham, and the useful discussions about the selection of promising paints with Dr. J. O. Cutter of the Paint Research Station, Teddington. The research was carried out for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, and the thanks of the authors are due to the Chairman, Professor Sir Harold Carpenter, Kt., F.R.S., and to Professor G. T. Morgan, F.R.S., Director of Chemical Research, for many facilities afforded and for permission to publish.

APPENDIX.

Some Properties of Selenium.

There is general agreement that elemental selenium is not poisonous,* but some of its compounds are stated to be so, and are believed to act analogously to those of arsenic and antimony. Hydrogen selenide is stated † to be more toxic than hydrogen sulphide or hydrogen telluride, but in the authors' experience no danger arises from it in the processes mentioned in this paper, partly perhaps owing to the extremely small concentrations in which it occurs, and partly to the rapidity with which it is decomposed in presence of moisture and oxygen ‡ with deposition of selenium. It seems probable, however, that the toxicity of selenium compounds has been over-estimated; certainly no ill effects were felt by Professor G. T. Morgan and his assistants in their extensive researches on organic compounds of selenium.

Selenium is extremely stable under all normal conditions of exposure; it is even less oxidized than sulphur by aerial oxygen,§ and is insoluble in water.‖ Unlike sulphurous acid, selenious acid solutions are not oxidized by aerial oxygen, and, moreover, do not deposit selenium on standing. Exposure to strong sunlight, however, is stated ¶ to result in a deposition of selenium, and to avoid gradual exhaustion of the bath by this means it should be kept covered when not in use.

Exhaustion of a selenious acid bath will occur in practice due to gradual removal of selenium and to saturation of the liquid with magnesium selenite, which will then be deposited on the surface of the metal as colourless crystals. At this stage it becomes a simple matter to recover all selenium remaining by addition of hydrochloric acid and passage of sulphur dioxide through the heated liquid. The selenium which is rapidly precipitated in this way, may be filtered off and re-converted to selenium dioxide by treatment with nitric acid.

* Czapek and Weil, *Arch. Exp. Path. Pharm.*, 1893, **32**, 438; Woodruff and Gies, *Amer. J. Physiol.*, 1902, **6**, 29; Lehrmann, *Biochem. Zeit.*, 1923, **134**, 390.

† Forcraud and Fonzes-Diacon, *Compt. rend.*, 1902, **134**, 171, 229, and 281.

‡ Moser and Doctor, *Z. anorg. Chem.*, 1921, **118**, 284.

§ Krafft and Steiner, *Ber.*, 1901, **34**, 560.

‖ Cross and Higgen, *J. Chem. Soc.*, 1879, **35**, 249.

¶ de Coninck, *Compt. rend.*, 1906, **142**, 511.

DISCUSSION.

Mr. H. Sutton,* M.Sc. (Member): This paper is of very great interest to me and to my colleagues at Farnborough. I should, in the first place, like to congratulate the authors on having conducted some most valuable experiments on the protection of magnesium against corrosion by surface treatment. The present paper introduces a surface treatment for magnesium alloys which is of great scientific interest, and one which seems to be capable of useful technical application. The problem is one of considerable difficulty; those who have actually had experience in this field best know the difficulties.

There now appears to be some accumulation of evidence to show that cleaning the surface of magnesium alloy samples in nitric or sulphuric acid, and the consequent removal of the surface layer of the alloy, usually more or less contaminated by foreign matter worked into the alloy during manufacture, has a pronounced benefit on the corrosion resistance; the removal of the contaminated surface layer is advantageous.

In this paper we are given some results of comparative tests of samples treated by the Jirotka, the selenium, and the bichromate treatment processes. If the Jirotka and the bichromate treatment processes were applied without previous acid cleaning of the wrought material, the results should not be compared directly with the rest, on account of the known benefit of acid cleaning. Process No. 1 (the I.G. process) entails, of course, the removal of a large amount of material from the surface.

Do the authors consider that the coating contains any selenious acid, and if so do they think that this helps in healing discontinuities at points where the film is damaged? I understand that they regard magnesium selenide as responsible for the self-healing process. This appears to me to be a novel and highly interesting example of self-healing of a protective film, and the mechanism of the self-healing action appears to be well worthy of close study.

In Table V, I observe a very great difference in the behaviour of duplicate samples treated by the alum dichromate process; one suffered a loss in weight of 4·72 grm. and the other of 0·42 grm. That seems an enormous difference. The corrosion observed on one of these samples was greater than that of the blanks, which to me is a very surprising result. It would be of considerable interest to know if the authors investigated the two samples I have mentioned, in order to ascertain, if possible, the reason for the very pronounced discrepancy in the results of the corrosion test. Occasionally we have found that local segregations in manganese have given very discordant results in duplicate or triplicate observations of corrosion resistance by sample tests such as these. We have further found that there is a very great difference in resistance to corrosion between alloys containing, say, 0·2 per cent. manganese and 0·5 per cent. manganese. In Table I those percentages are quoted as the limits of manganese content of one of the alloys used in the investigation, and we should have been very interested to see the results of actual chemical analyses made on the various batches of material used in the present research.

The importance of a high manganese content is clearly shown in Table IV, in which improved resistance to corrosion is shown by specimens treated by all the methods described and also by the blanks. The alloy investigated in this case contained 1·3 to 1·7 per cent. of manganese.

With regard to the failure of cellulose enamels our ideas may be a little different from those of the authors. We believe that they sometimes fail as a result of very considerable changes in volume under changes of humidity.

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* Senior Scientific Officer and Head of the Metallurgical Department, Royal Aircraft Establishment, Farnborough.

It would be interesting to us to know whether the authors have treated an alloy containing copper. In some of the chromate baths we have experienced difficulties in dealing with alloys containing copper. There is also, of course, difficulty in the nitric acid cleaning of alloys containing copper, owing to the tendency of copper to redeposit.

I am inclined to agree with Dr. Bengough's remarks in introducing the paper, that a good deal will depend on the behaviour of the protective film under coats of enamel and other organic protectives.

Captain R. H. Atkinson,* R.E.: I should like to inquire whether the authors have tried tellurium. It is so similar in properties to selenium that that is a question one is naturally led to ask, especially as so many different solutions were tried. If anything, tellurium is more "noble" than selenium; in fact, it is sufficiently "noble" to be a source of trouble in the refining of the platinum metals. As to its availability, I think there are considerable quantities in the anode slimes in the electrolytic copper refineries, and a certain amount is also obtained as a by-product in the refining of the platinum metals from nickel ores.

Dr. R. S. Hutton † (Vice-President): The authors' process for the protection of magnesium looks as though it might prove just as valuable and effective as the one Dr. Bengough gave the world some years ago for aluminium. The importance of these films, particularly if they possess any self-healing properties, is so great that I venture to ask the authors whether it would not be possible to evolve more rational methods of testing these coatings than the purely empirical ones which it seems still the custom to employ. Obviously we do want to know whether alloys when protected in this way will stand up to salt-spray tests and so on, but could we not get a little nearer to the fundamentals? It seems to me that the effective value of these films depends on several different properties. In the first place, surely they have to be thoroughly well bedded down on the basis metal. Mr. Sutton referred to the importance in that connection of the preliminary acid or other cleaning of the metal before the coating is applied. There are methods, which have been used already in another direction,‡ by which we can make a quantitative test of the adhesion of films to the underlying metal. Is it feasible to try to devise some standard test of this nature, suitable for protective coatings?

Another important property is the porosity of these films—how continuous and uniform or full of fissures and pores. Surely there again it ought to be possible to devise some simple test that would indicate the relative porosity of these films. The protective films have also to be chemically resistant to a range of corrosive materials.

All those three properties—and perhaps there are others—are quite distinctive, and demand individual tests; and, as we have the rare opportunity of Dr. Bengough's presence here to-day, I put forward these questions in the hope that now, or at some later period, he will work out for us some systematic series of rational tests which might be applied quite generally to problems of this nature.

Dr. W. Rosenhain,§ F.Inst.Met., F.R.S. (Past-President): I associate myself with what Mr. Sutton said about the extraordinary interest and practical importance of the work described in this paper, and also, from a little personal knowledge, I can support what he said as to the difficulties encountered in experiments on subjects of this kind.

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

‡ Nottage, *Proc. Roy. Soc.*, 1930, [A], **126**, 630.

§ London.

First of all, the alloys used, so far as I could gather from, I am afraid, a not too careful perusal of the paper, were always in the wrought condition, either sheet or extruded metal?

Dr. Bengough: There was one casting.

Dr. Rosenhain: That answers my question, because the magnesium alloys are largely used at the present time in the cast condition, and the behaviour might not be the same; but I am glad to hear it has been included.

With regard to the character of the film, Dr. Hutton has already put some of the questions that I wanted to ask, but one I might add concerns the electrical insulating properties of this film. I am not considering it so much from the corrosion protection point of view, although no doubt electrical insulating power is an important factor there, but from a much more general point of view, both as to the character of the film and as to its possible uses in other directions. Dr. Bengough is no doubt well aware, as many of you are, that the anodic film on aluminium is being used for electrical insulation purposes at the present time, and we may perhaps live to see magnesium being not exactly self-insulated, but almost so, in a similar manner.

That raises another question which attaches itself very closely to what Dr. Hutton has said; I refer to the question of what he called the porosity of the film. I am inclined to use a more general term, and say the permeability of the film as measured in this way. We saw the lightning-like rapidity with which that film is deposited when the solution is rubbed over a piece of clean magnesium. It reminded me very much of the action of mercuric chloride on aluminium; the attack is equally rapid. The question in my mind is, Does the film reach a limiting thickness very quickly? In other words, does one get in a few seconds as much protection and as great a weight or thickness of film as can be got at all, or does the action continue if the exposure to the reagent is prolonged, and can the film be strengthened, possibly, by some form of electrolytic action—the application of a current, for instance? These questions seem to me to be of importance in connection with the vital matter of the self-healing property of a film, because I think that it has been stated, and with a good deal of truth, that a protective film is of no use unless it is self-healing. Any other film is really nothing more than a paint, although it may be a very good paint, and therefore is liable to damage and the piece is liable to destruction because of slight local injury.

If the film can definitely be made to hold in some form or other the reagent from which selenium is further deposited in a sufficiently definitely attached form, so that it shall not be washed out readily, even if for that purpose it is necessary to protect the layer by a surface coating of some kind, then we should get the conditions under which self-healing could be very pronounced; otherwise I find it difficult to see how the mere presence of selenium in one part of the film will account for the film being reformed, except over very small fissures. I gather that at present its self-healing property is limited in that way.

Captain Atkinson referred to the use of tellurium. Personally, I am very grateful that tellurium was not used by Dr. Bengough and his colleagues. Some of his colleagues did work with tellurium for some time, and I had the misfortune for some months to sit at lunch in the same building with them. I kept as far away as possible, but really it became very difficult, because of the quite unavoidable unpleasant effluvium which workers in that material acquire. I think that it will not be used if it can possibly be avoided for any industrial purpose whatever, except possibly in an isolated island in the Atlantic or Pacific!

Mr. WHITBY (*in reply*): In reply to Mr. Sutton's question whether all the materials were first pickled, I would say that they were; those treated by the Jirotka process being first pickled in nitric acid before being sent for treatment. I cannot say whether the coating contained selenious acid. In every case the film was thoroughly washed before being submitted to the sea-water spray, and, in view of the high solubility of selenious acid, it seems rather doubtful if more than a trace could be left. On the question of the differences between certain duplicate specimens in Table V, I think that Mr. Sutton will find that many other duplicates besides those for the alum–dichromate process have exhibited fairly large differences. We think that it is almost undoubtedly due to the local segregation of manganese. We agree with Mr. Sutton that humidity may be a factor in producing the breakdown of cellulose films. We have not treated any alloys containing copper, but have confined ourselves almost entirely to alloys having the greatest commercial use.

Captain Atkinson asked whether we had used tellurium. We have used it, and I have a specimen here which has been coated with tellurium; I can assure Dr. Rosenhain that it has no objectionable properties. So far as tellurium is concerned, I should like to point out that the choice of compounds is very limited. Tellurium dioxide, unlike selenium dioxide, is insoluble in water. Tellurous acid is also insoluble in water for all practical purposes, so that one is confined mainly to the use of telluric acid or its salts. If a solution of potassium tellurite be acidified tellurium dioxide is precipitated. Another point against it is its higher cost.

Dr. Rosenhain asked whether castings had been treated. There were two castings among the specimens which we passed round, and we are also investigating castings of AZG alloy. As to the insulating properties of selenium, the film itself is usually a mixture of the red and grey forms; the grey form is, of course, a conductor, hence I do not think that the film would be so good an insulator as the anodic oxidation film on aluminium. The film can be thickened to a considerable extent by increasing the time of immersion, but begins to flake off after it has reached a certain thickness.

CORRESPONDENCE.

THE AUTHORS (*in further reply to the Discussion*): We agree with Dr. Hutton that it is desirable that the characteristic properties of protective films should be investigated in detail. It will take a long time to devise a set of tests of the properties which will predict behaviour in practice; the factors are probably numerous, and may include power of self-healing, insolubility, adhesion, continuity, low conductivity, and chemical and physical stability in fluctuating conditions. The relative importance of these factors has still to be ascertained, and until an immense mass of data has been collected and correlated with field tests it is necessary to depend mainly on the latter in spite of their apparent crudeness. Field tests may, indeed, be defended on the ground that they test the relevant properties *en bloc*, and the information obtainable from them is limited only because they usually include what is presumed to be typically bad, and not all possible, conditions of exposure, and because they do not usually throw much light on the mechanism of protection. Laboratory investigation is, therefore, desirable to quicken understanding of the problems involved.

Captain Atkinson will probably be interested in the following experiments with tellurium.

Films were formed on AZM alloy by immersion in potassium tellurate slightly acidified with sulphuric acid. The tellurate was made from metallic tellurium by oxidation to TeO_2 with nitric acid, evaporation to dryness, removal of copper, dissolution in potassium hydroxide, oxidation by hydrogen peroxide, and recrystallization from water. The films were dark brown or black, smooth and adherent, but much tellurium was deposited in the solution instead of on the alloy. Specimens were exposed for 5 weeks to the sea-water spray test described in the paper and the losses of weight in grams were :—

K_2TeO_4, %.	0·5	1·0	2·0	5·0	10·0
Laboratory Temperature.					
1 minute immersion	0·55	...	...	...	...
5 ,, ,,	...	0·88	0·52	0·82	0·84
10 ,, ,,	...	...	...	0·66	0·47
50° C.					
1 ,, ,,	...	...	...	0·58	0·93
5 ,, ,,	...	0·36	0·49	0·70	...
15 ,, ,,	...	0·64	...	0·63	...
75° C.					
1 ,, ,,	...	...	0·56	0·42	0·19
5 ,, ,,	...	0·35	0·28	0·41	...
100° C.					
1 ,, ,,	...	...	0·68	0·31	...
5 ,, ,,	...	0·51	0·28	...	...
Blank.					
1·21					
Selenium process.					
(10% SeO_2 + 0·5% NaCl, 5 minutes at laboratory temperature.)	0·08	0·13			

The tellurium films compare unfavourably with those of selenium; corrosion when once started does not stop.

INTERCRYSTALLINE CORROSION OF DURALUMIN.*

By A. J. SIDERY,† Assoc.Met. (Sheff.), MEMBER, K. G. LEWIS,‡ M.Sc., and H. SUTTON,§ M.Sc., MEMBER.

SYNOPSIS.

Experiments were carried out to determine the influence of overstrain in tension or in compression and of certain modifications of heat-treatment on the tendency of Duralumin to develop intercrystalline corrosion. For the purpose of evolving a reliable test which would permit the relative susceptibility of various samples of Duralumin to this form of corrosion to be estimated in a reasonable space of time several reagents were investigated. It was found that partial immersion in a N-1 solution of sodium chloride to which 1 per cent. (by weight) of hydrogen chloride had been added was capable of producing intercrystalline corrosion consistently in samples of Duralumin where a propensity towards this type of corrosion existed. The effect of overstrain was examined by subjecting to this test a number of specimens of heat-treated Duralumin sheet to which tensile stress had been applied to produce various degrees of permanent elongation and a number of longitudinal strips cut from samples of heat-treated Duralumin tube which had been compressed to arbitrarily selected stresses above the elastic limit in compression. The results of the experiments indicated that overstrain in tension increased slightly the tendency towards intercrystalline penetration, but no relation was observed between this tendency and the degree of elongation. There appeared, however, to be a critical range of stress in compression, viz., 14·0–16·9 tons/in.^{2}, for the material employed in the experiments. Samples which had been compressed in this range of stress showed the greatest susceptibility. Corrosion tests were made on samples of the sheet and tube which had been heated at various temperatures in the range 470°–520° C., quenched in cold or in boiling water, and aged at room temperature with a view to ascertain the influence of such modification of heat-treatment and of quenching medium on the susceptibility of the material to intercrystalline attack. It was observed that, in general, the higher the quenching temperature the smaller was the tendency of the material to develop intercrystalline corrosion, but there was, however, an increased tendency towards the pitting form of superficial corrosion under the conditions of test employed. Material quenched in boiling water showed a very much greater propensity towards the intercrystalline form of corrosion than did material quenched in cold water or in cold oil.

UNDER certain conditions of use Duralumin has sometimes been found to develop a form of corrosion which penetrates below the surface of the material and is not necessarily accompanied by visible corrosion

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product on the surface. In the early stages the general effect of this form of attack, which is intercrystalline in character, is a marked reduction in the ductility of the material and a somewhat smaller decrease in maximum stress.

Rawdon [1] asserts that this deterioration results from sources outside the Duralumin, and that it is not a spontaneous disintegration of the metal itself. He also states that no distinct evidence of a structural condition at the grain boundaries which would definitely account for the intercrystalline corrosive attack has yet been found in the microstructure of Duralumin sheet,[2] and that the propensity of the material for intercrystalline corrosion is intimately bound up with the method of heat-treatment used.[3]

Pessel [4] carried out some interesting experiments in which specimens of Duralumin sheet, which had been subjected to pressure shortly after heat-treatment and aged while under pressure, were submitted to corrosion tests in comparison with material similar as regards composition and heat-treatment, but which had been aged in the normal manner. His results indicated that material aged under pressure suffered a slightly smaller loss of tensile strength and ductility after corrosion than did the alloy aged without the application of pressure.

Grogan and Clayton [5] suggest that compressive stresses in the surface layers of cold-water-quenched Duralumin being much higher than those in boiling-water-quenched material account for the difference between these materials in resistance to intercrystalline corrosion.

Von Zeerleder [6] investigated the effect of cold- and warm-water quenching in the final heat-treatment of an alloy of the Duralumin type. Quenching in water at 50° C. and ageing at 50° C. were found to have no effect on resistance to corrosion.

Meissner [7] investigated the deterioration of "super-Duralumin" by corrosion as influenced by ageing temperature.

In the present paper experiments are described which were made to determine the effects of overstrain and also of certain modifications of heat-treatment on the tendency of Duralumin towards intercrystalline corrosion.

For the purpose of these experiments it was considered desirable to develop a form of corrosion test which would enable the susceptibility of the material to intercrystalline corrosion to be determined and which would give consistent results in a reasonable space of time.

A series of exploratory corrosion tests of the "water-line" type was made on samples of 20-S.W.G. British Duralumin sheet having three conditions of surface, viz., "as heat-treated," "sand-blasted," and "scratch-brushed," in order to afford information on the influence of the type of surface on the susceptibility to intercrystalline corrosion.

The samples had been previously heated for 15 minutes at 490° C. in an electric muffle furnace, then quenched in cold water (temperature 18°–20° C.) and allowed to " age " at room temperature for at least 8 days.

The sand-blasting was carried out with fine silica sand used at a pressure of 6–8 lb./in.^{2}, whilst in the scratch-brushing operation care was taken to obtain a uniform surface finish on the samples.

The suitability of the following reagents as corroding media was investigated :—

(1) Natural sea-water (obtained from the English Channel).
(2) *N*-1 solution of sodium chloride.
(3) Aqueous solution containing 1 per cent. (by weight) sodium chloride + 0·5 per cent. (by weight) sodium bicarbonate.
(4) Mylius' reagent, consisting of an aqueous solution containing 1 per cent. (by weight) sodium chloride + 3 per cent. (by weight) hydrogen peroxide.
(5) *N*-1 solution of sodium chloride to which 1 per cent. (by weight) of hydrogen chloride had been added.
(6) *N*-1 solution of sodium chloride to which 3 per cent. (by weight) of hydrogen chloride had been added.

A standard volume, viz. 250 c.c., of each of the above solutions was measured out into glass vessels which were supported in a large mechanically-stirred water-bath, the temperature of the solutions being maintained thermostatically at 20° C. ± 0·1° C. and losses due to evaporation being replaced by frequent additions of the requisite amounts of distilled water. Samples in each of the three surface conditions were suspended in each of the above reagents so that a total area of 50 cm.^{2} of rolled surface was immersed, the upper portions of the specimens being coated with paraffin wax down to approximately 5 mm. from the " water-line " in order to prevent creeping of the solution and to localize the formation of corrosion product.

The samples were immersed in this manner for 14 days, with the exception of those cases where Mylius' reagent was used. In these instances the period of immersion was 3 days.

At the conclusion of the test period the samples were sectioned longitudinally and examined microscopically.

The results of microscopical examination of these preliminary specimens indicated that, of the three surface conditions investigated, a sand-blasted surface afforded the greatest facility to intercrystalline attack of the material. As this type of surface could be produced reasonably consistently, the surfaces of subsequent specimens were prepared in this manner, except where otherwise stated. Further, a

N-1 solution of sodium chloride to which 1 per cent. (by weight) of hydrogen chloride had been added was capable of producing intercrystalline corrosion consistently in Duralumin, in cases where a tendency towards this type of corrosion existed, in short-time tests of the type employed. This solution was considered to be the best of the reagents investigated and was selected for subsequent experiments.

PART I.—INFLUENCE OF OVERSTRAIN IN TENSION OR IN COMPRESSION.

For information on the effect of overstrain in tension or in compression on the tendency of Duralumin to develop intercrystalline corrosion, a series of tests was made on samples of recently manufactured British Duralumin sheet and tube, the sheets being 6 ft. × 2 ft. × 0·036 in. thick and the tube 2 in. external diameter, 0·064 in. thick, and approximately 12 ft. long.

The composition of the materials as determined by chemical analysis was as follows :—

	Sheet No. 1.	Sheet No. 2.	Tube.
Silicon, per cent. . .	0·28	0·19	0·34
Copper, ,, . .	4·02	4·25	4·10
Manganese, ,, . .	0·63	0·59	0·59
Magnesium, ,, . .	0·59	0·40	0·40
Iron, ,, . .	0·48	0·48	0·42
Tin, ,, . .	nil	nil	nil
Zinc, ,, . .	nil	nil	nil
Nickel, ,, . .	nil	nil	nil
Aluminium, ,, . .	remainder	remainder	remainder

The results of mechanical tests made on samples of the materials in the condition "heated at 490° C. for 15 minutes in an electric muffle furnace, quenched in cold water and aged at room temperature for 8 days" were as follow :—

	Sheet No. 1.		Sheet No. 2.		Tube.
	In Direction of Rolling.	Normal to Direction of Rolling.	In Direction of Rolling.	Normal to Direction of Rolling.	Compression.
	Tension.	Tension.	Tension.	Tension.	
Elastic limit, tons/in.^{2} . . .	8·8	7·5	9·7	9·5	10·5
0·1 per cent. Proof Stress, tons/in.^{2}	14·7	14·2	15·6	13·2	14·9
0·5 per cent. Proof Stress, tons/in.^{2}	16·4	16·0	17·3	15·2	17·0
Maximum Stress, tons/in.^{2} . .	25·1	25·0	26·7	28·0	17·8
Elongation, per cent. . .	20·0	18·0	14·0	18·0	...

FIG. 1.—× 100.

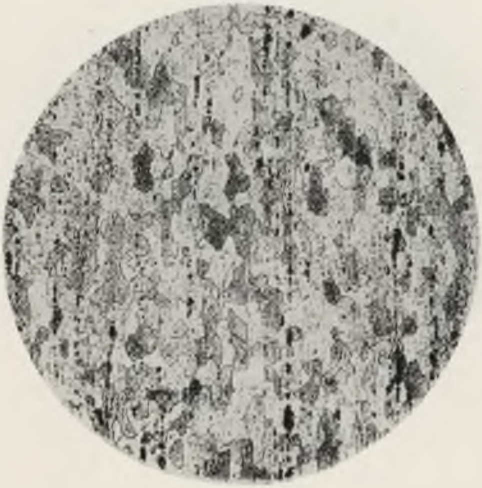


FIG. 2.—× 100.

[*To face p.* 168.

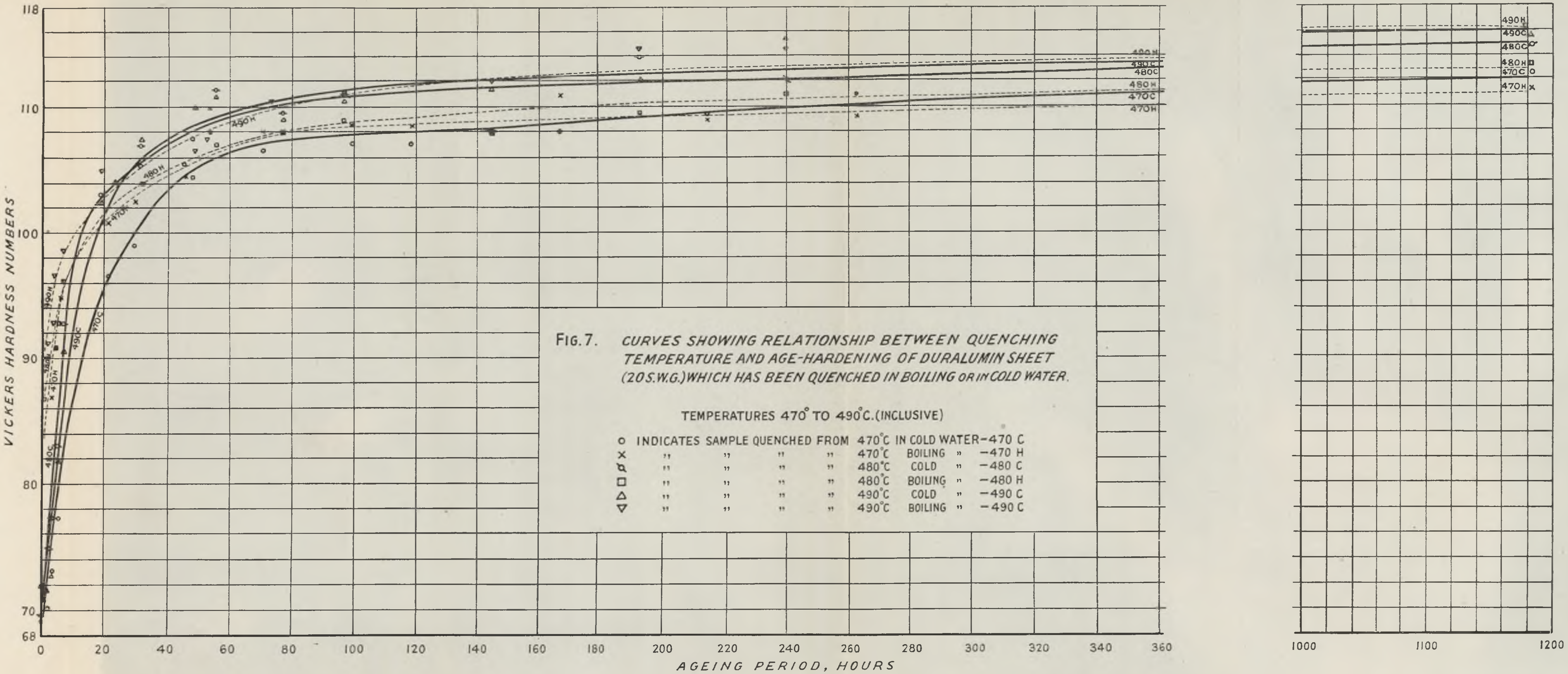


FIG. 7. *CURVES SHOWING RELATIONSHIP BETWEEN QUENCHING TEMPERATURE AND AGE-HARDENING OF DURALUMIN SHEET (20 S.W.G.) WHICH HAS BEEN QUENCHED IN BOILING OR IN COLD WATER.*

TEMPERATURES 470° TO 490°C. (INCLUSIVE)

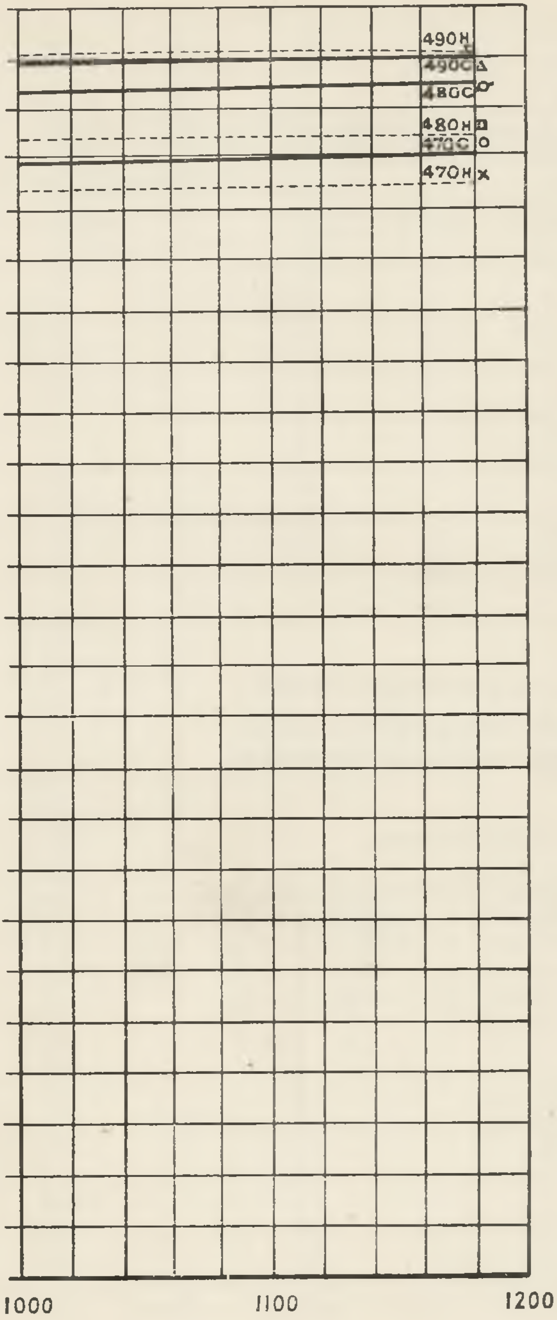
FIG. 4.—× 100.

FIG. 5.—× 100.

Samples of Duralumin Sheet after 14 days' immersion in *N*-1 Sodium Chloride solution to which 1 per cent. (by weight) of Hydrogen Chloride had been added.

Left. Quenched in boiling water in heat-treatment.
Right. ,, ,, cold ,, ,, ,, ,,

PLATE XIV.



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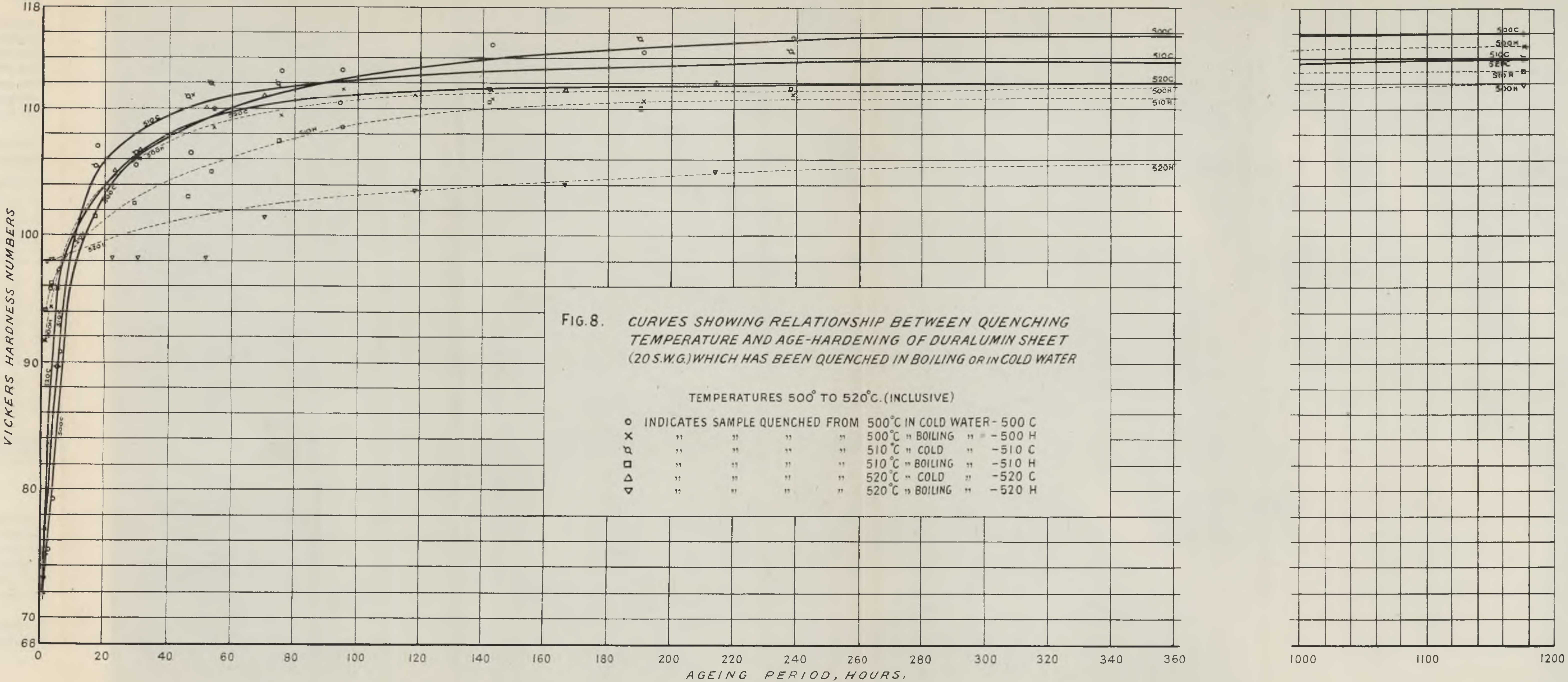


FIG. 8. CURVES SHOWING RELATIONSHIP BETWEEN QUENCHING TEMPERATURE AND AGE-HARDENING OF DURALUMIN SHEET (20 S.W.G.) WHICH HAS BEEN QUENCHED IN BOILING OR IN COLD WATER

The microstructure of a longitudinal section of the sheet cut perpendicularly to the rolled surface, polished, and etched with a reagent consisting of equal parts by volume of 5 per cent. hydrofluoric acid and 10 per cent. nitric acid is shown in Fig. 1 (Plate XII) × 100, and that of a section of the tube cut in a plane normal to the surface and parallel with the axis is shown in Fig. 2 (Plate XII) × 100. The grains of the tube were finer and more nearly equiaxed than those of the sheet.

For experiments on the influence of strain in tension, tensile test-pieces were prepared from sheet No. 1 having test-length dimensions of 10 × 1·25 cm. After stress had been applied to secure the desired degree of permanent elongation, the heads of the test-pieces were cut off, leaving a sample 10 × 1·25 cm. for corrosion test. Some of the test-pieces were cut with their axis in the direction of most rolling of the sheet and others with their axis normal to that direction. Unstressed samples were included in each series of corrosion tests for purposes of comparison.

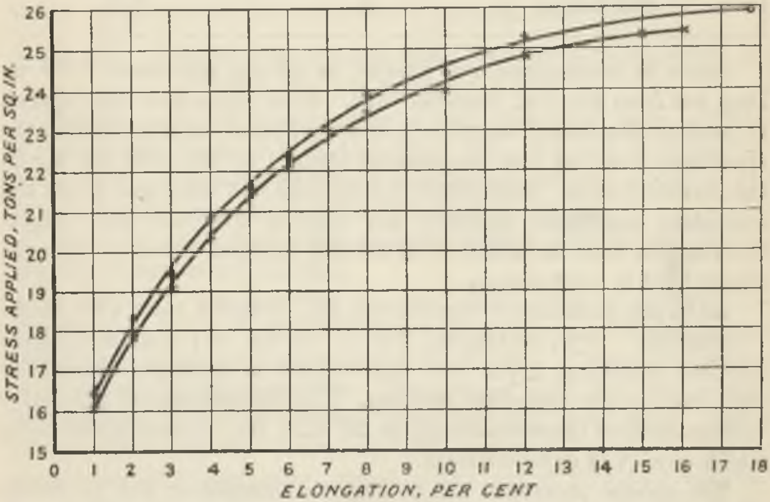


FIG. 3.—Curve showing the Relationship Percentage Elongation–Stress applied (tons/in.^{2}) in Duralumin which was given Normal Final Heat-Treatment, "Aged" in Air at Room Temperature, and Stressed in Tension to give various Degrees of Elongation.

——○—— Samples cut in the direction of rolling.
——×—— Samples cut normal to the direction of rolling.

The average stresses required to give the requisite amounts of permanent elongation are shown in Table I and are represented graphically in Fig. 3.

TABLE I.

Samples Stressed in the Direction of Rolling.	Samples Stressed Normal to the Direction of Rolling.	Elongation, per cent.
16·4	16·0	1
18·3	17·9	2
19·5	19·1	3
20·8	20·4	4
21·6	21·4	5
22·3	22·2	6
23·9	23·4	8
24·4	24·0	10
25·5	25·3	15
...	25·4 (failure)	16·1
25·9 (failure)	...	17·8

Strain in compression was applied to tubular specimens, 3·125 in. long, cut from the 2-in. diameter tube. After stress had been applied to produce the desired degree of permanent strain in compression, the specimens were cut into longitudinal strips 1·25 cm. wide for use in the corrosion tests. Since strain in compression of tubes was, under the conditions employed, probably not uniform over the test length, the samples were subjected to arbitrarily selected stresses above the elastic limit in compression.

As in the preliminary experiments, the corrosion tests were of the " water-line " type, employing 250 c.c. of the N-1 sodium chloride solution containing 1 per cent. (by weight) of hydrogen chloride in each case as the corroding medium. The temperature of the latter was maintained thermostatically at 20° C. ± 0·1° C. during the tests, which were of 14 days' duration.

The general procedure was to heat the samples at 490° C. for 15 minutes, quench in cold water (18°–20° C.), allow them to age for at least 8 days at room temperature, and then to give them the desired amount of strain, if any, in tension or compression. In some cases the specimens were stressed immediately after heat-treatment and allowed to " age " while in the corroding medium.

Before being subjected to corrosion test the surfaces of the specimens were sand-blasted and the upper portions of the samples coated with paraffin wax down to 5 mm. from the " water-line " to prevent excessive creeping of the solution. The following are observations made on the various batches of samples tested.

Series I. Samples Heat-Treated, Aged, Strained in Tension, and then Subjected to Corrosion Test.

After the samples had been cleaned and washed, it was seen that the pitted areas were elongated in the direction of rolling. Microscopical examination revealed severe pitting and coarse, irregular intercrystalline corrosion on all the samples. The samples stressed normally to the direction of rolling were the most severely attacked.

Series II. Samples Strained in Tension Immediately after Heat-Treatment and Quickly Transferred to Corroding Reagent.

The samples appeared superficially to have behaved in the same manner as normally aged material. Intercrystalline corrosion was fairly general throughout the series. The samples stressed normal to the direction of rolling to 8 and 12 per cent. elongation contained small areas of typical intercrystalline corrosion.

On the whole, corrosion was not quite so severe as in samples aged before being strained and subjected to corrosion test.

Series III. Samples Heat-Treated, Aged, Strained in Compression, and then Subjected to Corrosion Test.

Samples were cut from lengths of tube which had been subjected to compressive loads of 11·5, 13·0, 14·0, 15·5, 16·9, and 21·3 tons/in.^{2}, respectively, after heat-treatment and ageing. Under a load of 21·3 tons/in.^{2} buckling of the tube was observed at one end.

Corrosion tests were made on the strained samples and also on samples of unstrained material.

A tendency was observed for an "oval" form of corrosion, as illustrated in Fig. 4 (Plate XIII), to develop in the unstrained specimens and in those which had been most highly stressed. Pitting was observed on practically all the specimens. The samples which had been stressed in the range 14·0–16·9 tons/in.^{2} were the only ones which showed typical intercrystalline corrosion. The overstrain produced by the application of compressive stress in the range 14·0–16·9 tons/in.^{2} appeared to be critical as regards the tendency of the material towards intercrystalline corrosion. This observation was confirmed by the results of tests made with several other reagents.

In order to ascertain whether this range of stress when applied in tension would produce overstrain corresponding with a maximum degree of susceptibility of the material to intercrystalline attack, strips were cut from the tube, heat-treated, aged, and machined to the form of tensile test-pieces having a gauge-length of 10 cm. and a width over the gauge-length of 1·25 cm. These were then stressed as follows:—

Sample No.	Stress Applied. Tons/in.^{2}.	Permanent Elongation. Per cent.
1	14·0	0·1
2	15·5	0·2
3	16·9	1·2
4	21·9	5·0
5	25·0	10·0
6	27·7 (failure)	14·0

Corrosion tests of a similar nature to those employed in the case of previous samples strained in tension were then made on the specimens, which were subsequently examined microscopically.

The microscopical examination revealed very little typical intercrystalline corrosion among this series of samples as compared with the corresponding batch of specimens strained in compression. The samples stressed in the range 14·0–16·9 tons/in.^{2} did not exhibit any marked tendency towards the above form of corrosion; for instance, the sample which had been stressed at 15·5 tons/in.^{2} was merely pitted.

Effect of Aeration of Corroding Agent.

In order to ascertain the effect of aeration on the behaviour of Duralumin samples under corrosion test, a series of specimens of the sheet 10 cm. × 1·25 cm. was given the normal final heat-treatment (*i.e.*, heated at 490° C. for 15 minutes and quenched in cold water) and subjected to corrosion tests in the following conditions :—

Series A—Heat-treated and immediately subjected to corrosion test.
Series B—Heat-treated, aged, and subjected to corrosion test.
Series C—Heat-treated, aged, strained in tension, and subjected to corrosion test.

The reagents employed for series A and B consisted of :—

(1) Natural sea-water (from the English Channel).
(2) *N*-1 solution of sodium chloride.
(3) Solution containing 1 per cent. (by weight) of sodium chloride + 0·5 per cent. (by weight) of sodium bicarbonate.
(4) *N*-1 solution of sodium chloride to which 1 per cent. (by weight) of hydrogen chloride had been added.
(5) *N*-1 solution of sodium chloride to which 3 per cent. (by weight) of hydrogen chloride had been added.

In series A and B samples having three types of surface, viz., " as heat-treated," " sand-blasted," and " scratch-brushed," were subjected to test in each reagent. In the case of series C, " sand-blasted " surfaces and reagent (4) only were employed. The corrosion tests were of the " water-line " type hitherto employed, but bubbles of air were caused to impinge on a definite area of each sample at a depth of 4 cm. from the " water-line." The bubbles were ejected at regular intervals from glass capillary tubes. The tests were of 14 days' duration, at the end of which the specimens were microscopically examined.

Observations on the various series are given below.

Series A.

All the samples immersed in the acid solutions showed greater corrosion than the rest. The former all showed some coarse and irregular intercrystalline corrosion. The samples immersed in the solution containing sodium bicarbonate also showed irregular intercrystalline corrosion in places. Generally, the effect of aeration appeared to be to increase corrosion slightly near the point of impingement.

Series B.

A small amount of intercrystalline corrosion was observed on the samples immersed in the reagent containing sodium bicarbonate. Those immersed in the acid solutions showed much irregular intercrystalline corrosion of both the coarse and fine varieties and, also, the " oval " form of corrosion.

Series C.

This series included samples strained in tension in the direction of rolling and samples strained in tension normal to the direction of rolling, the range of elongation being similar to that employed in previous experiments.

Throughout the series pitting and irregular intercrystalline attack were fairly general. The " oval " form of corrosion predominated in the lower portions of those samples which had been strained in the direction normal to that of rolling.

PART II.—INFLUENCE OF QUENCHING IN BOILING WATER COMPARED WITH THAT OF QUENCHING IN COLD WATER IN FINAL HEAT-TREATMENT.

In view of the fact that hot water is sometimes used in practice as the quenching medium in the final heat-treatment of Duralumin, with the object of accelerating age-hardening or of reducing distortion due to internal stresses, the effect of quenching in boiling water on the corrosion-resistance of the material was compared with that of quenching in cold water. Samples 10 cm. × 1·25 cm. cut from sheet No. 2 and samples of tube as used in Part I of the paper were heated at 490° C. for 15 minutes in an electric muffle furnace and quenched in boiling water, or, alternatively, in cold water at 18°–20° C.

For information on the influence of strain in conjunction with the above modification of heat-treatment, samples of sheet which had been heat-treated, quenched in boiling or in cold water and aged, were strained in tension in or normal to the direction of most rolling so as to produce 1, 5, 10, and 15 per cent. permanent elongation, and samples of tube which had been heat-treated, quenched in boiling or in cold water and aged, were strained under compressive loads of 12, 15, and 17·7 tons/in.^{2} and then cut longitudinally into strips 1·25 cm. wide, as in the experiments described in Part I.

Both sets of samples were sand-blasted lightly and then subjected to corrosion test in a *N*-1 solution of sodium chloride containing 1 per cent. (by weight) of hydrogen chloride, the conditions of the tests being the same as those employed in Part I.

Observations made on the samples after microscopical examination at the conclusion of the corrosion tests were as follow :—

(i) *Unstrained Samples.*

The specimens which had been quenched in boiling water exhibited typical intercrystalline corrosion, the corrosion of the cold-water-quenched specimens being more of the nature of pitting.

Fig. 5 (Plate XIII) × 100, shows sections of two samples of Duralumin sheet cut normal to the direction of rolling. The specimen shown on the left was quenched in boiling water and that on the right quenched in cold water.

(ii) *Samples of Sheet Strained in Tension in the Direction of Rolling.*

The samples which had been quenched in boiling water were all severely attacked by intercrystalline corrosion, generally of the typical form. The cold-water-quenched specimens were more seriously pitted than those quenched in boiling water, but were relatively free from intercrystalline attack. Some areas exhibiting the " oval " form of corrosion were observed, however.

The further below the " water-line," the coarser was the corrosion both as regards pitting and intercrystalline attack and, in the cold-water-quenched samples, the greater the tendency to the " oval " form of corrosion.

(iii) *Samples of Sheet Strained in Tension Normal to the Direction of Rolling.*

The intercrystalline corrosion observed in this series was confined to the boiling-water-quenched specimens, from the immersed portions of which appreciable amounts of material had been removed. The specimens quenched in cold water were, in most cases, pitted severely.

(iv) *Samples of Tube Strained in Compression.*

Coarse and typical forms of intercrystalline corrosion were observed in all the boiling-water-quenched samples, and in the cold-water-quenched samples subjected to the heavier compressive loads the typical variety was also present. The remainder of the cold-water-quenched specimens showed somewhat irregular intercrystalline corrosion. Unstrained samples cut from cold-water-quenched pieces of the tube showed the "oval" form of corrosion at the lower portions, *i.e.*, the parts which had been more deeply immersed in the corroding medium. Intercrystalline corrosion was finest in the vicinity of the "water-line," and tended to become coarser towards the lower extremity of the specimens.

Effect of Quenching in Oil.

In order to ascertain whether quenching in oil affected the susceptibility to intercrystalline corrosion, samples of the sheet were heat-treated at 490° C. for 15 minutes and quenched in whale oil at room temperature. After removal of the oil, the samples were allowed to age at room temperature.

"Water-line" tests were then made on the specimens in natural sea-water and also in *N*-1 sodium chloride solution to which 1 per cent. (by weight) of hydrogen chloride had been added, the tests extending over a period of 14 days.

On examining the specimens microscopically, it was found that the extent and character of the corrosion were practically identical with those observed in the cold-water-quenched samples.

PART III.—EFFECT OF MODIFICATION OF TEMPERATURE OF HEAT-TREATMENT.

Samples cut from sheet No. 2 in the direction of rolling and samples of the tube were heated in an electric muffle furnace for 15 minutes at temperatures of 470°, 480°, 490°, 500°, 510°, and 520° C. and quenched in cold or in boiling water. Ageing of the specimens was then allowed to take place at room temperature over a period of at least 14 days.

Microscopical examination of sections taken from specimens quenched from the different temperatures and fully aged revealed no apparent differences in microstructure. No indications of incipient melting were observed in the specimens quenched from 520° C., which, in common with the other samples, showed fairly large grains of $CuAl_2$ which apparently had not been in solid solution.

Corrosion Tests.

Corrosion tests under conditions similar to those obtaining in the preceding experiments, and employing the acidified sodium chloride solution as corroding agent, were made on samples quenched from each of the above-mentioned temperatures in cold water (18°–20° C.) and on a corresponding set of samples quenched in boiling water.

The results of microscopical examination of the various groups of specimens after corrosion test were as follow :—

Sheet Quenched in Cold Water.

This series showed a greater tendency towards intercrystalline corrosion in the low-temperature-quenched than in the high-temperature-quenched samples, those quenched from 470°, 480°, and 490° C. being the only samples to exhibit any typical intercrystalline corrosion. The converse was true as regards superficial corrosion, the greatest amount of pitting and the " oval " form of corrosion being observed on the samples quenched from the three higher temperatures, namely, 500°, 510°, and 520° C. The " oval " form of corrosion was confined to areas well below the " water-line."

Tube Quenched in Cold Water.

Pitting was observed on all specimens. The tendency towards intercrystalline corrosion was again less on the specimens quenched from the higher temperatures. Irregular intercrystalline corrosion was fairly general throughout, but the typical variety was confined to the samples quenched from the two lowest temperatures, *i.e.*, from 470° and 480° C.

Sheet Quenched in Boiling Water.

This series was characterized by the irregularity of type and extent of corrosion. Pitting was present on all specimens. Typical and coarse intercrystalline corrosion was exhibited by the samples quenched from the three lowest temperatures, whilst on the remaining three the intercrystalline attack was irregular in character. The " oval " form of corrosion was again found only on the more deeply immersed portions of specimens quenched from the three highest temperatures.

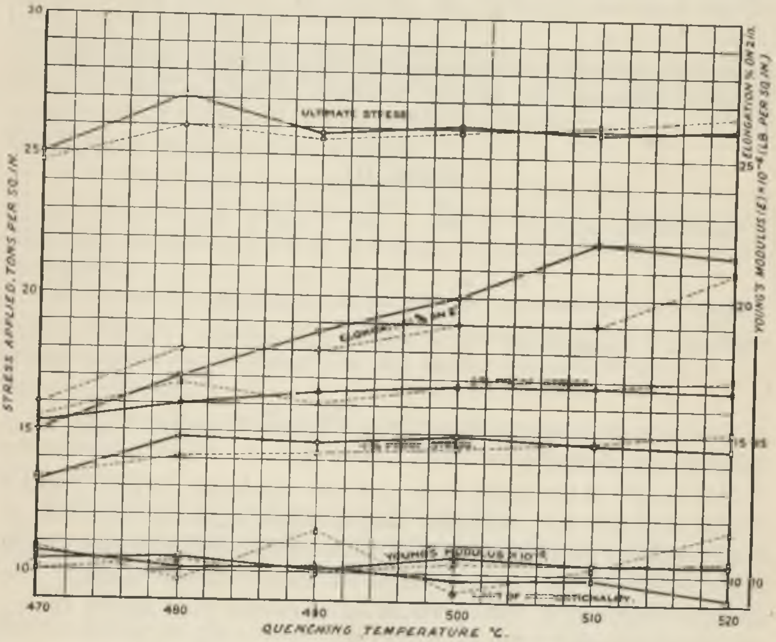
Tube Quenched in Boiling Water.

Typical and generally coarse intercrystalline corrosion was shown by all samples. The specimens quenched from the three higher temperatures exhibited irregular intercrystalline attack and also the " oval " form of corrosion.

Mechanical Tests.

With the object of ascertaining the influence of the above-mentioned modifications in heat-treatment on the mechanical properties of the material, tensile and " limiting radius " bend tests were made on specimens from sheet No. 2 after heat-treatment and ageing. Hardness tests were made on the samples with the aid of a Vickers diamond hardness testing machine immediately after heat-treatment, and then at intervals as age-hardening proceeded. The indentations were made by means of a 136° diamond pyramid under a load of 10 kg. applied for 30 seconds.

The results of the tensile tests, which are given in Table II and are shown graphically in Fig. 6, indicate generally that the cold-water-quenched material was very slightly superior to material quenched in boiling water, except as regards limit of proportionality, the values of which appeared to be somewhat erratic. The percentage elongation was greater on those specimens which were quenched from the higher temperatures.



CURVES SHOWING THE RELATIONSHIP BETWEEN QUENCHING TEMPERATURE AND MECHANICAL PROPERTIES OF DURALUMIN SHEET WHICH HAS BEEN QUENCHED IN BOILING OR IN COLD WATER

——— SIGNIFIES CURVE FOR SAMPLE QUENCHED IN COLD WATER
- - - - - " " " " " " BOILING "

POINTS ON THE ULTIMATE STRESS CURVE ARE DENOTED BY ○
" " " 0·5% PROOF STRESS " " " " ×
" " " 0·1% " " " " " " ⊙
" " " LIMIT OF PROPORTIONALITY " " " " △
" " " PERCENTAGE ELONGATION " " " " ▽
" " " YOUNG'S MODULUS " " " " ⌀

FIG. 6.

Table III shows the results of the limiting radius bend tests. The radius (r) of bend is given in terms of the thickness (t) of the sheet,

TABLE II.

Quenching Temperature (° C.).	Quenched in Cold Water.						Quenched in Boiling Water.					
	470.	480.	490.	500.	510.	520.	470.	480.	490.	500.	510.	520.
Acting Length, in. .	2	2	2	2	2	2	2	2	2	2	2	2
Limit of proportionality, tons/in.² . . .	10·6	10·1	10·2	9·8	9·9	9·2	10·8	9·7	11·5	9·4	10·3	11·6
0·1 per cent. Proof stress, tons/in.² . . .	13·2	14·8	14·7	15·0	14·7	14·6	13·3	14·1	14·3	14·5	14·8	15·1
0·5 per cent. Proof stress, tons/in.² . . .	15·3	16·0	16·5	16·8	16·8	16·7	15·5	16·8	16·1	16·8	16·8	17·1
Ultimate stress, tons/in.²	25·0	27·1	25·8	26·1	25·9	26·1	24·7	26·0	25·6	25·9	26·2	26·6
Elongation, per cent. .	15·0	17·0	18·7	20·0	22·0	21·5	16·0	18·0	18·0	19·0	19·0	21·0
Young's modulus × 10^{-6}, lb./in.² . . .	10·4	10·5	10·1	10·6	10·4	10·4	10·0	10·4	10·0	10·4	10·5	10·3

TABLE III.

Quenching Temperature, ° C.		470.	480.	940.	500.	510.	520.
Quenching Medium.	r = Cold Water	1t c 2t uc	1t c 2t uc	1t c 2t uc	1t c 2t uc	1t c 2t uc	½t c 1t uc
	Boiling Water	1t c 2t uc	½t c 1t uc	½t c 1t uc	½t c 1t uc	½t c 1t uc	½t c 1t uc

and the abbreviations "c" and "uc" denote "cracked" and "uncracked" respectively.

The results of the hardness tests, shown graphically in Figs. 7 and 8 (Plates XIV and XV), indicated that modification of the conditions of heat-treatment within the scope of these experiments had only a very slight effect on the hardness attained after complete ageing. The samples quenched in boiling water age-hardened very rapidly during the first few hours.

SUMMARY AND DISCUSSION OF RESULTS OBTAINED.

The tests have shown that it is possible to develop intercrystalline corrosion in Duralumin in laboratory tests of short duration.

Under the conditions of the corrosion tests, it was found that the corroding media employed in the earlier experiments showed differing degrees of activity in producing intercrystalline corrosion. Several reagents, viz., the Mylius solution, and the more strongly acid solution of sodium chloride, were very potent in producing in practically all the samples tested a form of intercrystalline corrosion differing somewhat from the typical form, and also the typical variety where the Duralumin was in a susceptible condition. The former, here described as "oval," appears to be a coarse form of intercrystalline corrosion, in which corrosion probably proceeds round small aggregates of grains.

In short-time tests of this kind, the *N*-1 solution of sodium chloride containing 1 per cent. (by weight) of hydrogen chloride was considered to be the most suitable of the reagents employed.

Samples of Duralumin which had been heat-treated, aged in air, and then subjected to attack by a suitable corrosive agent, showed somewhat greater susceptibility to intercrystalline corrosion than did samples which had been heat-treated and allowed to " age " during immersion in the reagent.

The results of the experiments on material strained in tension indicated that cold-work increased slightly the tendency towards intercrystalline corrosion, but no relation between this tendency and the degree of elongation was observed.

On the other hand, there appeared to be a critical range of stress in compression, viz., 14·0–16·9 tons/in.^{2}. The samples of Duralumin tube which had been compressed in this range of stress showed the greatest susceptibility.

On the whole, Duralumin sheet strained transversely with respect to the direction of rolling was found to be more liable to penetration by intercrystalline corrosion than was similar material strained in the direction of rolling.

It was observed that where intercrystalline corrosion occurred in non-aerated reagents, it was usually more abundant in the vicinity of the water-line.

When bubbles of air were caused to impinge on a specimen partly immersed in a corrosive reagent, the effect of aeration generally seemed to be to increase corrosion slightly near the point of impingement.

The results of corrosion tests on both sheet and tube indicated that the higher the quenching temperature, the smaller was the tendency of the material to develop intercrystalline corrosion. In the material quenched from the higher temperatures employed, there was, however, an increased tendency towards the pitting form of superficial corrosion. In samples quenched in boiling water, the tendency towards intercrystalline corrosion was much greater than in those quenched in cold water.

The results as regards the increased tendency of Duralumin quenched in hot water towards intercrystalline corrosion, and the reduced tendency of Duralumin quenched from temperatures of 500°–520° C. towards this form of corrosion compared with that quenched from lower temperatures, are in accordance with the experience of American investigators. Rawdon[3] states that " sheet material quenched in hot water shows a very much greater tendency towards intercrystalline corrosion than the same material after being quenched in cold water." On the influence of temperature in final heat-treatment the same author remarks:

"If the temperature is somewhat below that at which complete solubility of the alloy constituents is attained, the material will not be fully heat-treated, and the corrosion-resistance will be relatively low." This conclusion, however, appears to be based on tests of samples quenched either from 500°–510° C. or from 425° C. The results of the present experiments are to some extent confirmatory, but Rawdon's suggestion of the complete solution of the alloy constituents being the leading factor in securing low tendency to intercrystalline attack appears to be open to question, since Duralumin sheet heat-treated at 520° C. still contained particles of $CuAl_2$ which apparently had not been in solid solution. It seems probable that the rate of cooling through the range of temperature in which deposition of the $CuAl_2$ and other constituents would occur freely on slow cooling may be the governing factor. Since 490° C. lies very close to the upper limit of this range for Duralumin, quenching from this temperature would be expected to give a slower rate of cooling through the upper portion of the range.

As regards the greater tendency, observed in these experiments, of Duralumin quenched from 500° to 520° C. toward the pitting or superficial form of attack, the latter is the less serious of the two types of attack normally observed in corroded Duralumin, since the extent of the corrosion is much more apparent than in the intercrystalline type. Moreover, it is possible that the immersion tests employed in the present experiments are more favourable to this form of attack than exposure to marine atmosphere would be.

The experiments on the effect of variation of quenching temperature on the mechanical properties of finally heat-treated and aged Duralumin have been made so far only on samples cut from a single sheet of 20-S.W.G. material. The results indicate that the ultimate stress, 0·1 and 0·5 per cent. proof stresses, and Young's modulus values of the material cold-water-quenched and aged were nearly the same as, but very slightly higher in general than those obtained on the material boiling-water-quenched from corresponding temperatures and aged. In general, the effects of variation of quenching temperature in the range 490°–520° C. had very little effect on the tensile or on the bending properties. The hardness of heat-treated and aged material as recorded by Vickers hardness tests was not sensibly affected by modification of quenching temperature within this range.

ACKNOWLEDGMENTS.

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DISCUSSION.

Dr. W. Rosenhain,* F.Inst.Met., F.R.S. (Past-President): I know that there are others here who are probably more interested in the details of this paper than I am, and who really ought to commence this discussion, but, as they seem shy about doing so, I want to make one or two remarks in connection with one aspect of the subject. It has been my experience, in examining a good deal of Duralumin which has undergone intercrystalline corrosion, that apparently the structural elements which are formed by stamping immediately after quenching, and therefore during the ageing or before the ageing process has been completed, have suffered much more rapidly than other parts which were hot-rolled or cold-rolled and afterwards heat-treated and aged. That view, of course, has been stated before, and I have no doubt that its echo is to be seen in this paper in the experiments on the effect of over-strain. Those experiments are very interesting and their conclusions are also suggestive, but I should like to point out that they are not quite conclusive, because, in my view, the influence of over-strain, particularly if carried out before the ageing has been completed, does not lie in the fact that the metal has been subjected to plastic deformation, but in the fact that serious residual stresses have probably been left in it. Stamping and deformation into corrugated shapes almost inevitably leave the material in a self-stressed condition, and, if the ageing occurs after that, it may actually occur unevenly as a consequence of that state of affairs, and, in any case, it intensifies that self-stressed condition. I have always imagined, in the cases which I have seen, that it was this self-stressed condition which was the real cause of the acceleration of intercrystalline corro-

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* London.

sion. It is true that certain American observations appear to give the very reverse of the experience which I have described. The actual parts considered were the parts of some airships, and in my case the channel sections of the airship girders were practically uncorroded, whilst the thin bracing material was heavily attacked by intercrystalline corrosion, whereas the Americans described the exact converse from their observations. I can only think that the difference must be due to some very wide difference in the method of working adopted. I believe that they do their deforming in rather a different way, and a possible result is that in their case the channels were more severely self-stressed than the bracing stampings.

I repeat this experience, which I have mentioned before on various occasions, because I should very much like to have seen this paper completed by some experiments, which I admit are not easy to make, on the attack on Duralumin which was not strained so much as stressed. It can be done in one fairly simple way, which Archbutt and I adopted some years ago in another connection—that is, to take a strip of material and spring it. I confess that the amount of stress developed in that way, when it is held in a sprung condition, is not very definite, but its effects are very obvious. We investigated in that way an aluminium alloy with 20 per cent. of zinc, and we consistently produced intercrystalline attack in that manner, whereas, if left lying unstrained, the attack, although it did occur in time, happened much more slowly, and the analogous case of season-cracking in brass is another instance in which intercrystalline attack undoubtedly is very much affected by stress.

One would like, therefore, to know how far the fact that in the experiments described in the paper the over-strain was applied in a simple way—that is to say, purely tension or compression which left a minimum of residual stress in the deformed material—altered the effect as against a kind of mechanical plastic working which would leave behind it a considerable amount of self-stressing. In practice, in a great many applications of Duralumin, that kind of plastic working which is liable to leave self-stressing behind it is applied, and with Duralumin it is not possible to apply any relieving heat-treatment without damaging the material. Any heating sufficient to relieve stresses would inevitably alter the state of ageing of the material, possibly to its disadvantage.

However, that is asking for more, as one often does after having been given a great deal, because this paper is already full of interest. I am particularly interested that a reagent has been found which rapidly produces intercrystalline attack. I should like to ask the authors, however, whether they are satisfied that a material which undergoes relatively rapid attack under this somewhat fiercely corrosive agent is also the material which undergoes that attack most rapidly under ordinary conditions. I know that is a difficult question to answer, and I do not expect them to answer it, but I should like to know what degree of assurance they have on the subject, because it is important that we should not base our conclusions on an accelerated corrosion test of this kind, which has, no doubt, inherent in it all the defects which unfortunately attach to all accelerated tests in connection with the difficult subject of corrosion, unless we are fully satisfied about it.

This paper is one which I think everyone interested in light alloys must value very much.

Professor Dr. GEORG SACHS * (Member): The problem discussed here appears to me to be very complicated, and I should like to ask some questions on points which seem to be of fundamental importance in this connection.

In the first place, it is not clear whether intercrystalline fissures occur

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at all in the absence of stresses. This question, as far so I can see, cannot be answered definitely; but in my opinion the presence of stresses is a necessary condition for the formation of intercrystalline fracture.

An important factor which promotes the formation of fissures is undoubtedly the presence of precipitated particles. I think that recent work has definitely proved that the deleterious effect of heating on Duralumin and similar alloys is due to the precipitation of constituents from solid solution. On the other hand, practically no such precipitated constituents are present in the normally age-hardened state.*

Dr. C. H. Desch,† F.R.S. (Member of Council): I should like to ask whether the details of the structure have been examined during the process of corrosion, because the location of the corrosion at the grain boundaries may be to some extent a secondary effect due to the setting up of local couples between the impurities out of solution which accumulate at the grain boundaries and the surrounding metal. A number of years ago I showed a photograph ‡ of Duralumin taken in that way in the course of a study of the corrosion of certain metals under the microscope, and it was found that the corrosion began not exactly at the grain boundaries, but running in a line just parallel with each of these inclusions, obviously owing to the formation of local couples.

At that time the precipitation idea of the hardening of Duralumin had of course not been introduced, and was not considered, but, as Professor Sachs has just said, the effect of mechanical deformation on the precipitation is so great that one would have to take that influence into account.

Dr. H. Moore,§ C.B.E. (Vice-President): I feel that the large amount of information contained in this paper on the subject of the intercrystalline corrosion of Duralumin is of the very greatest value, and I think that we are much indebted to Mr. Sutton and his co-workers for the intensive study they are making of this question; but we still seem to be a long way from an explanation of what is the cause of this intercrystalline corrosion. The authors are extremely guarded in their suggestions on p. 180 as to the possible causes, and if Mr. Sutton will speculate a little more in his reply I shall be grateful, even though he may feel that he is on very uncertain ground.

Is this intercrystalline corrosion due to intercrystalline fissures, as Professor Sachs has suggested, or to the separation of some material at the crystal boundaries, or to some other cause? Dr. Rosenhain has suggested that internal stress may be an important factor. Personally, I think that the evidence is against the suggestion that stress is important. If a direct attack on the problem does not seem to be leading us to the solution, it is possible that analogies with other cases of intercrystalline corrosion, such as that of the austenitic stainless steels, may help us. The case there seems to be distinctly simpler. Austenitic stainless steels when subjected to certain forms of heat-treatment deposit a carbide—I am not certain of its nature—at the crystal boundaries, and the tendency to intercrystalline corrosion with these materials does appear to be bound up with the presence of this carbide. If steps are taken to prevent the separation of the carbide at the crystal boundaries, the intercrystalline corrosion does not occur.

I should like to emphasize the importance of a solution of this very wide and general question: what are really the causes of these intercrystalline corrosions which we get in various materials?

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* von Göler and G. Sachs, *Metallwirtschaft*, 1928, **8**, 671.

† Superintendent, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

‡ *Trans. Faraday Soc.*, 1916, **11**, 198.

§ Research Department, Woolwich.

Professor Dr. Sachs: In this connection perhaps some researches on other aluminium alloys may be of interest. Certain alloys with a high content of copper, zinc, and other hardening constituents and with a very high tensile strength show a strong tendency to crack. Strips in a bent or stressed state fracture after a short time in contact with water vapour, frequently when no signs of corrosion can be observed. I do not know whether the fracture is intercrystalline, but I think that this is the case, as the whole phenomenon is very similar to the season-cracking of brass.

The fracture is strongly dependent on various factors. An unbent strip generally does not fracture; with increasing amounts of bending the time that elapses before fracture at first rapidly decreases, then remains nearly constant. Like Duralumin, these alloys are self-hardening. After quenching, fracture takes place more and more rapidly with progress of the ageing process. The tendency to fracture is, however, not greatest in the state of maximum hardness. Of specimens aged at different temperatures, that treated at 150° C. fractures the most rapidly; this has an appreciably smaller tensile strength than that aged at room temperature. It must be assumed, however, that the amount of new constituent precipitated at 150° C. is much greater than that precipitated at room temperature. On the other hand, specimens annealed at 300° C. have practically no tendency to crack. The tendency to crack is therefore not greatest when the internal stress is greatest nor when precipitation is at a maximum, but with a certain combination of both these factors.

Mr. Sutton (*in reply*): Dr. Rosenhain referred to the influence of stresses, and we ourselves have paid attention to the possible influence of residual stresses in the metal. He also mentioned experience with channels in some of the American airships as compared with our own. I think that, generally speaking, in British practice we have had less trouble with the thick material than with the thin. I agree with Dr. Rosenhain, and I am sure that my co-authors would also agree, that small differences in technical practice make a vast difference to the final behaviour of the Duralumin sheet. We intend, if we are permitted to go further with this work, to determine by machining of measured pieces the residual stress in material about which we know something of the properties of resistance to intercrystalline corrosion.

Professor Sachs referred to the influence of the condition of no residual stress in the material. Fully-softened Duralumin seems to be rather highly susceptible to the intercrystalline form of corrosion; one might reasonably assume that the residual stress in that material would be small, and it seems clear that susceptibility is not due to residual stress.

It does appear possible, and indeed very probable, that one stage of the precipitation process or the various phenomena which lead up to it is of very great importance. The heat-treatment conditions, particularly the method of quenching and the temperature of the quenching medium, seem to be of considerable importance.

In reply to Dr. Desch, although at this stage we have not pursued the particular line of investigation to which he refers so carefully as probably the case warranted, we intend to go more closely into the question of the microscopic investigation of corrosion in Duralumin. It does, however, appear to be a fact that the corrosion does not necessarily always start from the edge of a crystal—that is, as observed on the surface under examination. That may perhaps be due to the large potential difference which may exist between an inclusion and the rest of the material.

The evidence is not all available at the moment for giving such a general statement on the conditions governing intercrystalline corrosion such as Dr. Moore would perhaps wish to have. Local stress may be influential, and doubtless frequently is. It is now well known that simultaneous operation of corrosion and tensile stress, may result in failure at low load, and the failure seems to occur by intercrystalline corrosion. Secondly, local externally applied stress is probably most important when the boundary conditions are favourable to intercrystalline corrosion. Thirdly, in certain cases the boundary conditions appear to be of predominating influence.

These remarks are very tentative at the moment. We feel it is desirable to establish each point as we go along, and in the present paper the point in our mind was to determine whether the effect of overstraining was likely to be permanently detrimental.

There is one matter of great importance which was raised by Dr. Rosenhain—namely, whether normal exposure conditions would reveal good correspondence to the result obtained by the accelerated tests; in other words, does the accelerated test show up as bad material that which would actually give a bad result, for instance, under marine conditions? The available data suggest that there is close agreement between the results of the accelerated test and the exposure tests we have been able to make to date, in respect of resistance to the intercrystalline form of corrosion.

CORRESPONDENCE.

THE AUTHORS (*in further reply to the Discussion at the Meeting*): In further reply to Dr. Rosenhain's remarks, we had intended to make experiments on pieces of Duralumin under externally applied stress, and hope later to investigate this field. Experiments by Rawdon [*] indicated that Duralumin subjected simultaneously to static tensile stress and corrosive influences deteriorated more quickly than Duralumin subjected to the same corrosive conditions but without the externally applied tensile stress. The additional effect produced by stressing the material in tension was, however, considerably less than the effect of corrosion alone. Rawdon considers that, under very mildly corrosive conditions, the effect of static tensile stress may be negligible so far as corrosion-acceleration is concerned.

On the subject of fissures, raised by Professor Sachs, we agree with him that precipitated particles appear to play an important part in the formation of intergranular fissures. The remarks of Professor Sachs on cracking of bent samples of high-strength aluminium alloys containing copper, zinc, and other hardening constituents are of much interest. Ageing of Duralumin and similar alloys in the range 140°–150° C. appears to be very detrimental from the corrosion point of view. The work of Meissner [†] and v. Zeerleder [‡] brings out clearly the greater susceptibility of material so treated to deterioration under corrosive conditions.

Dr.-Ing. K. L. MEISSNER [§] (Member): It is interesting to note that not only the conditions of heat-treatment and cold-working are important for the intercrystalline type of corrosion, but that the surface condition alone is also capable of affording this attack. The authors state that a sand-blasted surface afforded the greatest facility to intercrystalline attack. It is well known in practice that sand-blasting diminishes the corrosion-resistance of aluminium alloys. Hence, in connection with other considerations regarding the fatigue properties of the material, sand-blasting is prohibited in Germany for constructional material used in aircraft. On the other hand, sand-blasting is sometimes considered to be absolutely necessary for roughening the surface before the application of some lacquers and other corrosion

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[*] *U.S. Nat. Advisory Cttee. Aeronautics Tech. Note* No. **305**, 1929.

[†] *J Inst. Metals*, 1931, **45**, 187–208.

[‡] *J. Inst. Metals*, 1931, **46**, 169–186.

[§] Chief Metallurgist, Dürener Metallwerke A.G., Düren, Germany.

preventing media which cannot be put on the smooth surface of rolled material.

Further, it must be stated that the type of attack depends largely on the composition of the corroding medium. The authors mention that a solution of sodium chloride + hydrogen chloride is the most efficient for producing intercrystalline corrosion. The Mylius solution is also known to produce intercrystalline attack, and I think that it is for that reason that abbreviated laboratory corrosion tests are not always comparable with the behaviour of the material in practice—for example, if used in sea-water. It is to be expected that this will always be the case if the conditions of the material itself do not afford the tendency towards intercrystalline attack under normal conditions of corrosion, as, for example, in the atmosphere or in natural sea-water. In such cases material of this kind must give uncertain or misleading results when tested in solutions which are themselves capable of producing intercrystalline corrosion.

As regards the reason why material quenched from the highest possible soaking temperatures, *i.e.* from 500° to 520° C., tends less to intercrystalline corrosion than do materials quenched from slightly lower temperatures, as, for instance, from 490° C., the authors mention that the rate of cooling may be the governing factor rather than the more or less complete solution of the alloy constituents, since heterogenous particles of $CuAl_2$ can always be seen in heat-treated Duralumin. It must, however, be remembered that the attack of artificially aged material is always intercrystalline, but that the conditions of artificial ageing which produce deleterious intercrystalline attack are not sufficient to cause a remarkable segregation or precipitation of the constituents. Even if such precipitation occurred to a marked degree, the particles would separate out of the solid solution mostly *in* the crystals, and not on the crystal boundaries. It can easily be imagined that a material which is not fully heat-treated, for example, if quenched from 425° C., will have a lower corrosion-resistance than one quenched from a higher temperature, because the former has more heterogenous particles. It is, however, not so clear that the different quenching temperature produces a different type of corrosion instead of affording only corrosion of a different degree but of the same type.

THE AUTHORS (*in reply*): We are in agreement with Dr. Meissner that sand-blasting has a very adverse influence on the corrosion properties of light alloys when no protective is subsequently applied. We decided to employ sand-blasted surfaces on our specimens, since, as a result of preliminary experiments, we found that this type of surface provided more favourable conditions for intercrystalline attack than did either a scratch-brushed or an "as heat-treated" surface.

Regarding Dr. Meissner's remarks on the frequent incongruence of the results of short-period laboratory corrosion tests and those of normal exposure tests in sea-water, we have found that Duralumin in such a condition as to render it susceptible to severe intercrystalline attack on immersion in the sodium chloride–hydrogen chloride reagent is also susceptible when subjected to normal marine exposure.

In reply to Dr. Meissner's interesting remarks on the effect of heat-treatment, we are in agreement with him that the reason for the difference in the corrosion behaviour of material quenched from different temperatures is not yet clear. It appears reasonable to suppose that the use of the higher soaking temperatures (500°–520° C.) results in solution of most of the small particles of $CuAl_2$ and other hardening constituents, leaving only relatively large particles undissolved. The latter may be responsible for the more marked surface pitting experienced in the high-temperature quenched Duralumin.

NOTE ON THE INTERACTION OF ALUMINIUM AND WATER VAPOUR *

By RICHARD SELIGMAN, Ph.nat.D., Past-President, and
PERCY WILLIAMS, B.Sc., Member.

Synopsis.

The statement having been made recently that aluminium and its alloys are rapidly attacked by super-heated steam at 300°–350° C., the authors have made experiments, and have found that no such attack takes place under the conditions which they define.

Hanson and Slater [†] have recently put forward the view that pinholes in aluminium and its alloys are due to the absorption of hydrogen set free during the corrosion of the metals by water. They hold [‡] that the water must be liquid, and that above the dew-point no such corrosion takes place. So far as the present authors are aware, there are only two references to this subject in literature, and both are to experiments carried out at temperatures far higher than those which Hanson and Slater had in mind.

St. Claire Deville,[§] writing in 1859, says that an aluminium wire heated to red heat in a glass tube through which steam was passed showed no change after several hours, either by loss of brilliancy (éclat) or gain in weight. Seventy years later, Guillet and Ballay [||] wrote that aluminium and its alloys are heavily attacked by quick-flowing superheated steam, metal of 99·87 per cent. purity and 1·5 mm. thickness having been completely destroyed in 300 hrs. at a temperature of 300°-350° C., whilst in the same time a piece of rolled sheet of ordinary purity gained 3·25 grm. in weight per 100 cm.^{2} exposed.

This would be strange in the light of a statement by Pilling and Bedworth,[¶] that even at 600° C. oxidation of aluminium by oxygen ceased after 60–80 hrs., and that after heating for as much as 890 hrs. the weight of the film remained at 0·01 grm. per 100 cm.^{2}.

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* Manuscript received October 19, 1931. Presented at the Annual General Meeting, London, March 9, 1932.

[†] *J. Inst. Metals*, 1931, **46**, 216.

[‡] *J. Inst. Metals*, p. 226.

[§] " De l'Aluminium," **1859**, p. 25.

[||] *Compt. rend.*, 1929, **189**, 551.

[¶] *J. Inst. Metals*, 1923, **29**, 574.

The matter being of interest, both practically and theoretically, the authors have re-examined it, and as a result of their experiments hold that St. Claire Deville, who did not, as a rule, err on the side of under-estimating the resistance of aluminium to attack, was, nevertheless, right in this case, and that in Guillet and Ballay's experiments some other factor was at work which the present authors have no means of identifying.

Two experiments were necessary, because the method used by Guillet and Ballay differed from that of Deville in one particular, which might have been important. Whereas Deville used a tube which was presumably open at one end, Guillet and Ballay exposed their test-pieces in the steam main of an industrial installation, where the steam was at a pressure of 15 kg./cm.^{2} * and therefore in much greater concentration than in Deville's tube. The steam used in Guillet and Ballay's experiments was also flowing at an average speed of 30–35 metres per second, which must have been much faster than that of Deville, but they state that this cannot have affected their results, since a second series of test-pieces placed in the steam separator (ballon sécheur), where the steam was at rest, was similarly, though more slowly, attacked. Unfortunately, their paper gives no details of this second method of experimenting, but a private communication, for which the authors are much indebted to MM. Guillet and Ballay, shows that it had been carried on for 4500 hrs. One point seems to be important. In both cases the boiler was at work for only 9 hrs. out of the 24 hrs. It is difficult to understand, therefore, how MM. Guillet and Ballay can have made sure that their test-pieces were not in contact with liquid water for long periods. The possibility that boiler compounds were carried in the steam can also not be ignored.

The present authors were not concerned with quick movement of their steam, which, they hold, would only facilitate chemical attack by the mechanical removal of protective films, but they made sure that no liquid water touched their test-pieces. In one case the amount of air present was also reduced to far below that required to form the protective film described by Pilling and Bedworth.†

Under these conditions aluminium sheets of varying purity and a cast aluminium–silicon alloy exposed to superheated steam at temperatures of 200°–500° C. showed very slight fluctuations in weight from day to day, but no significant change when the time of heating was prolonged to more than 100 hrs.

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* Private communication.

† *Loc. cit.*

I. EXPERIMENT AT ATMOSPHERIC PRESSURE.

The samples, which had been dipped in caustic soda, washed, and then dried at 100° C., were supported on a silica plate in a silica muffle, close to the junction of a thermocouple. Steam was blown into the back of the muffle through a silica tube in sufficient volume to replace the contents of the muffle four times per minute, and escaped through crevices round the muffle door. In order to prevent liquid water from coming in contact with the specimens, a baffle was placed in front of the steam inlet. For the same reason the muffle was first heated each morning to the temperature of the experiment, the test-pieces were introduced, and 2 minutes later the steam was admitted. In the evening the test-pieces were removed hot from contact with the steam. The experiment was continued for 15 to 20 working days, and the total time of exposure of the specimens to steam was 103–133 hrs.

The following results were noted :—

TABLE I.

No. of Test-piece.	Composition.			Aluminium (by difference).	Area, cm.^{2}.	Length of Exposure, Hrs.	Total Change in Weight. Grm.		Change in Appearance.
	Copper.	Iron.	Silicon.				Actual.	Per 100 cm.^{2}.	
				A. Temperature 200° C.					
1	0·02	0·30	0·21	99·47	73	133	+0·0001	+0·00014	No change.
2	0·00	0·16	0·14	99·70	75·8	133	−0·0002	−0·00026	,,
3	0·02	0·01	0·01	99·96	26·5	133	no change	no change	,,
4	...	Alpax	...	...	59·5	133	−0·0006	−0·0010	,,
				B. Temperature 350° C.					
5	0·03	0·54	0·21	99·22	68	103	no change	no change	A few superficial blisters; otherwise no change.
6	0·00	0·16	0·14	99·70	68	103	+0·0007	+0·0010	
7	0·02	0·01	0·01	99·96	33	103	no change	no change	
8	...	Alpax	...	...	42	103	−0·0001	−0·0002	No change.
				C. Temperature 500° C.					
9	0·02	0·30	0·21	99·47	73	113	+0·0003	+0·00041	Surface dull.
10	0·00	0·16	0·14	99·70	75·8	113	−0·0001	−0·00013	A few blisters; surface bright.
11	0·02	0·01	0·01	99·96	26·5	113	+0·0001	+0·00038	A few blisters; surface tarnished. Interference colours.
12	...	Alpax	...	...	59·5	113	−0·0003	−0·00050	Surface slightly dulled.

II. EXPERIMENT UNDER PRESSURE.

A small strip of refined aluminium containing silicon 0·01, iron 0·01, copper 0·02, aluminium (by difference) 99·96 per cent., weighing 0·5276 grm., and having a surface of about 8·3 cm.^{2}, was placed in a thick-walled tube of Pyrex combustion glass, closed at one end, together with a sealed glass capillary containing a weighed quantity of water. The open end of the tube was drawn out, the air exhausted to 0·001 atm. by a Geryk pump, and the tube, which then had a capacity of 36·9 c.c., sealed. It was wrapped in wire gauze and placed in a steel tube within an electrically-controlled furnace, in which it was held at 300° C. continuously for 217½ hrs. The dimensions of the capillary were such as to ensure that it burst at a temperature of about 250° C., so that the conversion of its contents into vapour would be very rapid, and the risk of the aluminium being attacked by liquid water small. The weight of water (0·1 grm.) was sufficient to fill the Pyrex tube with dry saturated steam at a temperature of 152·5° C., at which temperature the pressure would have been 5 atm. Therefore, at 300° C. the pressure will have been about 6·7 atm. and the superheat about 136° C.

At the end of the experiment the Pyrex tube was opened while still hot, so as to avoid condensation on the surface of the metal. No change in the appearance or weight of the sample could be detected.

Calculation showed that the weight of the air derived from the capillary (0·05 c.c.), together with that remaining in the Pyrex tube after exhaustion, was about 0·0001 grm., which would contain only about one-twentieth of the oxygen found by Pilling and Bedworth to be necessary to inhibit further oxidation at 600° C. There is therefore little likelihood that the immunity of the aluminium from attack was due to oxidation prior to the admission of the steam.

DISCUSSION.

Dr. Richard Seligman (*introducing the paper*): This is a very small contribution to a very large subject, and I do not propose to do more than to direct your attention to the four lines of the synopsis and then to add three further observations.

The first of these is that Mr. Williams and I have not made any attempt to do what I consider must be the impossible in this case—namely, to give a proof that interaction between solid aluminium and water vapour cannot in any circumstances take place. All we have done is to select certain conditions under which we felt that, if any interaction did take place, it would be the one for which we were looking. We established those conditions and found no such interaction. That is the limit of what this note purports to describe.

The second point I should like to make is, that the experiments were originally carried out at the temperature which Guillet and Ballay lay down in their paper. After we had completed these, at the request of certain members of the Publications Committee the experiments were repeated at the temperatures of 200° and 500° C.

My third and last point is that, whereas we have been able to find no such action as Guillet and Ballay describe, we are not absolutely certain that some change does not take place at the highest temperature named in the note and at the still higher temperature (620° C.) at which we have since been working. We direct attention in the note to the occasional appearance of blisters. It is quite possible that it is—and we assume it to be—the blistering of sheet which occurs from time to time even with the best sheet at high temperatures. Having gone on to a higher temperature—we are not absolutely certain that some other change is not taking place. We cannot reconcile the appearance of some of the test-pieces with the mere development of what I have called original sin in the metal. We can offer no explanation. We do not even know if it is a fact that the water vapour plays a part, but I have brought one sample with me which shook our confidence.

That is all I desire to say, except to remind you that this little paper owed its origin to a question which you, Mr. President, asked me some time ago, and to which we have here attempted to give the answer.

Professor D. **Hanson**,* D.Sc. (Vice-President) : I think that our immediate Past-President need offer no apologies for bringing this short paper to our notice, because the results do contribute to the solution of a very important practical problem, and it is, I am quite sure, satisfactory to those members who are interested in aluminium to know that the experiments described by Guillet and Ballay are not characteristic, at any rate, of all aluminium when exposed to steam at high temperatures. I find this particularly interesting, because it deals with a type of experiment which is somewhat analogous to some with which I have been connected. Mr. Slater and I have studied the action of water on aluminium for different purposes, and we have most definite evidence that reactions can occur between aluminium and many of its alloys at ordinary temperatures where there is contact with liquid water, and at much higher temperatures than those with which the authors have been concerned—namely, when the metal is molten. Molten aluminium will decompose water very readily, generating hydrogen and aluminium oxide, and certain reactions of the nature of electrolytic corrosion between water and aluminium and its alloys at low temperature will also produce hydrogen and, I suppose, aluminium oxide, or hydrated products.

It is very interesting to have this evidence from Dr. Seligman, that there is an intermediate region in which the action does not appear at any rate to be rapid. If one considers the chemical nature of aluminium, one would expect it to react with water at all temperatures, whether that water were liquid or vapour, and I suggest to Dr. Seligman that the cause of this failure to develop any appreciable action under the conditions of his experiments must be due to something which prevents the water from coming into proper contact with the aluminium. It does suggest that the protective film, although it may be very thin, is sufficiently continuous and sufficiently impervious to aqueous vapour within the range of his experiments to act as a real protection.

I think that the subject is by no means closed, and that it may be that, under other conditions, and possibly in the case of certain alloys, the protection may not be so perfect, and there may possibly be some action.

I listened with interest to Dr. Seligman's additional information, that he and Mr. Williams obtained some evidence of action at the higher ranges of temperature even between the solid metal and steam. I think that I am right in understanding that?

Dr. **Seligman** : Some indication that we could not definitely say there was none.

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* Professor of Metallurgy, The University, Birmingham.

Professor HANSON: You do not exclude the possibility of some action?

Dr. SELIGMAN: No.

Professor HANSON: The subject is, I feel, one of practical importance and also of theoretical importance. I hope that Dr. Seligman will be able to contribute further to this subject, or, at any rate, to use his influence to see that someone else does. I hope we shall not regard the matter as closed.

Mr. T. HENRY TURNER,* M.Sc. (Member): A practical application of the results reported in this paper would seem to lie in the use of aluminium alloys for reciprocating steam engines or possibly turbines. Experiments have been carried out in full-scale commercial practice for some considerable time, where aluminium has worked nominally in contact with steam in reciprocating engines.

There is always a film of oil, or carbon deposit, in commercial practice, and it may be that the film was so continuous in the case to which I refer, that in effect the steam never did come, as in Dr. Seligman's carefully conducted experiments, in contact with the aluminium. It is a fact, however, that, so far as the steam engine experiments go, an aluminium alloy can stand up to steam under practical conditions for a considerable time. I cannot say whether it will become a regular practice to use aluminium or its alloys under such conditions, but I know that such alloys have stood up for a much longer time than would have been thought possible on the basis of the French work, and to that extent practical trials appear to confirm Dr. Seligman's findings.

Dr. A. G. C. GWYER † (Vice-President): I am naturally very interested in this paper, but have very little comment to make on it, as Dr. Seligman has already anticipated, in his introductory remarks, the one question which I had to ask. Bearing in mind that the authors reported no action at 500° C., whilst we know from Professor Hanson's work that if steam is passed into molten aluminium at 700° C. there is definite action, I intended to inquire at what intermediate temperature action definitely started. It is now clear, however, that there is very little if any action at, say, 600° C. or 620° C.

I should imagine that the absence of chemical action was to be attributed to the fact that the steam was dry, and I take it that the authors took every precaution to ensure that no water condensed on the metal; the samples were also heated, I think.

Dr. SELIGMAN: Yes, for quite a short time.

Dr. W. ROSENHAIN,‡ F.Inst.Met., F.R.S. (Past-President): This is a very interesting question and the paper raises a number of points for further inquiry. The immunity of attack which is shown in Dr. Seligman's experiments is, of course, due not only to the fact that the steam was dry, because at temperatures from 300° C. upwards it would probably be dry unless the pressure were very high indeed, but also to the fact that there is no abrasive action of any kind. I think that industrial steam might carry particles of solid or liquid with it, and that the action might be quite different, because, clearly, if the protective film is continuously removed from the surface, continuous action would occur.

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† Chief Metallurgist, The British Aluminium Co., Ltd., Warrington.

‡ London.

So far as the higher temperatures are concerned, the specimen which Dr. Seligman has shown is very interesting, and it bears a resemblance to several specimens of aluminium alloy which I have seen which have not been subjected to steam precisely, but to a furnace atmosphere no doubt containing steam, for a very prolonged period, and which blistered even more markedly than the present sample. Whether that blistering was really due to steam we do not know, but I think that the evidence that we now have suggests that it was. One felt that it must be something entering the metal from outside, and therefore, if it happens in an atmosphere of pure dry steam, the only thing that can enter, apparently, is the hydrogen produced by reaction with the water vapour. One is inclined to speculate on that matter from the point of view of what Dr. C. A. Edwards has shown to happen in steel—namely, that the hydrogen enters the metal possibly in atomic form from the nascent state and that it then combines into molecules inside and is unable to escape except by blowing bubbles. That specimen looks as if somebody had tried to blow bubbles inside it!

The question why the metal at 620° C. should react only slowly, while at 700° C., if steam is blown into it, it reacts very quickly, is one to which I think the answer is obvious. In the one case there is a solid with a more or less fixed surface film, and in the other case a liquid in which the surface film is continuously being broken by every fresh bubble. I think that this view is confirmed by the fact that the surface film does act as a very potent barrier to interchange of gas between the metal and the surrounding atmosphere, and the importance of that fact from the practical point of view is very great.

We are very much indebted to Dr. Seligman for bringing forward this evidence, but I cannot help thinking there must be some factor in the matter which we do not understand, because I can scarcely suppose that Guillet and Ballay simply made misstatements. They must have found what they describe, and evidently there was some difference in the conditions. Possibly the steam moving at a high velocity carried with it some particles, liquid or otherwise, which acted as an abrasive and destroyed the surface film in their case, but not in the case described in this paper. That is a hypothetical explanation of the discrepancy, which is much too big to be due to anything but a real and important cause.

Mr. T. **Henry Turner**: In that connection may I add that Dr. Seligman's reference to the boiler compound might be very much to the point, and in the case to which I referred, the water was untreated and there was little or no priming.

Mr. I. D. **Taverner**, B.E.* (Member): I do not think that I have anything theoretical to say, but it does seem that this paper which Dr. Seligman has put forward will be of very great interest to those people who are dealing with the development of the use of aluminium and its alloys for high-pressure steam engines, and it is to be hoped, as previous speakers have already said, that the investigation may be carried forward to deal with the alloys which are commonly used at the present time for internal combustion engines.

Mention has been made of the possibility of particles of water being carried over with superheated steam, and I think that experience in the past with turbines has shown that this is certainly the case. Whether it occurs also in reciprocating engines—and whether the velocity of the steam is sufficient—are points on which I cannot express a definite opinion, but there can be no doubt that such particles would have a very severe abrasive action if the velocity of the steam were sufficient.

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* Engineer, The British Aluminium Co., Ltd., London.

The **President**: I had some experience bearing on this some years ago, but unfortunately the evidence of it has disappeared. We had a commercially pure aluminium piston put in a locomotive which did not use superheated steam, and undoubtedly a considerable amount of water was carried over, enough, I think, to wash away any film of oil, which, with due respect, I do not think is of any appreciable thickness, and the water carried over would, I feel sure, wash it off. Having some trouble one day, we took the cylinder cover off, and found that we had not got a piston! Similar experiments have lately been carried out with an aluminium alloy, and I have seen the pistons quite recently. There was no trace of oil on them, and the condition was not that of superheated steam, for they were used in shunting engines, where plenty of water is carried over, as every time the engine starts one has to warm up again with consequent condensation, and probably there is complete washing off of the oil film. These cylinder pistons are all right after four or five months' use.

Mr. Taverner mentioned internal combustion engines, and the effect of using aluminium pistons in the early days in aeronautical engines with high temperatures is probably well known. Some of those pistons gave one the impression that the ordinary worm which eats into our furniture had been getting at them. I take it that one may assume that there was not sufficient water vapour present to do any harm.

Dr. **Seligman** (*in reply*): I am really surprised beyond measure that this paper should have aroused so much interest.

I should like to deal first with Mr. Taverner's point. He must not read into this contribution an attempt to pass judgment on the possibility of applying aluminium or its alloys to steam-engine practice; that was not in our minds when Mr. Williams and I started this work. As Dr. Rosenhain has said, you there have rapidly moving steam and totally different conditions, and that is why I started my remarks by limiting our claims to specified conditions designed to show one thing, and one thing only.

If I may now deal with what the President said, I suppose that one might say that " a long time " has something in common with " the length of a piece of string." What is a long time? Professor Guillet has carried some of his experiments very much further than we did ours. We only tried to show that in the time he gave in his paper nothing happened. That was 300 hrs., but now he has carried on for 4000 hrs., as he has told me privately, and no doubt he will publish his results later.

With regard to Professor Hanson's remarks, we feel convinced ourselves that it is a question of the protective film. We had in mind some views of his with regard to the method by which hydrogen enters into aluminium. We concluded from what he had said that it only goes in where the film is broken by the attack of liquid water. We thought it well to inquire whether, if there were no liquid water present, attack would still occur, for we could not see why, if, as Pilling and Bedworth showed, oxygen ceased to attack aluminium after a certain number of hours, water vapour should be more active.

That the work is closed I cannot believe. Whether we shall be able to carry it on I do not know, but it is open to anybody who would like to examine the matter further to do so, and I only hope they will, for our own opportunities are naturally very limited.

I think that also deals to some extent with what Mr. Turner said. I am very interested to hear that his experiments are still being carried on, but there he must surely have liquid water, and our results would not hold.

On the question of boiler compound, of course I do not know whether there was any boiler compound spewed up with the steam with which Guillet and Ballay were working. It was an industrial installation, but they do definitely

a *b*

Fig. A.

[*To face p.* 194.

state that speed did not enter into their problem, except as to the degree of attack. They worked with high speed and with what they called stationary water vapour—that is to say, in the separator of the boiler, and they say that attrition was not responsible for their results. If it was, then our results do not apply.

Dr. Gwyer raised the question of the higher temperature and the absence of liquid water. We were expressly excluding that. Dr. Gwyer himself asked us to go higher, and we did go higher, to see if we could find where the boundary lay between Professor Hanson's and our earlier results. Probably we are just on the border.

Dr. Rosenhain, as he always does, has contributed remarks of the greatest possible interest. He has referred to the furnace atmosphere in which the ordinary heating of aluminium is done and to the development of blisters under such conditions. We are very familiar with that, I am sorry to say, but there is just this small difficulty—that a sample similar to that which I showed was in an ordinary furnace atmosphere for a very long time without showing any blisters. We removed it, cleaned it, and put it into a steam atmosphere, and some very small blisters appeared. Whether that is accidental or not, I do not know. It has only just occurred, and I mention it now, perhaps prematurely, but it does shake one's confidence in stating that nothing is going on which is due to the steam.

CORRESPONDENCE.

The Authors: Since this paper was presented the experiments at 620° C. have been repeated, and as a result it seems clear that some interaction takes place at that temperature between solid aluminium and steam.

Fig. A (Plate XVI) shows :—

(*a*) One of four pieces of aluminium sheet heated for 63 hrs. in air, and
(*b*) One of four samples of the same sheet heated for 56 hrs. in steam ;

in both cases at atmospheric pressure. The metal had the composition given in Table I for test-piece No. 2.

THE AGE-HARDENING OF SOME ALUMINIUM ALLOYS OF HIGH PURITY *

By MARIE L. V. GAYLER,† D.Sc., MEMBER, and G. D. PRESTON,† B.A.

SYNOPSIS.

An investigation into the age-hardening of a series of alloys made with high-purity aluminium containing 4 per cent. copper, to which iron, silicon, and magnesium have been added either independently or together, has confirmed the results of previous investigators. It has been shown that the addition of 0·35 per cent. iron inhibits the age-hardening at room temperature of the binary copper–aluminium alloys: this effect is partly removed by the addition of 0·25 per cent. silicon, and is entirely removed by the addition of 0·5 per cent. magnesium. X-ray and microscopic examination have failed to give an explanation of the phenomena observed during age-hardening at room temperature.

The conclusions are drawn that (1) age-hardening of a Duralumin at room temperature and at 200° C. is due to some process, as yet undefined, which takes place prior to actual precipitation of $CuAl_2$ or Mg_2Si from the aluminium lattice; (2) in conjunction with existing equilibrium data, it is suggested that Mg_2Si as well as $CuAl_2$ plays an important part in the process of age-hardening.

THIS paper forms part of a research carried out for the Alloys Sub-Committee of the Aeronautical Research Committee with the support of the Metallurgy Research Board of the Department of Scientific and Industrial Research. Both of these bodies have given permission for publication.

INTRODUCTION.

Attention has been directed to the so-called anomalous behaviour of alloys of high-purity aluminium with copper ‡ which age-harden at room temperature, in contrast to similar alloys made from commercial aluminium. No satisfactory explanation of this phenomenon has yet been given, but data regarding the age-hardening of alloys of high-purity aluminium are being acquired. Fraenkel § has recently studied the age-hardening of some such alloys, and has shown that in the case

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‡ Archer, "The Hardening of Metals," *Trans. Amer. Soc. Steel Treat.*, 1926, **10**, 718; Meissner, Discussion, *J. Inst. Metals*, 1929, **41**, 191.

§ Fraenkel, *Z. Metallkunde*, 1930, **22**, 84–89.

of one containing 5 per cent. copper, the presence of 0·5 per cent. silicon causes a small increase in the hardness value obtained after quenching and ageing at room temperature, whilst the addition of 1 per cent. iron affects the ageing phenomenon in the reverse direction, causing practically no increase in hardness to take place at room temperature. He also shows the effect of 0·5 per cent. magnesium on the age-hardening of a 4 per cent. copper alloy, and finds that the increase in hardness corresponds with that which takes place in Duralumin.

Meissner * has also studied the effect of additions of small percentages of iron, silicon, and manganese on an aluminium alloy containing 4·2 per cent. copper and 0·5 per cent. magnesium. The aluminium used, however, was not the purest, since the silicon and iron content in the alloys varied from 0·018 to 0·032 per cent. and 0·033 to 0·046 per cent., respectively. As a result of his experiments, Meissner has drawn the following conclusions :—

(1) None of the three constituents, iron, silicon, or manganese, is necessary for the age-hardening of Duralumin at room temperature. On the other hand, the addition of magnesium to copper–aluminium alloys which do not age-harden so intensively at room temperature causes marked age-hardening at room temperature.

(2) The addition of silicon in an amount sufficient for the conversion of the magnesium into Mg_2Si has no influence on ageing; at most the tensile strength is slightly increased.

(3) The presence of iron, which adversely affects the age-hardening of copper–aluminium alloys at room temperature, does not affect that of copper–magnesium alloys.

The present research was already started before the results of the above investigations were published, but it is thought worth while to publish the results which have been obtained. Only the very purest materials have been used, and the effect of the addition of various elements, either singly or in pairs, has been very carefully studied in relation to age-hardening at room temperature and at 200° C., together with accompanying changes in lattice structure, if any, as determined by X-ray analysis.

1. Experimental Data.

The alloys used in this research were made from the very purest material available, as follows :—

(1) Aluminium of high purity 99·96 per cent. which has been kindly presented by the Aluminum Company of America.

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* Meissner, *Z. Metallkunde*, 1929, **21**, 328.

(2) Electrolytic copper.

(3) Silicon of high purity 99·94 per cent. prepared at the National Physical Laboratory.

(4) Electrolytic iron 99·9 per cent., prepared at the National Physical Laboratory.

The alloys were made up in pure alumina pots to ensure that no contamination of the melt took place. The molten alloys were cast into ½-in. chill moulds, as the supply of aluminium available was insufficient for 1-in. chill castings.

The alloys were made up to the following compositions :—

(*a*) *Copper Alloys.*

(1) 4 per cent. copper.

(2) 4 per cent. copper + 0·5 per cent. magnesium.

(3) 4 per cent. copper + 0·25 per cent. silicon.

(4) 4 per cent. copper + 0·32 per cent. iron.

(5) 4 per cent. copper + 0·25 per cent. silicon + 0·32 per cent. iron.

(*b*) *Copper and Magnesium Alloys.*

(1) 4 per cent. copper + 0·5 per cent. magnesium + 0·32 per cent. iron.

(2) A series of alloys containing 0·5 per cent. magnesium with 1, 2, 3, and 4 per cent. copper.

The alloys were heated at 450° C. for 5–6 hrs. and forged to about 3/16 in. thick, and the surfaces were then prepared for hardness measurements. After prolonged soaking at 500° C. for 20–24 hrs. they were quenched in water at room temperature. One specimen of each alloy was aged at room temperature and then heat-treated at 200° C., whilst the other was heat-treated at 200° C. immediately after quenching. The specific heat-treatment and the Brinell hardness numbers thus obtained are embodied in Figs. 1 and 2 (Plates XVII and XVIII).

It was found almost impossible to obtain regular hardness values from the alloy containing 4 per cent. copper only. The full black circles in the figure represent the values obtained from three different forgings. Great care was taken in forging the alloys to ensure that the specimen should be uniformly worked, but it seemed to have no effect. Immediately other additions were made to the alloy this difficulty more or less disappeared. It was thought that segregation of the copper was a possible cause of this irregularity, a view that is supported by the difficulty of obtaining good X-ray photographs of this alloy. Turnings of the alloy FY, containing 4 per cent. copper, 0·32 per cent.

iron, 0·008 per cent. silicon, taken from the outside of the chill to a depth of 1/16 in., gave on analysis 4·15 per cent. copper, whilst turnings taken from a central portion of radius 1/16 in. gave the value 3·95 per cent. copper. These results confirmed the deductions from the X-ray analysis.

2. DISCUSSION OF RESULTS.

(*a*) *Copper Alloys.*—From the values obtained, it is seen, as already observed by previous investigators,* that a 4 per cent. copper alloy made with very pure materials age-hardens at room temperature to a marked extent.

Fraenkel † has observed the extraordinary effect which takes place on heat-treating a 4 per cent. copper alloy after age-hardening at room temperature, *i.e.* the initial softening which occurs, followed by an increase in hardness. This phenomenon has been frequently observed in aluminium alloys of the Duralumin type,‡ and is very noticeable in the case of each alloy investigated in the present research.

In agreement with Fraenkel's results, the addition of 0·25 per cent. silicon has practically no effect on the age-hardening of a 4 per cent. copper alloy. It follows, therefore, from the above results that silicon alone is insufficient to account for the fact that alloys made with commercial aluminium do not age-harden at room temperature. The amount of iron present in commercial aluminium is of the order 0·35 per cent., so the effect of that amount of iron in the 4 per cent. copper alloy was next studied. Here, in agreement with Fraenkel's results, which were, however, obtained by the addition of 1 per cent. iron, the age-hardening is greatly reduced, and even subsequent heat-treatment does not raise the hardness to the value obtained from the alloy without iron.

It seems highly probable, therefore, that the iron content is responsible for the fact that commercial copper–aluminium alloys do not age-harden at room temperature, and to check this conclusion an alloy was made up containing the same percentages of silicon and iron as in the previous experiments. The results show that when silicon and iron are present together the deleterious effect of the iron is reduced by the presence of silicon, and that although the hardness obtained after quenching and ageing at room temperature is small in comparison with that obtained in the alloy free from silicon and iron, the ageing at 200° C. produces a greater maximum hardness in less time than in the case of the alloy containing 0·32 per cent. iron only.

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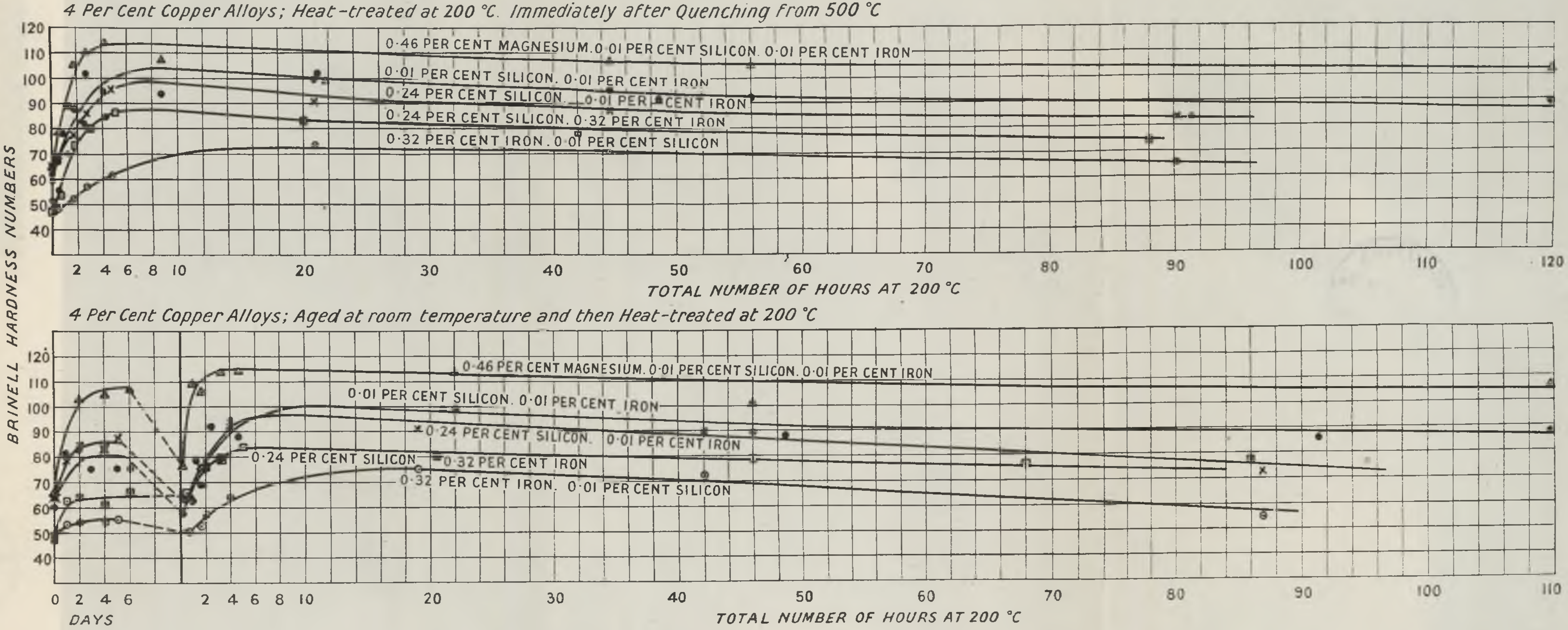
* *Loc. cit.*

† *Loc. cit.*

‡ Gayler, *J. Inst. Metals*, 1922, **28**, 213; 1929, **41**, 191; Meissner, *J. Inst. Metals*, 1930, **44**, 207.

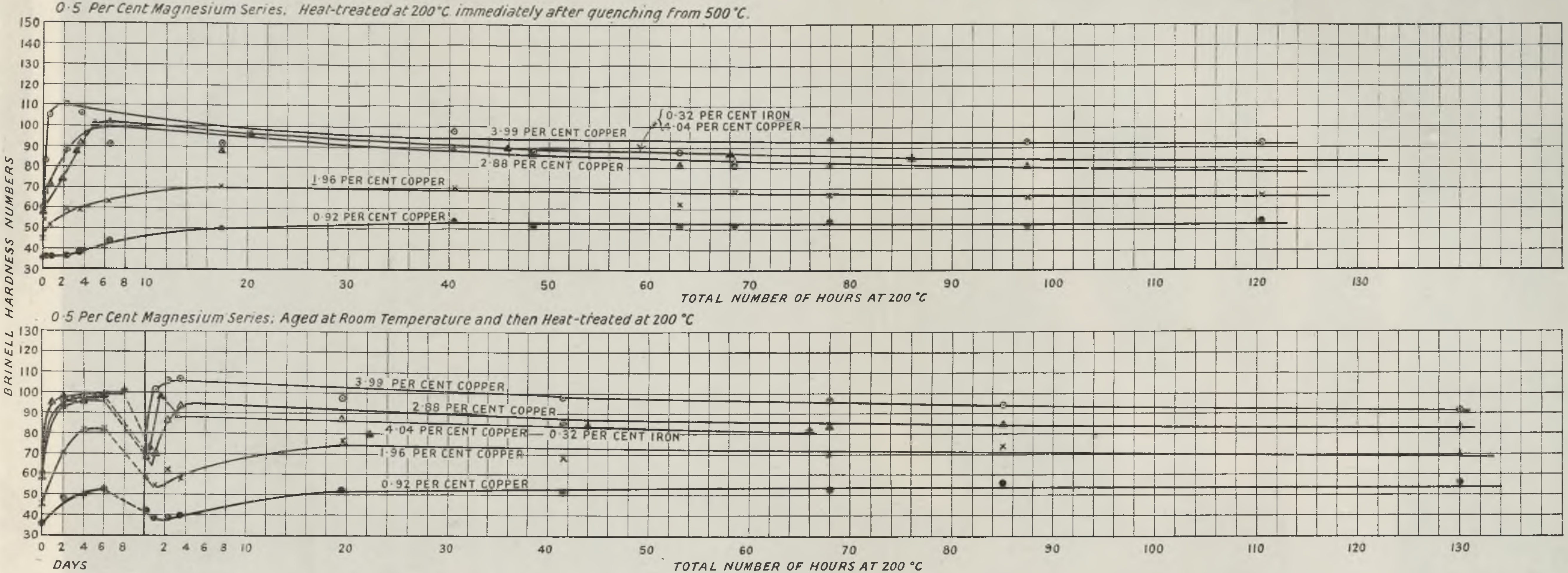
PLATE XVII.



[*To face p.* 200.

FIG. 1.

PLATE XVIII.



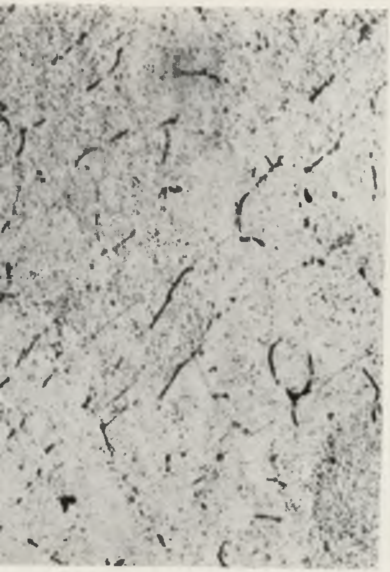
0·5 Per Cent Magnesium Series. Heat-treated at 200 °C. immediately after quenching from 500 °C.

0·5 Per Cent Magnesium Series: Aged at Room Temperature and then Heat-treated at 200 °C

FIG. 2.

[Between pp. 200 and 201.

PLATE XIX.



3.—4 per cent. Copper; 0·32 per cent. Iron. × 300.

FIG. 4.—4 per cent. Copper; 0·32 per cent. Iron; 0·5 per cent. Magnesium. × 300.

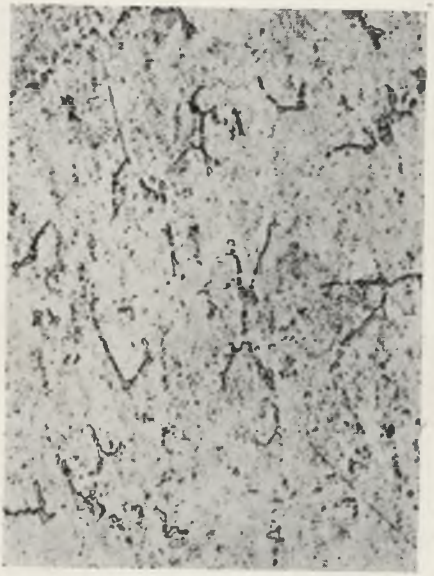
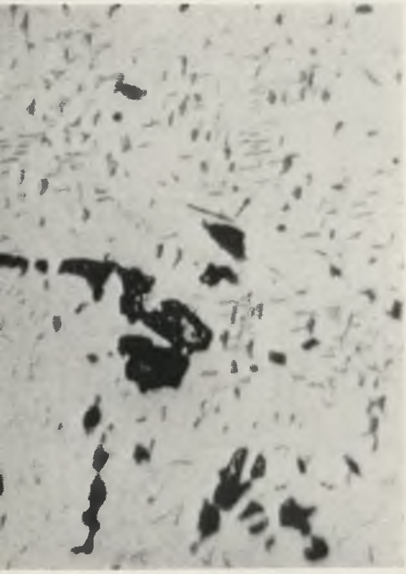


FIG. 5.—4 per cent. Copper; 0·32 per cent. Iron; 0·24 per cent. Silicon. × 300.

l three specimens had been aged at room temperature and then heat-treated for 4 to 6 days at 200° C., followed by a further heat-treatment for 1 day at 250° C. Specimens were etched with ½ per cent. HF.

[*Between pp.* 200 *and* 201.



IG. 6.—4 per cent. Copper; 0·32 per cent. Iron. × 1500.

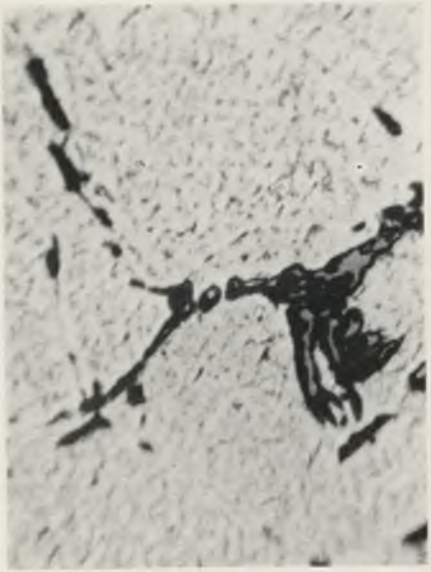


Fig. 7.—4 per cent. Copper; 0·32 per cent. Iron; 0·5 per cent. Magnesium. × 1500.

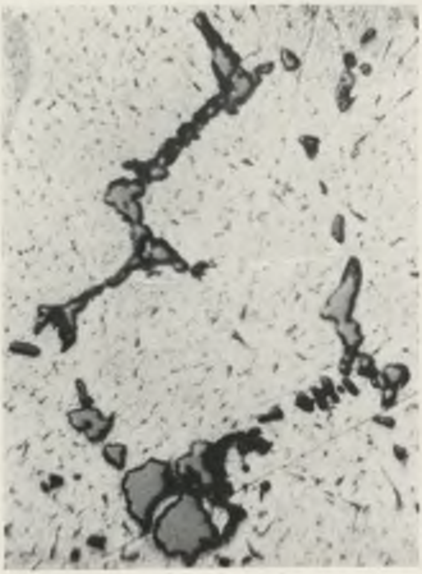


Fig. 8.—4 per cent. Copper; 0·32 per cent. Iron; 0·24 per cent. Silicon. × 1500.

Same specimens as in Figs. 1–3, but etched with 12½ per cent. NaOH.

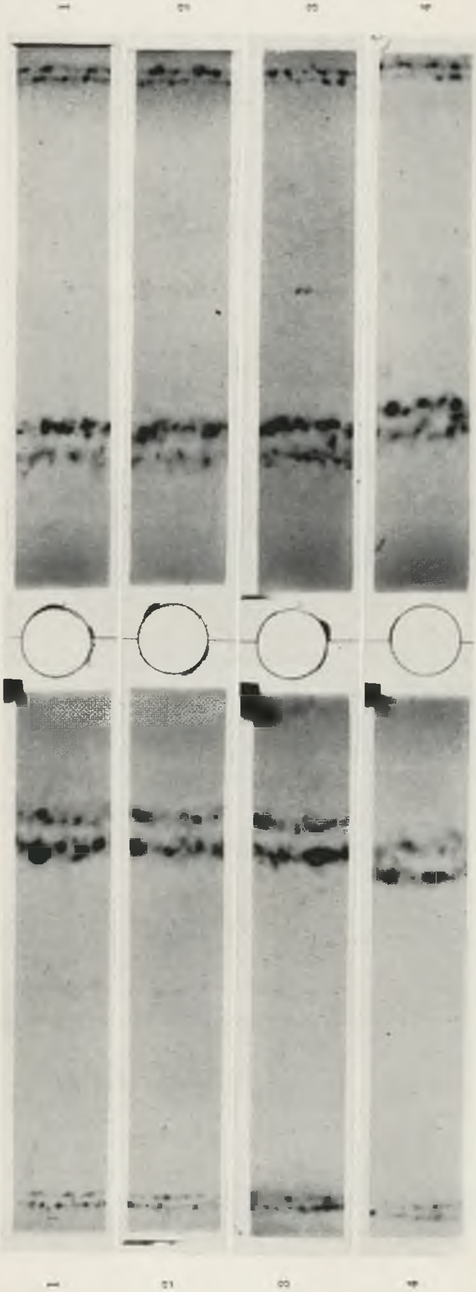


FIG. 9.—4 per cent. Copper. CuK radiation.

1. Immediately after quenching from 500° C.
2. Aged one week at room temperature.
3. ,, ,, ,, ,, and then 20 minutes at 200° C.
4. ,, ,, ,, ,, and then 24 hrs. at 200° C.

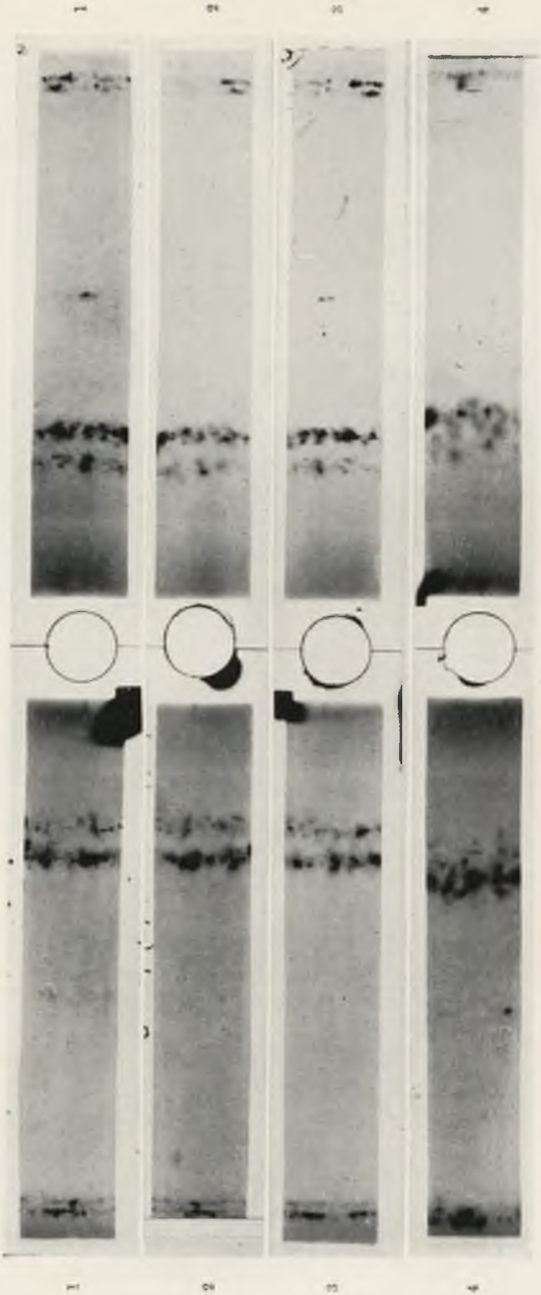


FIG. 10.—4 per cent. Copper; 0·5 per cent. Magnesium. CuK radiation.

1. Immediately after quenching from 500° C.
2. Aged one week at room temperature.
3. ,, ,, ,, ,, and then 20 minutes at 200° C.
4. ,, ,, ,, ,, and then 18 hrs. at 200° C.

The phases which, according to Gwyer and his colleagues,[*] should exist in the alloy in equilibrium at room temperature are given in the following table.

TABLE I.

No.	Composition by Analysis. Per cent.			Phases.
	Copper.	Iron.	Silicon.	
1	4·12	0·01	0·01	$Al + CuAl_2$
2	3·94	0·007	0·25	$Al + CuAl_2 + Si$
3	4·09	0·32	0·008	$Al + CuAl_2 +$ " N "
4	3·89	0·32	0·24	$Al + CuAl_2 +$ " N "

From these data it appears that possibly the formation or the presence of the constituent " N " in the alloy is in some obscure way responsible for the behaviour of commercial copper–aluminium alloys, since $CuAl_2$ can be precipitated in the ternary alloys only at the expense of " N." Up to the present there has been no exception to the rule that alloys belonging to binary systems, in which the solid solubility of one constituent in the other decreases with fall in temperature, possess the property of age-hardening. Pure copper–aluminium alloys follow this general rule, and age-harden at room temperature, but alloys made from commercial aluminium age-harden appreciably only at higher temperatures. This difference might be ascribed to the fact that the latter are not binary alloys, but are at least quaternary alloys, and that the separation of the compound $CuAl_2$ must be influenced by the presence of other constituents. It was thought that microscopic examination might perhaps throw some light on these results, but apart from the fact that the iron constituent appears different in character, as shown in Figs. 3–5 (Plate XIX), under a magnification of 300 diameters, there is nothing to account for the fact that iron alone or iron and silicon together prevent the ageing of the copper–aluminium alloy at room temperature, and that the addition of 0·5 per cent. magnesium to the alloy containing 0·32 per cent. of iron removes the inhibiting effect of the iron on the age-hardening phenomenon.

Under a magnification of 1500 diameters the micro-structures of these alloys, which had been annealed until the copper compound had become visible, showed that the peritectic reactions

(*a*) liq. + $FeAl_3 \longrightarrow$ " N "
(*b*) liq. + $FeAl_3 \longrightarrow$ " X " (which is isomorphous with " N ")

[†] Gwyer, Phillips, and Mann, *J. Inst. Metals*, 1928, **40**, 297.

which commence while the greater part of the alloy is in the liquid state, and proceed to completion in the solid state, had not been completed, and that the heat-treatment given the alloys in the solid state was not sufficient to convert the whole of the $FeAl_3$ into " N " or " X." The photomicrographs given in Figs. 6–8 (Plate XX) appear to indicate that the reaction has proceeded most completely in the copper–aluminium alloy containing iron only, and least completely in that containing 0·32 per cent. iron and 0·24 per cent. silicon. In all three cases no marked difference could be observed in the quantity of $CuAl_2$ precipitated. Reference was made to the researches of Gwyer, Phillips, and Mann,* in order to identify the various constituents, but it was found extremely difficult to be sure of the identification of the compounds.

(*b*) *Copper–Magnesium Alloys.*—Hardness measurements were made on a series of alloys containing 0·5 per cent. magnesium with 1, 2, 3, and 4 per cent. copper. The forged bars were (*a*) quenched from 500° C., aged at room temperature, and then heat-treated at 200° C.; (*b*) heat-treated at 200° C. immediately after quenching. The respective heat-treatments and the results obtained are embodied in Fig. 2 (Plate XVIII). It will be noticed that there is quite appreciable age-hardening in the alloy containing only 2 per cent. copper; an alloy containing the same amount of copper but made with commercial aluminium † shows no age-hardening either at room temperature or at higher temperatures. All these alloys show the initial softening on heat-treating the material after age-hardening at room temperature.

X-Ray Examination.

The X-ray examination of the alloys of high-purity aluminium with copper has been undertaken with a view to ascertain whether any changes of lattice parameter are associated with the marked age-hardening which occurs in these alloys at room temperature. In the discussion of our previous contribution (to which reference may be made for a description of the method employed),‡ Fraenkel and Scheuer suggested the desirability of the comparison of X-ray photographs of the alloy H_3 (commercial aluminium and 4 per cent. copper) immediately after quenching and after ageing at room temperature. In our reply § we stated that this had been done, and that a period of three months' ageing at room temperature produced no change that could be detected in the X-ray photographs. As the

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* Gwyer, Phillips, and Mann, *J. Inst. Metals*, 1928, **40**, 297.

† Hanson and Gayler, *ibid.*, 1923, **29**, 491.

‡ Gayler and Preston, *ibid.*, 1929, **41**, 191.

§ *Ibid.*, p. 246.

degree of age-hardening at room temperature which takes place in alloys of commercial aluminium and copper is quite small compared with that of a similar alloy of high-purity aluminium, it appeared possible that some effect might be observable in the latter case, but the X-ray photographs which have now been taken show no appreciable change.

The alloy containing 4 per cent. copper was examined in four conditions. First, immediately after quenching from 500° C.; secondly, after ageing at room temperature for seven days; thirdly, after annealing the aged specimen at 200° C. for 20 minutes, and finally after a further annealing at 200° C. for 24 hrs. The first three photographs (Fig. 9, Plate XXI) are indistinguishable, although marked hardness differences are found for alloys in the three conditions. In the first and third the Brinell numbers are in the neighbourhood of 60, whilst in the second condition the figure is of the order of 80 or thereabouts, as shown in the graph (Fig. 1, Plate XVIII). In the fourth condition the hardness number has a value of about 100, and the displacement of the lines in the X-ray photograph shows that the copper has been to a large extent precipitated, leaving a matrix, of which the parameter does not differ appreciably from that of pure aluminium.

A second series of photographs was obtained from an alloy containing 4 per cent. copper and 0·5 per cent. magnesium, the X-ray examination being carried out immediately after quenching from 500° C. after 7 days' ageing at room temperature, after a subsequent anneal for 20 minutes at 200° C., and after further annealing for 18 hrs. at 200° C. (Fig. 10, Plate XXII). In this case, too, no appreciable difference is observable in the X-ray photographs of the material in the first three conditions, although the hardness changes are still more marked than in the case of the alloy without magnesium.

A noticeable feature of the photographs of the quenched material is the breadth of the lines. The diffraction spots from individual crystals do not all fall on a line in the film. This has been interpreted as an indication of lack of homogeneity in the material, different crystals having slightly different composition. Efforts to reduce the width of the lines by repeated cold-work and annealing proved fruitless, so that it has not been possible to obtain parameter measurements of the desired accuracy. The changes of length during ageing at room temperature of a 4 per cent. alloy of copper with commercial aluminium have been determined by Chevenard, Portevin, and Waché,* and amount to a contraction of about 50 parts in a million. This figure is of the same order as that given by the density measurements in our

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* *J. Inst. Metals*, 1929, **42**, 337.

previous paper—namely, a change of 2·7894–2·7897 grm./cm.^{3}, or about 110 parts in one million, the length change being one-third of this quantity, or about 36 parts in one million. Parameter changes of this magnitude could not be detected by the X-ray method employed in the present investigation. A change in the distance between the lines on the film of 1 mm. corresponds with a change of parameter of 400 parts in a million, and this is the smallest change which we could hope to detect with such broad lines.

The net result of the investigation is that, within the limits of accuracy attainable by the method of investigation, no change in the X-ray spectra accompanies the hardening of these alloys at room temperature or the softening caused by short annealing at 200° C. The hardening which is produced by a further period of annealing at 200° C. is accompanied by a displacement of the diffraction lines, which has been interpreted as indicating the precipitation of copper from solid solution.

Conclusions from Experimental Data.

1. The examination of a series of alloys containing 4 per cent. copper made with high-purity aluminium has shown that:

(*a*) The presence of 0·32 per cent. iron inhibits the age-hardening of the alloy at room temperature and decreases the maximum hardness attainable on heat-treating at 200° C.

(*b*) The addition of 0·25 per cent. silicon has little or no effect on the age-hardening of the copper–aluminium alloy.

(*c*) The addition of 0·25 per cent. silicon to the alloy containing 0·32 per cent. iron reduces the deleterious effect of the iron.

(*d*) X-ray examination of alloys containing 4 per cent. copper and 4 per cent. copper with 0·5 per cent. magnesium has failed to detect any change of parameter during ageing at room temperature. On heat-treating at 200° C. the alloys previously age-hardened at room temperature, no change in parameter occurs until after maximum hardness has been obtained.

(*e*) A series of alloys containing 1, 2, 3, and 4 per cent. copper and 0·5 per cent. magnesium, respectively, all age-harden at room temperature and at 200° C.

(*f*) All the alloys age-hardened at room temperature show a marked decrease in hardness as a result of heat-treatment at 200° C. for about 20 minutes. The Brinell hardness obtained approaches that observed immediately after quenching.

DISCUSSION.

It has been stated above that the phenomenon of age-hardening is exhibited by an alloy when the solubility of the alloyed metal decreases with decreasing temperature. In such a case the quenched alloy is, at room temperature, a supersaturated solution, and a rise of temperature or the passage of time will be accompanied by a reaction in which the alloy will proceed to a state of equilibrium. An attempt to correlate the experimental results described above with existing knowledge of the equilibria of the different systems involved is a matter of considerable difficulty. In those cases where the equilibrium diagrams have been investigated the aluminium has been impure, and the exact effects of the small quantities of iron and silicon on the solubility limit of copper are not known. The work of Dix and Richardson on the binary Al–Cu system is an exception, very pure materials having been used in the determination of the solubility limit of copper in aluminium (Fig. 11). The dotted line in this figure is taken from an investigation * of the Cu–Al–Mg system in which the aluminium was of "commercial" quality. It suggests that the only effect of magnesium is to reduce the solid solubility of copper by about $\frac{1}{4}$ or $\frac{1}{2}$ per cent. The hardness curves in Fig. 2 (Plate XVIII) also indicate that the solubility of copper in aluminium in the presence of 0·5 per cent. magnesium is in the neighbourhood of 4 per cent. at 500° C., which does not differ appreciably from the value shown in Fig. 11.

We do not know what the effect of approximately 0·1 per cent. iron, present as impurity in the aluminium, would have on this. If it is legitimate to neglect the effect of magnesium on the solubility of copper, then it becomes difficult to explain the greater and more rapid age-hardening of an alloy with 0·5 per cent. magnesium compared with one without this element, if the ageing is ascribed to the formation of $CuAl_2$. It has been suggested † that the expansion of the space lattice of aluminium by the comparatively large magnesium atom facilitates the precipitation of $CuAl_2$. The X-ray evidence suggests that hardening at room temperature takes place without the rejection of copper from solution, whilst at higher temperatures (200° C.) the hardening is accompanied by some precipitation. It cannot, however, in the light of the present work, be assumed that the precipitation is the cause of this hardening—both phenomena may arise from a common cause, and the hardening may result from the mechanism of incipient precipitation,‡ as we have previously suggested.

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* Gayler, *J. Inst. Metals*, 1923, **29**, 507.

† Archer, *loc. cit.*

‡ Gayler and Preston, *loc. cit.*

With regard to the alloys containing magnesium and silicon, the only available data as to their equilibria are contained in the investigations of the systems Al–Cu–Mg_2Si,* Al–Cu–Mg–Mg_2Si. Here again the results are rendered uncertain by the presence of iron in the aluminium, but taking the evidence for what it is worth, it appears that at 500° C. the solubility of copper in aluminium in the presence of about 1 per cent. of Mg_2Si is reduced to 2 per cent. from the 4 per cent. which can be retained in solution in the absence of Mg_2Si. This fact, if true,

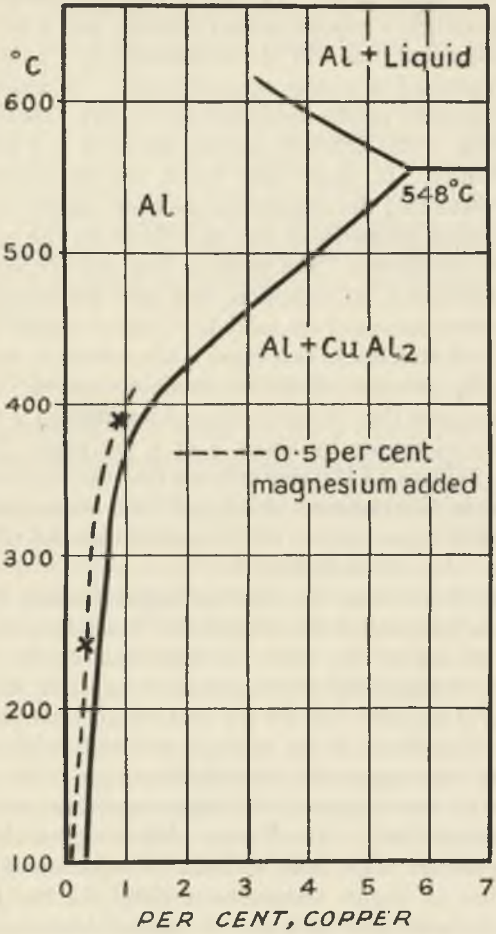

FIG. 11.

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* Gayler, *J. Inst. Metals*, 1922, **28**, 213; 1923, **30**, 139.

has an important bearing on the part played by Mg_2Si in the age-hardening of Duralumin made with commercial aluminium. Meissner has found that the hardening of 4 per cent. copper alloy with magnesium is not effected appreciably by the addition of silicon, and has concluded that Mg_2Si plays no part in the hardening, which is to be ascribed wholly to the copper. In the light of the evidence cited above, however, a Cu–Mg–Al alloy of the Duralumin type would have 4 per cent. copper in solution—a similar alloy with the addition of 0·3 per cent. silicon only 2 per cent., so that if the two alloys harden to the same extent, some other explanation must be sought, since an alloy containing 2 per cent. copper does not harden to the same extent as one containing 4 per cent. (Fig. 2).

ACKNOWLEDGMENTS.

The authors are indebted to Mr. P. Ward, B.Sc., who has analyzed the alloys used, and acknowledge with pleasure the assistance of Mr. R. P. Garner in the course of this investigation. They also desire to express their indebtedness to Dr. W. Rosenhain, F.R.S., for his continued interest and encouragement, and to offer their cordial thanks to Dr. J. D. Edwards of the Aluminum Company of America, who very kindly arranged for some aluminium of high purity to be sent to them.

APPENDIX I.

Analysis of Aluminium.

	Per cent.
Silicon	0·007
Iron	0·009
Copper	0·024

Analysis of Alloys Made Up.

Stamp.	Copper, %.	Iron, %.	Silicon, %.	Magnesium, %.
C_4 (2)	4·12	0·01	0·01	...
C_4 (3)	3·96	...	0·01	...
S	3·94	...	0·25	...
FY	4·09	0·32	0·008	...
FZ	3·89	0·32	0·24	...
CMF	4·04	0·32	0·012	0·58
C_1M_5	0·92	...	...	0·51
C_2M_5	1·96	...	...	0·54
C_3M_5	2·88	...	...	0·55
C_4M_5	3·99	...	...	0·54
C_4M_5 (2)	4·12	0·01	0·01	0·46

APPENDIX II.

Brinell Hardness Measurements : 2 mm. ball, 40 kg. load for 30 seconds.

Half-inch chill castings were annealed for 5–6 hrs. at 450° C., and then forged down to 3/16 in. approximately. The surfaces were then prepared for hardness measurements and the bars were soaked for 20 hrs. at 500° C. After quenching in water at room temperature one set of bars was aged at room temperature and then heat-treated at 200° C., and the other set was heat-treated at 200° C. immediately after quenching.

DISCUSSION.

Professor Dr.-Ing. Georg Sachs * (Member): There is also another factor which acts in the same peculiar manner as the presence of impurities in the age-hardening of aluminium alloys; this is the grain size. Researches on a magnesium-free alloy with 5 per cent. copper have shown that hardening starts earlier and is greater with single crystals than with finely crystalline material.† In both cases a reduction in the ageing temperature is accompanied by an enhanced hardening effect.

At this point I should like to mention that in recent researches a remarkable agreement has been reached as to the mechanism of the hardening process in Duralumin. According to this, precipitation begins only at high temperatures, about 150° C., and the mechanical effect in self-hardening is quite different from that produced by artificial ageing at high temperatures.‡ Recent work at the Kaiser-Wilhelm-Institut für Metallforschung in Berlin-Dahlem has shown that at high temperatures a hardening effect occurs at first, then disappears, and is finally followed by a hardening of a different type.

According to these results it appears to me to be established definitely that the characteristic Duralumin hardening depends on effects which occur within the solid solution. This has been confirmed by X-ray intensity measurements by means of which differences in the quenched and hardened states have been established which correspond with changes in the position of the atoms in the solid solution probably preparatory to precipitation. §

Dr. A. G. C. Gwyer || (Vice-President): I do not propose to discuss this paper in any great detail. I have talked the matter over with my colleagues —especially with Mr. H. W. L. Phillips—and have read the paper carefully, but the observations which I wish to make are of a rather general nature. It seems to me that this paper may be regarded as another milestone on the long road towards the clearing up of this theory of age-hardening. As such, the paper is to be welcomed, and it has undoubtedly established and settled one or two further points, notably the inhibiting effect of iron on the age-hardening of pure aluminium. There are also interesting points in regard to the sluggishness of the reaction and so on, but I do not wish to labour them at the moment.

I think that the extraordinary difficulty of this problem is emphasized more

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* Leiter des Metall-Laboratoriums der Metallgesellschaft A.-G., Frankfurt-am-Main, Germany.

† R. Karnop and G. Sachs, *Z. Physik*, 1928, **49**, 480.

‡ von Göler and G. Sachs, *Metallwirtschaft*, 1928, **8**, 671.

§ J. Hengstenberg and G. Wassermann, *Z. Metallkunde*, 1931, **23**, 114.

|| Chief Metallurgist, British Aluminium Co., Ltd., Warrington.

clearly than ever by the enormous amount of work which has been done and the fact that undoubtedly a great deal more remains to be done before the matter will be cleared up, whilst there still remain very striking divergencies, even, one might say, as to the facts, between some of the most competent workers, among whom the authors of this paper must unquestionably be ranked.

Recently a paper has been read—I have seen only an advance note of it—by E. H. Dix and his colleagues,* who confirm Dr. Gayler in her conclusion that magnesium only very slightly lowers the solid solubility of copper; but whereas Dr. Gayler finds that the solid solubility of copper is very materially lowered by the addition to it of Mg_2Si, Dix and his colleagues find the direct opposite, and say that the effect is negligible. They publish a photomicrograph, the explanation of which is not clear, but the photomicrograph itself is clear, and shows the presence of yet another constituent which I think is a new one—a quaternary one with aluminium, copper, magnesium, and silicon.

When one sees such a divergence with regard to the statement of apparent facts by two such competent workers, the conclusion that I have reached in this matter—I say it for the moment rather out of hand—is that it would seem that the time is ripe for a symposium between the leading American, German, and British workers on this subject, or alternatively they should get together in some way.

Dr. C. H. M. **Jenkins** † (Member): I congratulate the authors on the further work contained in this paper, and would like to ask them for a little more information on one or two points of special interest. The first concerns the general relationship of the changes in microstructure to the hardness changes which are mentioned. In reading various papers on age-hardening phenomena in aluminium alloys, one observes that the various authors deal with hardness changes, but do not definitely state at what point the first visible separation of new constituents can be observed in relation to those hardness changes. It is probable from the point of view considered in regard to aluminium alloys that the information given is what is desired, but if a study is being made of the age-hardening phenomena in other materials, such as perhaps in copper or in nickel–chromium alloys, it is important to understand the inter-relationship of the various factors in age-hardening. I think that this is a point which will receive more attention in the future, as the sequence of events, noticed in the age-hardening of alloys of other basis metals, does not, on the present evidence, appear to be the same as that obtained for aluminium alloys.

The other point to which I wish to refer is of a different nature, and relates to the actual interpretation of the Brinell hardness changes shown in the diagrams. It is to be observed that the authors express the changes in the alloys by means of Brinell hardness tests, and in support they show changes in hardness with the progress of time. There is no doubt that this result represents some change within the alloys, but it is not clear that this necessarily means a change of strength in the absence of all forms of externally applied deformation.

I have in mind an instance where there is an appreciable change in the Brinell hardness of a material without there being any difference in the hardness of the metal if the work-hardness due to making the impression is removed. In the case of tests on commercially pure ingot iron which has

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* E. H. Dix, Jr., G. F. Sager, and M. P. Sager, *Amer. Inst. Min. Met. Eng. Tech. Publ.* No. 472.

† Senior Assistant, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

been tested by actually impressing the material at various temperatures, one finds that the hardness values obtained in the ordinary way rise to a maximum at about 300° C. and afterwards fall. This at first sight appears to be caused by a change in the strength of the alloy, but if the specimens are brought to their original condition by being normalized—that is to say heated to 950° C. and then cooled in air—and then a further impression is made in the same ball holes, lower hardness values are of course found, but, what is more noticeable, the maximum is less prominently marked. If these re-impressions are made eight to ten times, it is found that the maximum has disappeared and there is no marked change in hardness from 0° to 300° C. This work shows that initially there is no great change in hardness with temperature before the Brinell impressions were made, but the marked rise in hardness in the usual Brinell test is due to a marked difference in the degree of work hardenability imparted to different specimens of the metal as the Brinell ball is forced in.

In the case of quenched, *i.e.* unhardened, aluminium alloys of compositions which normally age-harden, it is already known that the action of deformation by rolling, &c., brings about marked age-hardening. It would be a matter of interest to know whether some of the reported hardness changes in this and other papers are not due to changes in the susceptibility to work-hardening during the act of impressing the ball, and are not truly changes in the real hardness of the alloys as the ageing proceeds. Undoubtedly age-hardening results in a difference of the condition of the material, but it is extremely difficult to devise a method of test which would eliminate the effect of deformation.

Dr. C. H. Desch,* F.R.S. (Member of Council) (*replying on behalf of the authors*): I will leave the points concerning solubility and so on to be dealt with by the authors of this paper when they see the discussion. In view, however, of what Professor Sachs has said, I should like to say a few words on the X-ray evidence. It seems to me that, so far as these questions regarding the initial stages of age-hardening are concerned, we have almost reached the limit of what the ordinary method of X-ray examination will reveal. Professor Sachs referred to the recent work of Mark and Hengstenberg on the distribution of intensities in the different orders of X-ray reflections, and that seems to me to open up a means of penetrating much more deeply into the mechanism of minute changes of this kind than has hitherto been possible. During the last few months I have had an opportunity of seeing, in two American X-ray laboratories at Cornell University and Chicago, work which is being done on the measurement of the distribution of intensity within the lines on an X-ray pattern, and, although the apparatus required is elaborate, it is remarkable how much information can be obtained in that way. With those experimental means available, we may be able to determine much more satisfactorily than at present what is happening in these very difficult initial stages of the age-hardening process.

CORRESPONDENCE.

The Authors (*in reply to the discussion at the meeting*): We are much interested in Professor Sachs' remarks. The fact that grain-size affects the age-hardening is of great importance, and may account for irregularities which occur but which are attributed by some workers to other molecular or atomic disturbances. We are in complete agreement with Professor Sachs that it

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* Superintendent, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

is definitely established that the characteristic Duralumin hardening depends on effects which occur in the solid solution.

In reply to Dr. Gwyer, we had not seen the preprint of the paper by E. H. Dix and his colleagues until after our paper was in print. The results given in that paper certainly indicate the formation of a new constituent, but the diagram given by these authors needs careful interpretation. The effect of iron on the formation of the new phase is as yet not determined, and until it has been investigated one must keep an open mind as to the effect of Mg_2Si on the solubility of $CuAl_2$. It is interesting to note from the diagram given by E. H. Dix and his colleagues that the limit of solubility at 500° C. of the copper-rich constituent (Al–Cu–Mg–Si) is 2 per cent., which solubility rapidly decreases with fall in temperature.

In reply to Dr. C. H. M. Jenkins we would say that aluminium alloys do not lend themselves so readily to micro-examination during age-hardening as those of other metals. We have tried to follow up the age-hardening of the alloys we have been using, by careful microscopic examination during the period of maximum age-hardening and after. It is only after marked softening has set in that any visible microstructural changes can be observed. In the case of those alloys where a eutectoid decomposition takes place, *viz.*, aluminium–zinc alloys, it is possible, however, to follow the changes in microstructure from a time shortly after maximum hardness has been attained.

Dr. Jenkins rather suggests that microstructural changes have not received much attention. We can assure him that both here and in America and Germany every effort has been made to produce evidence of changes in microstructure during the early stages of age-hardening.

The change in Brinell hardness in the case of ingot iron at high temperatures due to work-hardening is very interesting. In our case the hardness measurement is made at one temperature, *i.e.*, room temperature. It is highly probable that work-hardening due to the impression of the ball does cause local age-hardening, but as the material age-hardens at room temperature (or higher temperatures as the case may be), the degree of hardening caused by the Brinell ball will decrease in effect and ultimately will have little or no effect. It is very possible that in the initial stages the effect of work-hardening may be more marked, but it must be small, since the hardness, in certain cases, of the quenched material is very often equal to or less than that of the material in the annealed state.

Dr. Jenkins has raised an interesting point, but it is difficult to see what test could be devised for hardness measurements, which would overcome the difficulty mentioned.

Mr. Edward G. Herbert,* B.Sc. (Member): The authors are to be congratulated on having so clearly differentiated between the age-hardening due to precipitation and that due to "some process as yet undefined which takes place prior to actual precipitation." My own researches have led to precisely the same conclusion—namely, that in the age-hardening of Duralumin there are two quite distinct processes, the one superimposed upon the other, *viz.*:—

(*a*) Precipitation hardening, which by itself would cause a uniform increase of hardness.

(*b*) Atomic hardening, due to the disturbance produced by quenching from a high temperature, and characterized by periodic fluctuations of hardness—alternate hardening and softening—the fluctuations being at first relatively rapid, but gradually slowing down and damping out. These fluctuations are almost certainly periodic changes of inter-atomic attraction

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* Director, Edward G. Herbert, Ltd., Levenshulme, Manchester.

or cohesion, and are therefore electromagnetic in character and responsive to the influence of magnetism.

The occurrence of hardness fluctuations—alternate hardening and softening—in the age-hardening of the aluminium alloys is well known. They have been made the subject of special study by Bollenrath, and are shown in the work of Meissner and other investigators, but it is not necessary to look beyond the work of the present authors for evidence of their occurrence. They are shown very clearly in the two top curves in Fig. 1, a rise to a maximum 3 to 4 hrs. after quenching, a fall to a minimum at 9 hrs., a rise to a further maximum, and a slow fall. An equally clear case is the top curve in Fig. 2. All these are perfectly normal quench fluctuations. In drawing their curves the authors have generally ignored the evidence of hardness fluctuations, although in one case, in the lower diagram of Fig. 2, the fluctuation was too violent to be altogether ignored.

In a paper which I offered to the Institute of Metals in August 1931, a description was given of a series of experiments designed to elucidate the processes concerned in the age-hardening of Duralumin. The experiments consisted generally in the application of various magnetic treatments to Duralumin during the ageing period. The primary object was to stabilize the metal in its freshly quenched condition, either by ageing in a magnetic field, or by magnetic treatment for short periods such as one minute, the treatment being accompanied in some cases by the application of heat. The outcome of the experiments was that while it was not possible by any application of magnetism to inhibit the general increase of hardness (precipitation hardening), the periodic fluctuations could be profoundly modified by placing the freshly quenched specimen in a constant magnetic field for a short period. In general, the result of the magnetic treatment was to set up new fluctuations of shorter periodicity and greater amplitude than those due to the shock of quenching.

The fact that precipitation hardening and atomic fluctuations are superimposed during the age-hardening of Duralumin somewhat complicates the study of either, but a simplification has been found possible. Atomic fluctuations can be set up not only by quenching, but also by magnetic disturbance or by severe mechanical deformation. They were, in fact, first observed in the ageing of hard steel which had been superhardened by bombardment with steel balls, and it was found that when they had damped out they could be started up afresh by an appropriate magnetic treatment.

In the work referred to above I have shown that fluctuations similar in character and believed to be essentially identical with those induced by quenching, can be set up in Duralumin by severe mechanical deformation. A Duralumin sheet was rolled down to 40 per cent. of its original thickness, and periodic hardness tests showed that during the subsequent period of ageing marked hardness fluctuations occurred. It was shown that the course of these fluctuations could be profoundly modified by placing the specimen at a selected phase, such as a maximum, in the magnetic field for 5 minutes.

It is to be hoped that the authors, having arrived at the conclusion that two distinct processes are involved in the age-hardening of the aluminium alloys, and having produced such clear evidence of both—the general hardness increase due to precipitation and the hardness fluctuations due to the shock of quenching—will follow the matter up by a separate investigation of the latter, inducing the periodic changes either by mechanical or magnetic means, and thus avoiding the complication of simultaneous precipitation hardening. In pursuing this subject it will be found useful to make the hardness tests at considerably shorter intervals than those used in the present investigation—half-hourly tests have been adopted in my own work, and it is possible to offer a further suggestion, based on experience. The specimen having been set in a state of atomic fluctuation, say by rolling, it will be found useful to divide it into two and apply the magnetic treatment to one portion only. Simultaneous hardness tests on the two halves will then allow of a comparison between the original mechanical fluctuations and the modified fluctuations set up by the magnetic treatment. A field of 6000 gauss has been found effective, but in recent experiments stronger fields up to 24,000 gauss have given even more marked results.

Mr. L. W. **Kempf**,* M.S., and Dr. W. A. **Dean** *: We have read this excellent paper with great interest, not only because of its value as an addition to our knowledge of age-hardening, but also because data collected in our laboratories agree closely with those presented in this paper. Our materials and procedure were somewhat different from those used by the present authors, and our investigation of hardening at room temperature was somewhat more extensive. In view of these differences, it is felt that some of these data may be of sufficient interest to be submitted for consideration here.

The alloys used by us were of somewhat lower purity than those of the authors, but were made from aluminium produced by the same process. Ingots about 3½ in. square by 12 in. long were cast in iron moulds and solidified progressively with circulating water. The ingots were heated for 15 hrs. at about 500° C., cooled to 450° C., and forged to ¾-in. square rod. Sections about ½ in. long were cut from this rod, heat-treated, and aged as indicated on the accompanying diagrams (Figs. A–C). Brinell impressions were made on the cross-sections of the rod, and each point represents the average of at least three impressions.

It is believed that the difficulties experienced by the authors in obtaining uniform hardness values on the binary 4 per cent. copper alloy may be attributable to grain-size variations. The difficulties would be accentuated, especially where larger grains are present, by the use of a small Brinell ball and load. Additions of iron, silicon, and magnesium tend to exert a grain-refining effect on this alloy.

The results are in close agreement with those of the authors, indicating that small differences in procedure and composition do not alter the character of the effects. The statement that aluminium–copper alloys of commercial purity do not harden at room temperature should perhaps be modified somewhat, inasmuch as the data indicate a definite age-hardening, although at a slower rate and to a smaller extent than if iron or iron and silicon are absent.

Among the additional points of interest brought out by consideration of our curves in conjunction with those of the authors the following may be mentioned:

(1) 0·5 per cent. of iron exhibits much less effect on the maximum hardness and hardening rate of an alloy containing 5·8 per cent. copper than on one containing 4 per cent. copper.

(2) The simultaneous addition of both magnesium and silicon to an alloy containing 4 per cent. copper is decidedly more effective in increasing maximum hardness and hardening rate than the addition of magnesium alone.

(3) The addition of silicon to an alloy containing 5·8 per cent. copper appears to increase the maximum hardness, whilst the simultaneous addition of silicon and iron has but little effect.

(4) In the aluminium–copper, aluminium–copper–magnesium, aluminium–copper–magnesium–iron, or aluminium–copper–iron–silicon alloys, prolonged ageing at room temperature results in hardnesses as high as the maximum

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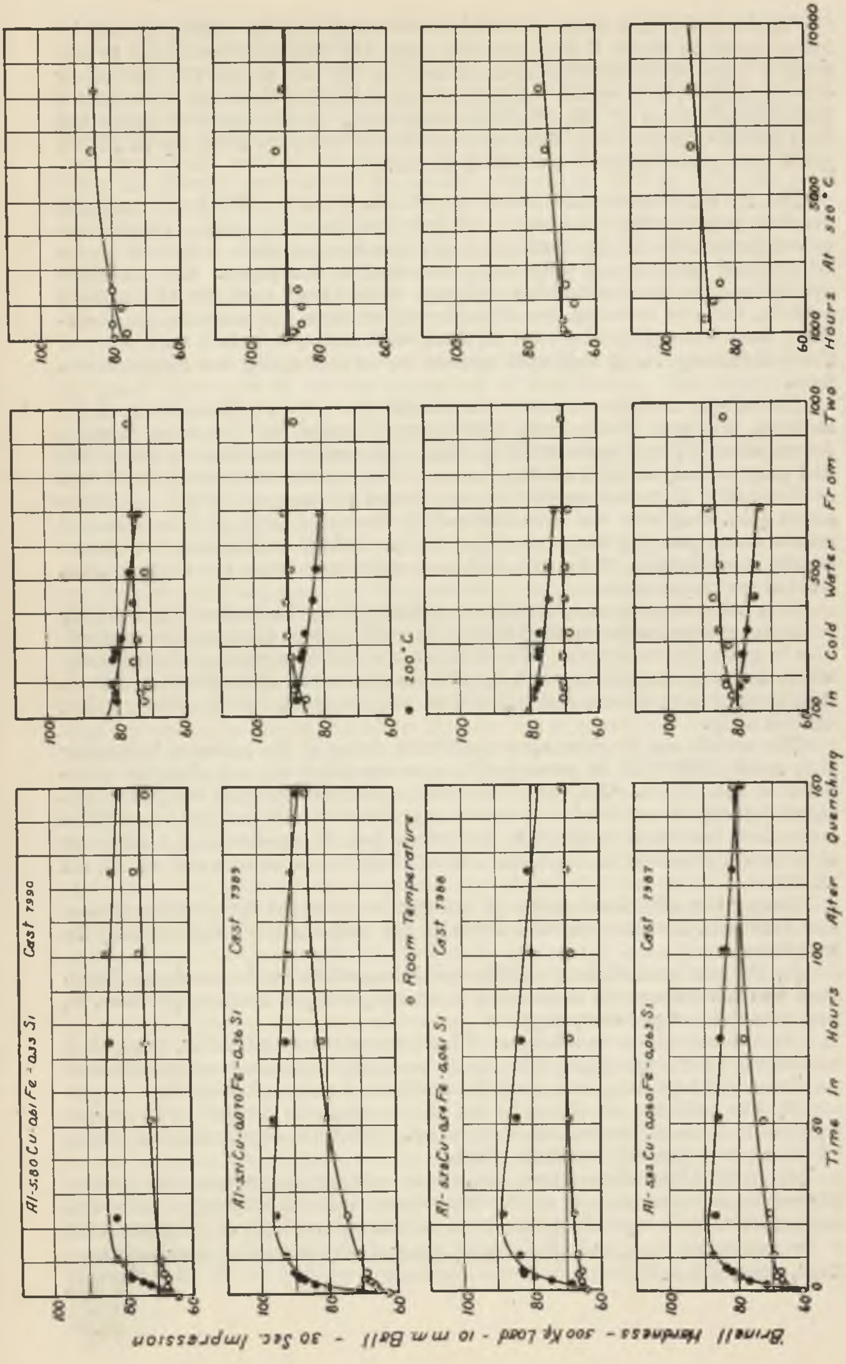

FIG. A.—Effect of Iron and Silicon on the Age-Hardening of an Al-5·8 Cu Alloy.

hardness attained on the same alloys aged at 200° C. The hardnesses attained to date at room temperature by the aluminium–copper–silicon, aluminium–copper–iron, aluminium–copper–magnesium–silicon, and aluminium–copper–magnesium–iron–silicon alloys are lower than the maximum hardness at 200° C.

(5) The hardness of all the alloys investigated appears to increase, although slowly, up to 10,000 hrs. at room temperature.

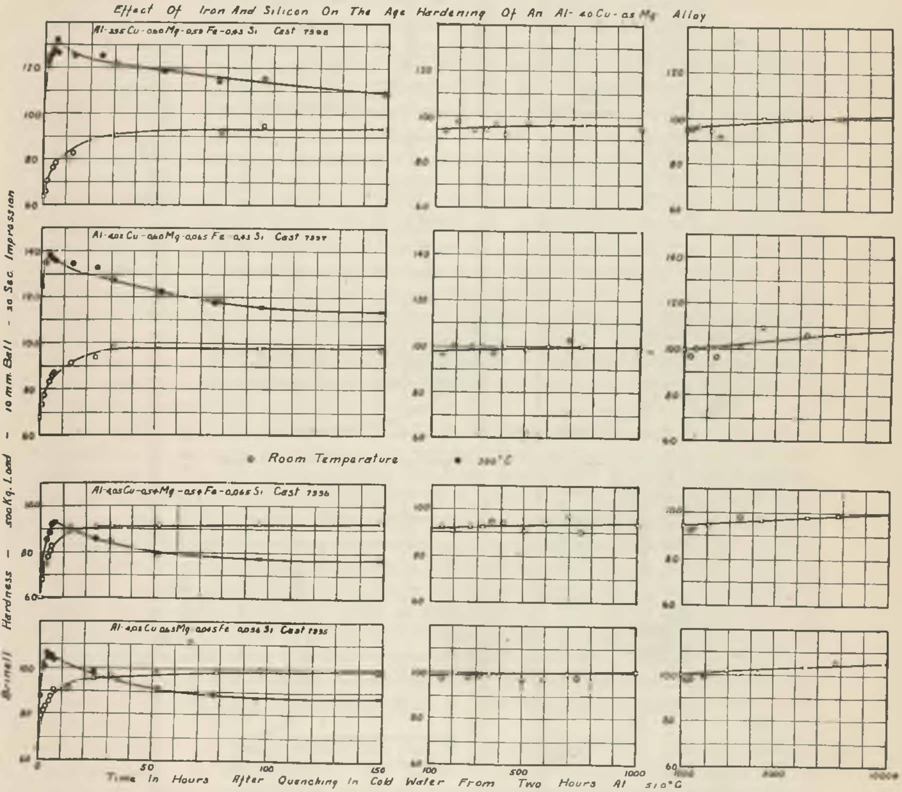

FIG. B.—Effect of Iron and Silicon on the Age-Hardening of an Al–4·0 Cu–0·5 Mg Alloy.

It has been shown * that a number of complex constituents may exist in alloys containing concentrations of copper, magnesium, silicon, and iron in the range of the commercial Duralumin alloys. Phases containing aluminium, copper, and iron; aluminium, iron, and silicon; aluminium, magnesium,

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* Dix and Keith, *Proc. Amer. Soc. Test. Mat.*, 1926, **26**, 317; Gwyer, Phillips, and Mann, *J. Inst. Metals*, 1928, **40**, 297; Dix and Heath, *Proc. Inst. Metals Div., Amer. Inst. Min. Met. Eng.*, **1928**, 164; Fink and Van Horn, *Trans. Inst. Metals Div., Amer. Inst. Min. Met. Eng.*, **1931**, 383; Dix, Sager, and Sager, *Amer. Inst. Min. Met. Eng. Tech. Publ.* No. **472**, 1932.

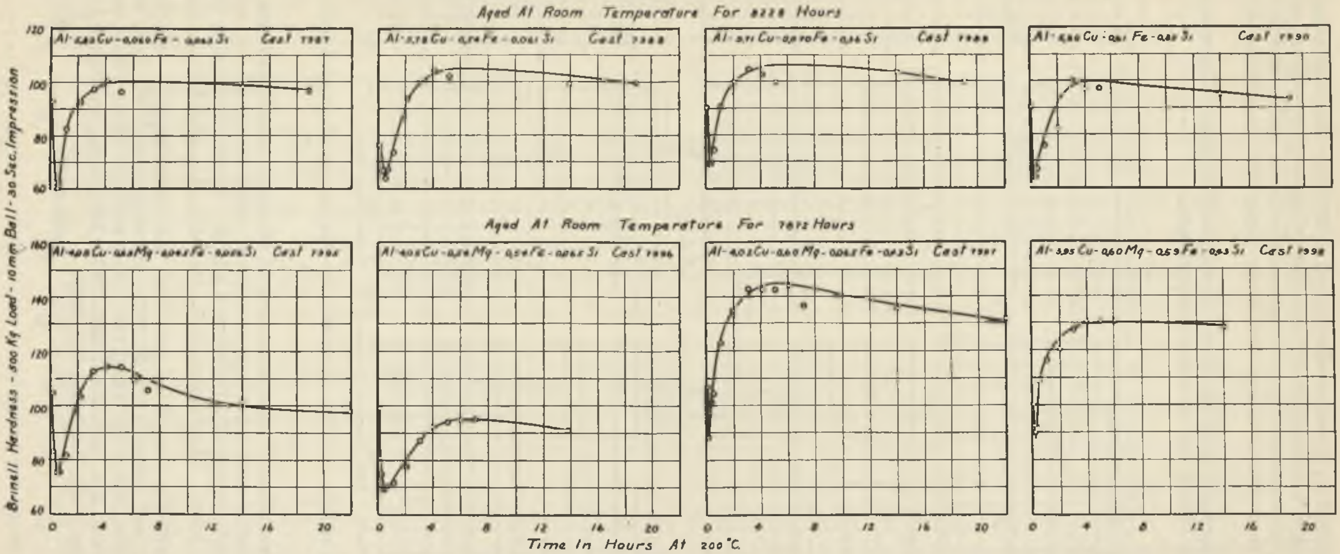

FIG. C.—Specimens Aged at Room Temperature and then Artificially Aged at 200° C.

copper, and silicon have been identified and unpublished work in these laboratories has indicated the presence of constituents containing aluminium, copper, and magnesium. We can by no means be certain that the list has been completed, especially since equilibrium relationships are probably never reached in commercial heat-treated alloys. The recently published work of E. H. Dix, Jr., G. F. Sager, and B. P. Sager definitely indicates the presence of a constituent containing aluminium, copper, magnesium, and silicon in alloys similar in composition to those under discussion here. It is shown that the solubility of this new constituent varies with temperature, and thus probably plays an important rôle in the hardening of commercial Duralumin.

The superior hardenability of the aluminium–copper–magnesium–silicon alloys was somewhat puzzling in view of the reported * lower solid solubility of copper in aluminium in the presence of Mg_2Si. These new data make the hardening of these alloys somewhat more explicable, but it becomes exceedingly improbable that such hardening can be ascribed to precipitation of any one or two simple constituents. It is rather more probable that hardening under any specific set of conditions is the result of a number of reactions, each of which may proceed at various rates depending on a number of factors, such as availability of atoms, rates of diffusion, complexity of the constituents, stability of compounds formed, degree of supersaturation, &c. At a low temperature, for example, a relatively unstable hardening constituent may be formed, because atoms may be readily available for its formation or its degree of supersaturation may be relatively great, whereas at slightly elevated temperatures with greater freedom of diffusion and a different relationship between the various degrees of supersaturation a more stable constituent may be formed simultaneously with the disintegration of the one formed at the lower temperature.

In spite of the probable complexity of the processes, certain effects appear consistently enough to warrant the hazarding of an explanation. Thus the influence of iron on the hardening of alloys containing copper would appear to be consistent with the formation of a relatively stable constituent containing iron and copper. When the copper concentration is below the solid solubility limit at the temperature of solution treatment, the influence of iron is relatively great, giving in effect a solid solution of lower copper content. With a copper concentration sufficiently above the solid solubility limit no copper is removed from the solid solution and the effect on hardenability is relatively slight. The constituent containing silicon and iron appears to be even more stable than the iron–copper. The addition of silicon to an alloy containing iron and copper within the solid solubility limit counteracts the effect of the iron by combining with it and releasing copper to the solid solution.

The effect of magnesium and Mg_2Si on the hardening of aluminium–copper alloys is undoubtedly the result of more complex reactions which probably vary considerably with the conditions under which hardening is brought about. The explanation of these phenomena must await not only accurate identification of the end products, but also the determination of the rate under various conditions at which the reactions leading to these products proceeds. The initial softening on ageing at elevated temperatures following ageing at room temperature is undoubtedly evidence of the great influence of temperature on these exceedingly complex reactions.

Whether or not the hardening under discussion is brought about by precipitation depends largely on our definition of the word. We prefer the use of the word in the broad sense as applying to the entire process of atomic readjustment between supersaturated solvent and solute as evidenced by

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* Gayler, *J. Inst. Metals*, 1922, **28**, 213; 1923, **30**, 139.

measurable changes in properties. It would seem as unduly restrictive to limit its use to changes in atomic space lattice visible to the X-ray as to limit its use in aqueous solutions to processes visible to the naked eye.

If the hardening of Duralumin-type alloys appears to be becoming more complex, this may be evidence that some progress is being made towards more complete understanding of the process. The usual sequence of such investigations is from simple conceptions to complex and back again. We seem at present to be leaving simple and advancing to complex conceptions.

Dr. HUGH O'NEILL,* M.Met. (Member): It appears from this interesting paper that at the present moment we are still in doubt concerning the full explanation of the age-hardening of Duralumin alloys. Whatever that explanation may be, it naturally must fit all the facts associated with the whole phenomenon, including, presumably, certain observations of Grard's † to which attention may perhaps be directed. This worker quenched specimens of Duralumin from 475° C. and then determined the following mechanical properties after the metal had aged for increasing lengths of time at room temperature: Brinell hardness (10 mm. ball; 500 and 1000 kg. load), elastic limit, ultimate stress, elongation, and resilience. Grard found in the case of his experiments that the ageing process may be divided roughly into two periods. His own words best describe the form of the graphs connecting time and mechanical properties as observed during the first four days: "Cette période est caractérisée par des oscillations très accusées, qui ne sauraient être attribuées aux erreurs expérimentales, dénotant un travail moléculaire notable pendant cette période de gestation." The behaviour during the next four days is described as follows: "Pendant cette période les écarts s'atténuent, la courbe d'allure sinusoïdale s'aplatit, et l'état d'équilibre s'affirme."

Since Grard was apparently quite convinced of the existence of fluctuations in the mechanical properties during ageing, it is natural to look for similar ups and downs in the Brinell results of the present authors. I believe that they are in evidence, and particularly in the upper diagram of Fig. 2. A smooth curve has been drawn for the alloy containing 3·99 per cent. copper, but some of the points are displaced both above and below that curve by an amount which is greater than legitimate experimental error in the Brinell test.

Interesting results in connection with age-hardening have recently been observed ‡ in nickel–manganese austenitic steels containing 3 or more per cent. of titanium. The hardness values during ageing are often displaced from the usual smooth curves, and in one case, whilst the hardness property was indicating a general *increase*, the electrical resistivity showed first an increase, followed later by a decrease.|| This curious behaviour may eventually provide a clue to the more complete understanding of the important phenomenon of age-hardening.

THE AUTHORS (*in reply*): We are much indebted to Mr. E. G. Herbert for his interesting contribution. The fluctuations which we have ignored in our curves are apparent only in some of those of alloys which age-harden to a very marked extent. Irregularities, such as were found, were not considered other than experimental, since they probably could be attributed to variation in composition due to inverse segregation. Mr. Herbert attributes these fluctuations to the shock of quenching, but surely in our case this is not so, for they do not occur either in the curves in Fig. 1 or Fig. 2 until *after* maximum hardness has

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* Senior Lecturer, Department of Metallurgy, The University, Manchester.

† *Rev. Mét.*, 1920, **17**, 286.

‡ F. R. Hensel, *Trans. Iron Steel Div., Amer. Inst. Min. Met. Eng.*, **1931**, 255.

|| H. Esser and W. Eilender, *Arch. Eisenhüttenwesen*, 1929–30, **4**, 142.

been attained, *i.e.*, until actual precipitation of small crystals of the separating phase occurs. Hence the fluctuations pointed out, if genuine, are not due to what Mr. Herbert terms " shock of quenching," since these should occur before precipitation hardening sets in.

We thank Mr. Kempf and Dr. Dean for their extremely interesting contribution, and we are very pleased that our results agree closely with theirs. Their suggestion that the difficulties experienced by us in obtaining uniform hardness values on the binary 4 per cent. alloy are due to variation in grain-size occurred to us, but on etching the specimens no marked difference in grain-size was apparent and we therefore came to the conclusion that inverse segregation was the most possible cause. In this case after heat-treatment some crystals would be richer in copper than others, for under the conditions of the experiments equilibrium conditions would probably not have been attained. The statement that aluminium–copper alloys do not harden at room temperature was an error. We intended to put " do not age-harden very appreciably."

It is interesting to note that Mr. Kempf and Dr. Dean have found that the effect of 0·5 per cent. iron on the maximum hardness and rate of hardening is less with an alloy containing 5·8 per cent. copper than on one containing 4 per cent. The whole problem of age-hardening when considered from the point of view of the constitutional diagram is extremely complex, particularly in view of the fact that the heat-treatments given to the alloys are not necessarily sufficient for equilibrium to be definitely established. The recently published work of E. H. Dix, Jr., G. F. Sager, and B. P. Sager is another contribution to the study of the equilibrium of these complex alloys, and it has yet to be shown that the new compound which they identify is present or is precipitated during the age-hardening of Duralumin. Until X-ray technique is developed sufficiently so that Mg_2Si can be identified on the X-ray spectra, there seems little likelihood that the effect of this new compound can be isolated apart from that of either constituents present in Duralumin. It is hoped that this development will throw much more light on this problem which appears to be getting more and more complex as further research is carried out.

We are in agreement with the writers when they say that " . . . it becomes exceedingly improbable that such hardening can be ascribed to precipitation of any one or two simple constituents." It always has seemed improbable that, for instance, $CuAl_2$ alone was responsible for the age-hardening of Duralumin: where two or more constituents may be present in contact with a solid solution, their effects on the solid solution are interdependent and should not be regarded otherwise.

The influence of iron on age-hardening of aluminium–copper alloys is curious. The writers suggest the formation of a relatively stable constituent containing iron and copper as being consistent with the influence of iron. Do they suggest a compound other than " N," which is known to be formed on prolonged annealing of the solid or some other compound? Also, if their explanation is correct, why does the addition of a small amount of magnesium annul the effect of iron, when, up to the present, evidence shows that magnesium does not combine with iron and cannot, therefore, counteract the effect of iron by combining with it?

Dr. O'Neill is quite correct when he says, " We are still in doubt concerning the full explanation of the age-hardening of Duralumin alloys," but we are gradually getting nearer our goal. We thank him for bringing to our notice Grard's observations. Fluctuations on curves certainly need following up, but in our experiments we did not feel justified in drawing other than a smooth curve through the points. Such facts as segregation, grain-size, &c., would have to be examined very carefully before attributing an up or down in the curves in Fig. 2 to some fundamental cause. It is interesting that both Dr. O'Neill and Mr. Herbert have directed our attention to the above fact.

THE SOLUBILITY OF ALUMINIUM IN MAGNESIUM IN THE SOLID STATE AT DIFFERENT TEMPERATURES *

By Professor P. SALDAU †, Member, and M. ZAMOTORIN ‡, Member.

Synopsis.

The solubility of aluminium in magnesium of 99·68 per cent. purity has been determined at temperatures up to 420° C. The solubility limit at room temperature is 6·08 per cent. aluminium by weight, and this is maintained unchanged until 300° C. after which a rapid increase occurs, the solubility line passing through 10·9 per cent. by weight of aluminium at 400° C., and intersecting the eutectic line (436° C.) at the point corresponding with 12·6 per cent. aluminium by weight.

Introduction and Summary of Previous Work.

The solubility of aluminium in solid magnesium is of interest in connection with the structure of alloys of the Elektron type, in which magnesium is the principal constituent, and the age-hardening properties are the result of changes of the solubility of the other elements with temperature.

After preliminary work by Grube,§ who failed to detect any solubility in solid magnesium, the system aluminium–magnesium was investigated by Hanson and Gayler,|| and more recently by Schmidt and Spitaler.¶ Both these investigations agree in placing the eutectic temperature on the magnesium side of the system at 436° C., at which temperature the solid solution in magnesium contains approximately 11 per cent. aluminium by weight. According to Hanson and Gayler, the solubility limit falls to 9 per cent. aluminium at room temperature, whereas according to Schmidt and Spitaler the solubility at room temperature is only 7·5 per cent. by weight of aluminium, this concentration being preserved unchanged up to 300° C., from which temperature it increases rapidly until the limit of 11 per cent. is reached

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† Chemical Laboratory, Mining Institute, Leningrad, U.S.S.R.

‡ Metallurgical Institute, Leningrad, U.S.S.R.

§ Grube, *Z. anorg. Chem.*, 1905, **45**, 229.

|| Hanson and Gayler, *J. Inst. Metals*, 1920, **24**, 201.

¶ Schmidt and Spitaler, *Z. Metallkunde*, 1927, **19**, 452.

at the eutectic temperature. In view of the differences between the results of these two investigations, the present research was undertaken in the hope of throwing further light upon the problem.

EXPERIMENTAL.

The metals used in the present investigation were as follows :—

(1) Aluminium, supplied by the British Aluminium Company.

	Per cent.
Silicon	0·08
Iron	0·06
Aluminium (by difference)	99·86

(2) Magnesium, from Kahlbaum.

Silicon	0·21
Aluminium	0·09
Iron	0·02
Magnesium (by difference)	99·68

The alloys were prepared in quantities of 50 grm. by melting in carbon crucibles under a flux of magnesium and potassium chloride containing 37 per cent. of the latter. The alloys were cast into metal moulds, and the ingots thus obtained were cut up into test-pieces weighing about 1 grm., which were annealed in sealed evacuated glass tubes in order to prevent oxidation. The aluminium contents of the specimens were determined by analysis after the annealing and quenching treatment.

The annealed and quenched specimens were carefully polished, and etched with a 0·1 per cent. alcoholic solution of nitric acid, after which the structure was examined microscopically.

EXPERIMENTAL RESULTS.

The alloys the compositions of which are given in Table I were first annealed at 420° C. for 14 days, and were then slowly cooled over a period of 4 hrs. to the required quenching temperature, at which they were maintained for 24 hrs., and then quenched in cold water. In another experiment, the alloys, after annealing for 14 days at 420° C., were slowly cooled to room temperature (15° C.) over a period of 7 days.

The results of the microscopic investigations are given in Table I, and are plotted graphically in Fig. 1.

As can be seen from Plate XXIII, the change in microstructure on passing from the homogeneous to the two-phase area was well marked, although many of the alloys classed as homogeneous contained small particles of impurities in the grain boundaries. Thus Figs. 3 and 4

TABLE I.

Quenching Temperature. (° C.)	Composition of Alloy (% Al) and Microstructure.								
	13·15	12·32	11·12	10·68	9·24	8·47	7·93	6·48	5·67
420	$\gamma + \delta$	$\gamma + \delta$	δ	δ	δ	δ	...	...	...
400	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	δ	δ	δ	...	...	...
380	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	δ	δ	δ	δ	δ
340	...	...	...	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	δ	δ
320	...	...	...	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	δ	δ
300	...	...	...	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	δ
280	...	...	...	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	δ
250	...	...	...	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	δ
Annealed and slowly cooled.	...	...	...	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	$\gamma + \delta$	δ

(Plate XXIII) refer to alloys containing 5·67 and 9·24 per cent. aluminium quenched from 300° C. and 380° C., respectively, and in each case there are distinct traces of additional constituents in the grain boundaries, presumably owing to the silicon and iron which are present as impurities. These particles were, however, easily distinguishable from the magnesium–aluminium γ constituent when the latter was present. Fig. 5 (Plate XXIII) shows the structure of the alloy containing 10·68 per cent. aluminium after quenching from 380° C. In this case the specimen was homogeneous at the temperature of the preliminary anneal (420° C.), but became two-phase at the lower temperature, the particles precipitating chiefly in the grain boundaries and along cleavage planes. Fig. 6 (Plate XXIII) shows the structure of the alloy containing 13·15 per cent. aluminium after quenching from 420° C. In this case the alloy was outside the homogeneous area at the temperature of the anneal (420° C.) and the comparatively large particles present at this temperature are readily distinguishable from the smaller particles precipitated during the slow cooling in the alloy shown in Fig. 5. As these structures are quite typical, further photographs are not reproduced.

By extrapolating the solubility curve in Fig. 1 until it intersects the eutectic line at 436° C., the limiting concentration at the eutectic temperature is estimated at about 12·6 per cent. aluminium.

DISCUSSION.

In Fig. 2 the solubility curve obtained in the present work is compared with those of Hanson and Gayler, and of Schmidt and Spitaler. It will be noted that the results of the present work indicate a slightly higher solubility at the eutectic line, and a lower solubility below

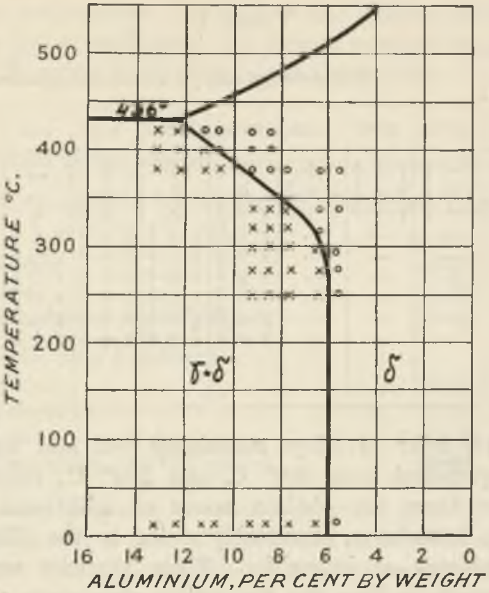
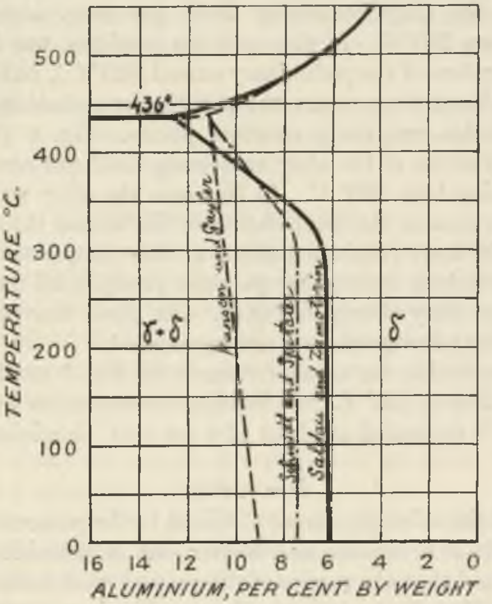

500
400
300
200
100
0
TEMPERATURE °C.
436°
γ+δ
δ
16
14
12
10
8
6
4
2
0
ALUMINIUM, PER CENT BY WEIGHT

Fig. 1.


500
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TEMPERATURE °C.
436°
γ+δ
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Hanson and Gayler
Schmidt and Spittle
Saldau and Zamotorin
16
14
12
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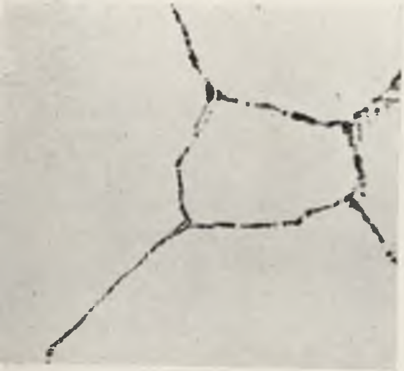
2
0
ALUMINIUM, PER CENT BY WEIGHT

Fig. 2.

PLATE XXIII.



IG. 3.—5·67 per cent. Aluminium quenched from 300° C. × 520.

FIG. 4.—9·24 per cent. Aluminium quenched from 380° C. × 520.

G. 5.—10·68 per cent. Aluminium quenched from 380° C. × 520.

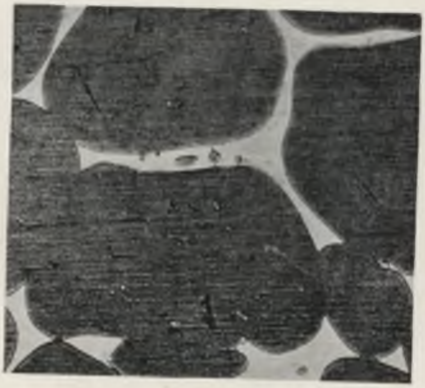


FIG. 6.—13·15 per cent. Aluminium quenched from 420° C. × 520.

ote.—All these alloys were annealed at 420° C. for 14 days before cooling to the quenching temperature.

[*To face p.* 224.

350° C. than the determinations of the previous investigators. One possible cause of this difference is that the present authors used a higher magnification in the microscopic examination of the alloys, and this might be expected to reveal particles which would otherwise not be observed. In this connection it is significant that in the three researches the scale of magnifications employed is in the inverse order of the solubility limits at the lower temperatures. Thus whilst Hanson and Gayler usually employed magnifications of 150, those of Schmidt and Spitaler were 250, and in the present investigation a magnification of 520 was used. It must further be noted that in the work of Hanson and Gayler the annealing times at the lower temperatures were comparatively short, and this might account for incomplete precipitation. A point which cannot, however, be ignored is the difference in the purity of magnesium used by the different investigators. The magnesium used by Hanson and Gayler was of 99·75 per cent. purity, the chief impurity being iron (0·1 per cent.), followed by copper (0·069 per cent.), and silicon (0·033 per cent.). Details of the metal used by Schmidt and Spitaler could not be found, but, as previously stated, the metal in the present work was of 99·68 per cent. purity, with silicon as the principal foreign element. In view of the slight solubility of these metals in solid magnesium, it is clear that their presence in amounts of the order 0·1–0·2 per cent. may well be important.

It is noteworthy that the solubility limit determined in the present work is apparently constant from 300° C. to room temperature. From some points of view this may be considered as improbable, and the reason may be that at low temperatures the precipitated particles were too small to be observed, or that the term of annealing was not sufficiently great to produce complete precipitation.

Summary and Acknowledgments.

The solubility of aluminium in magnesium of 99·68 per cent. purity has been determined at temperatures up to 420° C. The solubility limit at room temperature is 6·08 per cent. aluminium by weight, and this is maintained unchanged until 300° C., after which a rapid increase occurs, the solubility line passing through 10·9 per cent. by weight of aluminium at 400° C., and intersecting the eutectic line (436° C.) at the point corresponding with 12·6 per cent. aluminium by weight.

In conclusion, we should like to express our sincere gratitude to the Leningrad State Institute of Non-Ferrous Metals for permission to publish the results of this investigation.

Leningrad,
April 1931.

CORRESPONDENCE.

Professor E. Schmid * (Member): Supplementing the careful researches of Professor Saldau and Mr. Zamotorin, I should like to mention that, in collaboration with Dr.-Ing. H. Seliger,† I have recently determined röntgenographically the solubility of aluminium in magnesium by precision measurements of the lattice constants.‡ The purity of our magnesium was 99·95 per cent. and the results of our work are shown in Fig. A. From this it will be seen that the solubility limit at the eutectic temperature is about 12·1 per cent. and at room temperature about 2 per cent. The solubility curve of the present authors agrees with ours at temperatures above 300° C., but, at lower temperatures, considerable differences are noticeable in that the X-ray method indicates a much more rapid decrease of solubility. By the X-ray method it is possible to detect by measurements of the lattice, precipitations of particles much smaller than can be detected by microscopic examination, and hence the former method is to be preferred for this type of work.

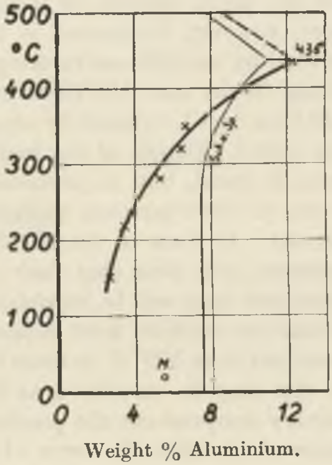


Fig. A.

The Authors (*in reply*): We desire to express our gratitude to Professor Schmid for the communication of his very interesting data obtained by X-ray analysis. We are of the opinion that the results obtained with the purer magnesium, also (99·95 per cent.) above 300° C., almost entirely coincide with our own. We are, also, very glad to note that the results of X-ray analysis below 300° C. confirm our theoretical conclusions that the solubility curve of aluminium in magnesium below 300° C. must represent not a vertical straight line, but a curve approaching more to the magnesium ordinate.

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‡ *Z. Elektrochem.*, 1931, 37, 447; this J., 1932, 50, 2.

THE BEHAVIOUR OF SINGLE CRYSTALS OF BISMUTH SUBJECTED TO ALTERNATING TORSIONAL STRESSES.*

By H. J. GOUGH,† M.B.E., D.Sc., MEMBER, and H. L. COX,‡ B.A.

SYNOPSIS.

Two single crystals of bismuth have been tested under alternating torsional couples with the object of studying the phenomena, particularly the slip phenomena, associated with fatigue. Throughout the tests, however, no slip bands were observed. In the early stages of the tests numerous bands were produced parallel to the twinning planes, and finally cleavage cracking occurred. The bands parallel to the twinning planes could not be definitely identified as twin bands by metallographic examination; but evidence as to this identity was finally found in the cracks observed on the surface of one of the specimens. Some signs of recrystallization were observed, the effect tending to extend along the sites of twin bands.

The production of twin bands appeared to depend on the shear stresses on the twinning plane, and consideration is given to the theoretical reasons for this dependence. It is shown that on the basis of minimum energy there is no reason to associate any type of movement with stresses tending to cause this movement by the shortest geometrical path, and that the process of twinning may be due to stresses which at first sight appear to be incapable of affecting the process.

INTRODUCTION.

FOR some years past there has been in progress at the National Physical Laboratory a research into the characteristics of the deformation of large single crystals of metals under various types of static and repeated stresses. The chief aim of the research is to determine the nature and causes of the failure of metals by fatigue action, and in all the experiments attention is directed primarily to the phenomena directly connected with fatigue failure. On the other hand, in several experiments recently performed a number of phenomena have been observed, which, whilst having little or no bearing on the actual problem of fatigue failure, appear to be of considerable interest from a purely metallurgical

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* Manuscript received November 23, 1931. Presented at the Annual General Meeting, London, March 10, 1932.

† Superintendent, Engineering Department, National Physical Laboratory, Teddington.

‡ Assistant, Engineering Department, National Physical Laboratory, Teddington.

point of view. Thus in the case of zinc * † and antimony ‡ information was obtained as to the mode of formation of twin bands, whilst in the case of silver § the entire absence of mechanical twinning on the surface of a single crystal fractured under alternating torsional stresses has been recorded. Again, in the tests on bismuth herein described the primary object of the experiments was to determine the slip plane and direction; but whilst, owing to the complete absence of slip, this object was not achieved, the profuse twinning caused by the alternating torsional stresses enabled the factors governing the formation of twin bands to be investigated in some considerable detail.

The enlargement of scope of the research, which the observation of mechanical twinning has necessitated, has led to a reconsideration of the factors determining the deformation of metals. Whilst attention was confined to the simple homogeneous || lattices, typified by the face-centred arrangement, consideration of the atoms in terms of planes and lines appeared to be quite satisfactory. The fields of force of the atoms in such a lattice are probably almost spherically symmetrical,¶ and it is reasonable at once to infer that the planes least resistant to slip will be those planes that are spaced farthest apart, and that the directions of easiest glide will be along the lines of densest atomic packing. Even in the case of zinc, which crystallizes in the close-packed hexagonal lattice—a lattice which is not truly homogeneous—consideration of atomic densities is sufficient to determine the slip plane; but, on the other hand, the failure of iron ** †† to develop well-marked slip planes shows that, even in such a relatively simple lattice as the body-centred cubic, the planar atomic densities cannot be the fundamental factor determining deformation by slip. In the more complex lattices, such as the face-centred rhombohedral lattice (to which antimony and bismuth conform), the fields of force of the atoms are certainly not spherically symmetrical, and simple consideration merely of inter-atomic distances cannot present a true view of the interatomic forces.

In these circumstances it is obvious that a more direct appeal to the actual variation in potential of the atoms during the translational movement becomes imperative; moreover, such consideration of potential can be applied not only to slip, but also to twinning, and even

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* *Proc. Roy. Soc.*, 1929, [A], **123**, 143.

† *Ibid.*, 1930, [A], **127**, 453.

‡ *Ibid.*, 1930, [A], **127**, 431.

§ *J. Inst. Metals*, 1931, **45**, 71.

|| A homogeneous lattice is defined as a lattice in which every atom is similarly situated with regard to every other atom.

¶ They cannot be *exactly* symmetrical, or the Cauchy relations between the elastic constants would be satisfied.

** Taylor and Elam, *Proc. Roy. Soc.*, 1926, [A], **112**, 337.

†† Gough, *ibid.*, 1928, [A], **118**, 498.

to actual cleavage. Unfortunately, a definite theory of the stability of an atomic lattice cannot be constructed without a complete knowledge of the atomic fields of force, and at the moment there appears to be very little hope that these fields will be determined by direct experiment. Nevertheless, even a general consideration of the changes of potential involved shows that the energies involved in slip and in twinning are probably of the same order, and that the occurrence of one phenomenon before or to the exclusion of the other depends on small differences between these energies. The processes of slip and of twinning are associated with definite atomic group movements, of each of which there are a finite number symmetrically distributed in the lattice, corresponding severally with the possible slip-plane directions and twinning planes. It is obvious, therefore, that the relative values of the vector potentials corresponding with the vector displacements associated with the various group movements will depend on the applied stress system, and that, if the number of slip or twinning planes is limited and/or if the difference between the energies associated with slip and twinning is small, both types of deformation may be produced by but slightly different systems of stress.

Now, to turn from generalities to particular cases, for all the metals crystallizing in the face-centred lattice that have so far been tested, the maximum shear stress resolved on the octahedral planes in the dodecahedral directions yields a very accurate criterion of the actual deformation; but it is by no means certain that this shear stress is the only criterion. The possibility is considered that the true condition may be of a more general type, including perhaps the normal stress [*] [†] on the slip plane, and/or other factors. From the accuracy with which the shear stress criterion predicts the actual slip distribution, it is apparent that these other factors must be of secondary importance; but the accuracy is not sufficient to deny them any influence whatever, and consideration of the fundamental atomic nature of the slip certainly indicates that these factors must have some effect. No definite record of the production of twin bands by purely mechanical action in any metal crystallizing in the face-centred cubic lattice has yet been found. This may be considered to indicate that the energy (change of potential) involved in twinning is much greater than that involved in slip; but the multiplicity of slip-plane directions would render even a small difference effective in inhibiting twinning under normal test conditions.[‡]

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[*] *Vide* Taylor and Farren, *Proc. Roy. Soc.*, 1926, [A], **111**, 529, and Taylor, *ibid.*, 1927, [A], **116**, 16.

[†] A research on this question has just been completed, and the results will shortly be published.

[‡] *I.e.* in static tests and in fatigue and impact tests with fairly low rates of change of stress.

Omitting consideration of the body-centred cubic lattice, concerning which the experimental evidence is somewhat conflicting, the case of the close-packed hexagonal lattice as instanced by zinc has next to be considered. In both static and fatigue tests on zinc both slip and twinning occur. As in the face-centred cubic lattice, the slip is determined to a high degree of accuracy by the shear stress on the plane of maximum density in the line of maximum density; but again there is no certainty that this shear stress is the *complete* criterion. Twinning in zinc appears to be dependent on slip. It is probable that the configurations of maximum potential (*i.e.* unstable equilibrium) in the processes of slip and twinning are very similar, and that the process of slip brings the atoms into positions where secondary factors can cause the small further increase of energy by which twinning is produced.*

Finally, in the case of antimony, under the action of alternating torsional stresses, twinning and cleavage cracking occur to the exclusion of slip.* It is possible that slip could be produced by suitably orientated static stresses, if by no other stress condition, but the behaviour of the material under reversed shear stresses is sufficient to show that the energy associated with twinning is probably lower than that associated with slip, and that this latter energy may indeed be greater than the energy involved in cleavage cracking.

The present paper describes experiments on two single crystals of bismuth, the results of which are in general accordance with the results of the experiment on a single crystal of antimony. It is proposed to describe these experiments, and subsequently to discuss the bearing of the results on the general ideas summarized in this introduction.

LATTICE STRUCTURE.

The lattice structure of bismuth has trigonal symmetry and is composed of two similar and similarly orientated face-centred rhombohedral lattices, displaced relative to each other along the longest diagonal of the rhombohedron (the axis of trigonal symmetry). The angle between any pair of edges of the rhombohedron is 87° 34′, and the atoms are spaced along these edges at points 6·52 A. apart.† The relative position of the interlaced lattice has not yet been definitely determined. From approximate figures given by James,‡ it can be deduced that the lattice points of the interlaced lattice divide the long diagonals of the elementary rhombohedra of the primary lattice in the approximate ratio 0·47 : 0·53.

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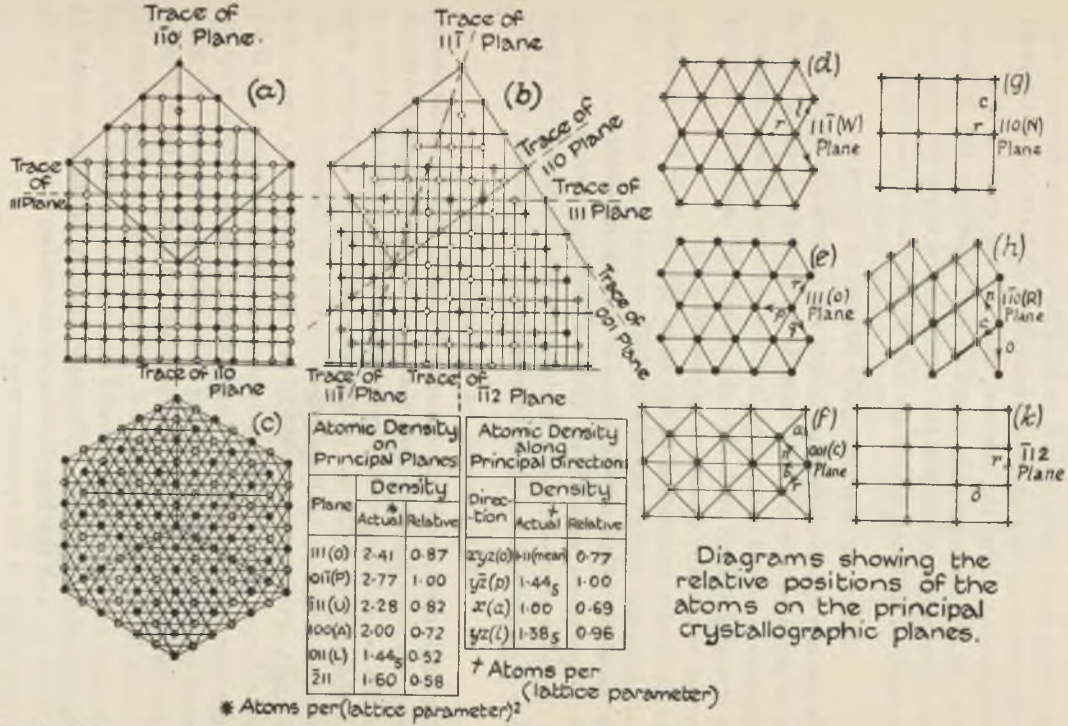
* *Loc. cit.*

† A. Ogg, *Phil. Mag.*, 1921, **42**, 165.

‡ *Phil. Mag.*, 1921, **42**, 193.

Fig. 1 shows three views of a model of the rhombohedral lattice, together with diagrams of the arrangement of atoms on the principal planes. The tables in Fig. 1 give the densities of atoms on the principal planes and along the principal directions.



Atomic Density on Principal Planes		
Plane	Density	
	Actual*	Relative
111 (O)	2·41	0·87
$01\bar{1}$(P)	2·77	1·00
$\bar{1}11$(U)	2·28	0·82
100(A)	2·00	0·72
011 (L)	$1·44_5$	0·52
$\bar{2}11$	1·60	0·58

Atomic Density along Principal Directions		
Direc-tion	Density	
	Actual†	Relative
xyz(o)	1·11(mean)	0·77
$y\bar{z}$(p)	$1·44_5$	1·00
x(a)	1·00	0·69
yz(l)	$1·38_5$	0·96

† Atoms per (lattice parameter)

* Atoms per(lattice parameter)^2

Fig. 1.—Diagrammatic Representation of the Structure of Bismuth. Rhombohedral lattice (face-centred): Angle 87° 34′. Parameter 6·52 A. with interlaced lattice displaced along trigonal lattice.

CONVENTIONS AND SYMBOLS.

The conventions and symbols used in the present report are as follows : each plane considered is designated by a capital letter, and the corresponding small letter is used to describe the lattice direction with which the normal to the plane would coincide if the lattice were deformed (by compression along the trigonal axis) to the cubic system. In addition, in the stereographic diagrams and elsewhere the Millerian indices of the planes referred to the rhombohedral edges are employed, whilst modified Millerian indices are used for the lattice directions.*

CHOICE OF SPECIMEN AND STRESSING SYSTEM.

The primary object of the experiments was to cause slip by the application of repeated stresses, and in order to provide a critical test of the maximum resolved shear stress law, it was desired to use a specimen and a stressing system such that slip should be caused on as many planes and in as many directions as possible.

No particular orientation of specimen appeared to be necessary, so that, from the limited number of single-crystal bars available, two bars of as widely different orientations as possible were chosen.

Both specimens were tested under alternating torsional stresses, since this type of stressing can produce slip (and twinning) on a large number of planes with but little deformation of the specimen as a whole.

PREPARATION OF SPECIMENS, &C.

The single crystals (reference marks B.1 and B.2) used in the present experiments were prepared from the liquid by the Bridgman method. From the bar B.1, a specimen (reference mark B.1A) was machined to a cylindrical form, 0·331 in. in diameter and 0·5 in. in length, with enlarged ends (joined by large radius curves) of diameter 0·5 in., the total length of the specimen being 2·7 in. Reference marks were scribed on the enlarged ends. In the process of machining the specimen B.1A, a large number of small twin bands were produced, which were not removed by the subsequent etching and polishing processes. To avoid the production of such twins, the specimen cut from the bar B.2 (reference mark B.2A) was not machined. A length was merely cut from the bar as cast, and the reference marks were scribed on brass collars fitted to the ends of the specimen. The mean diameter of the specimen B.2A was 0·515 in. and the length between the collars was about 1·75 in. The total length of the specimen was 2·8 in.

Both specimens were etched deeply and then X-rayed, and finally polished preparatory to test.

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* *Proc. Roy. Soc.*, 1930, [A], **127**, 434

Figs. 2 and 3 are stereographic projections showing the orientations of the principal crystallographic planes and directions of the specimens

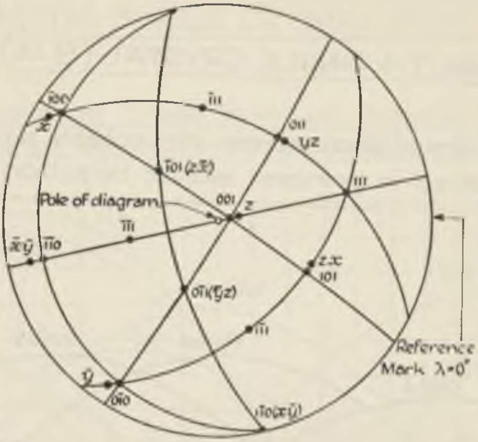


FIG. 2.—Bismuth Single Crystal (B.1A). Stereographic projection showing positions of principal planes.

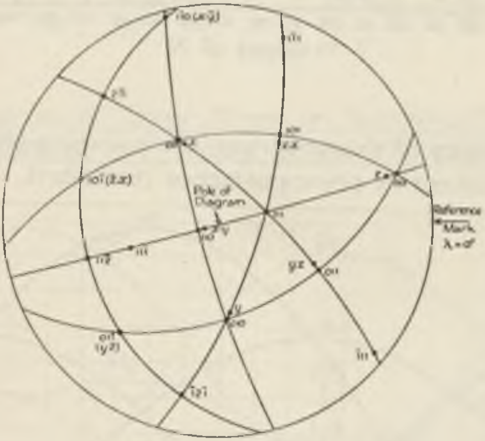
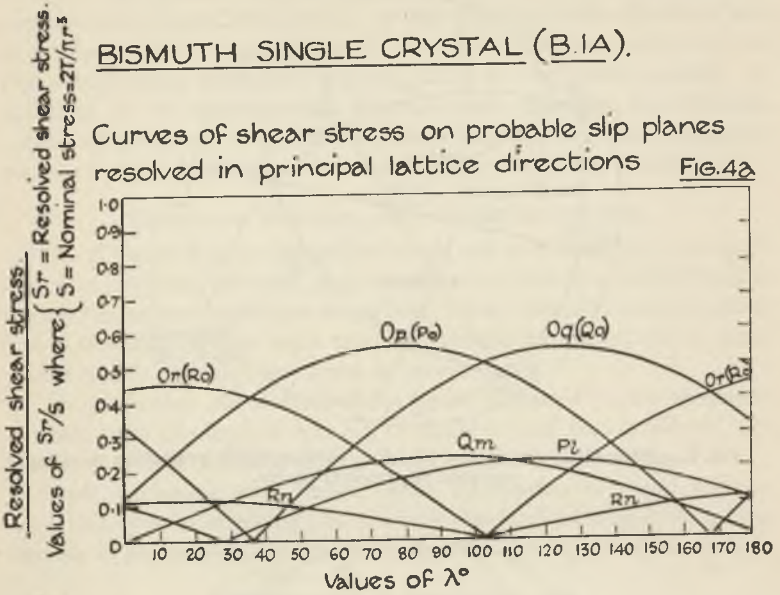


FIG. 3.—Bismuth Single Crystal (B.2A). Stereographic projection showing positions of principal planes.

B.1A and B.2A, respectively. The pole of each diagram represents the axis of the specimen, and the arrow one of the reference marks on the ends of the specimen.

Stress Analyses of Bismuth Single Crystals B.1A and B.2A.

Shear Stress.—The constants in the equations to the shear stresses on the principal crystallographic planes resolved in the principal



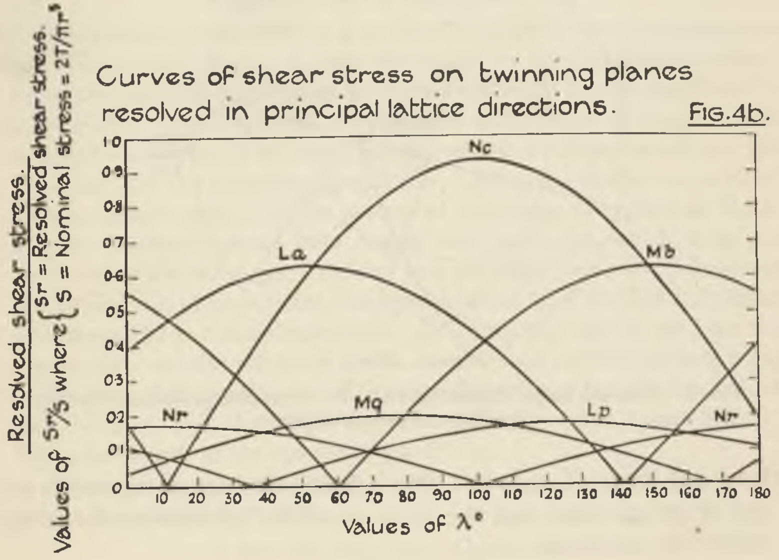


Fig. 4.

directions were evaluated for each specimen, using the co-ordinates found by X-ray analysis. The ratio of the "resolved shear stress S_r" at any point to the nominal maximum shear stress $S = 2T/\pi r^3$, where

BISMUTH SINGLE CRYSTAL (B.2a).

FIG. 5 (a).

Curves of Shear Stress on Probable Slip Planes Resolved in Principal Lattice Directions.

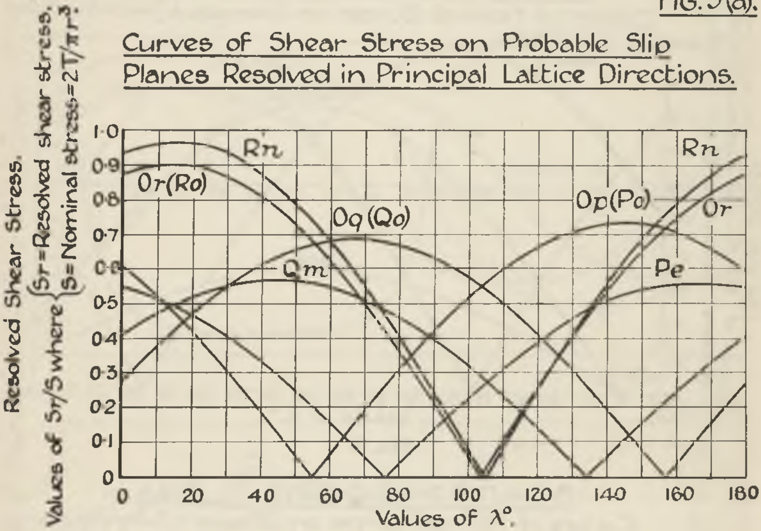


FIG. 5 (b).

Curves of Shear Stress on Twinning Planes Resolved in Principal Lattice Directions.

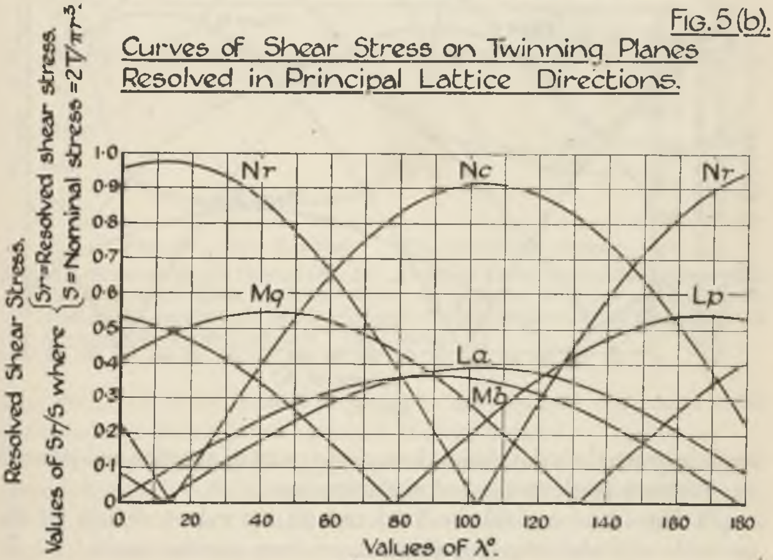


FIG. 5.

T is the applied torque and r the radius of the specimen, is given by the formula $S_r/S = A \cos(\lambda - a)$, where A and a depend only on the orientations of the plane and directions considered, and where λ is the angle between the axial planes through the point in question and through the reference mark on the end of the specimen.

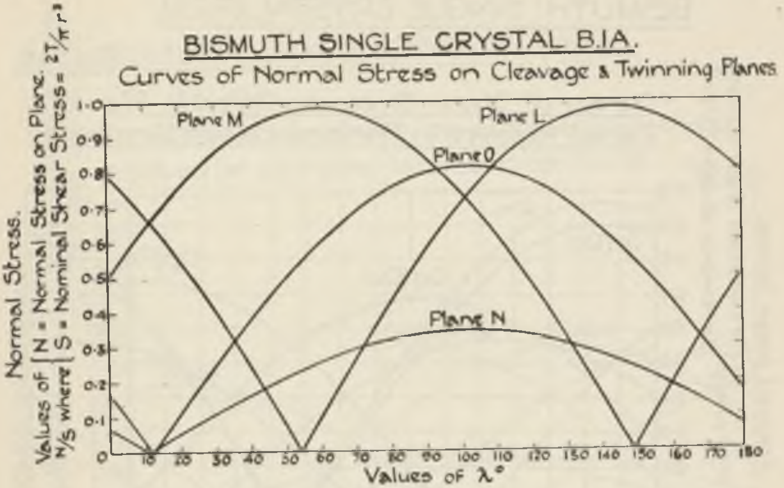


FIG. 6.

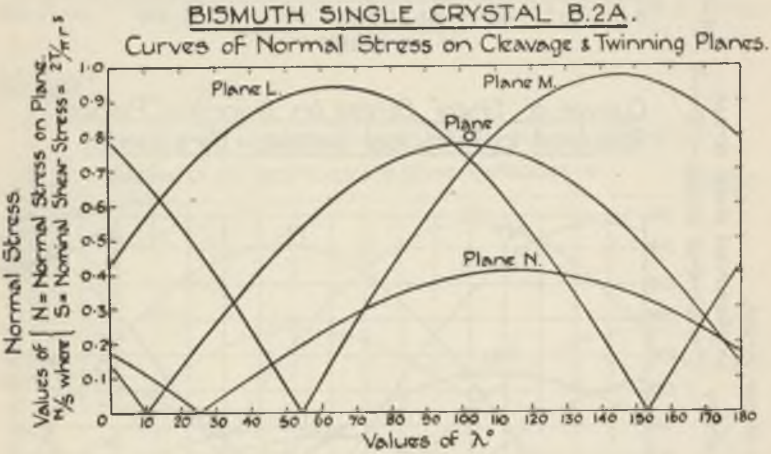


FIG. 7.

In Figs. 4 (*a*) and (*b*) also 5 (*a*) and (*b*) the values of S_r/S for the probable slip and twinning planes have been plotted against λ. In these figures, as elsewhere, the capital letter represents the plane and the small letter the direction of the resolved shear stress.

Normal Stress.—The normal stresses on the 111 planes and on the twinning planes (of the type 011) were evaluated for both specimens.

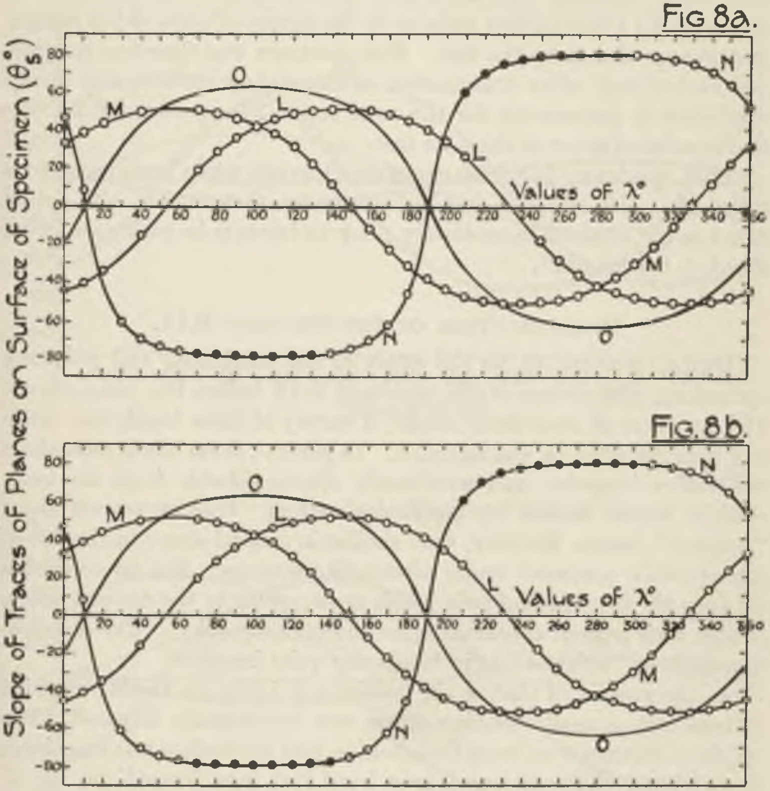


Fig. 8*a*.—After first test. Fig. 8*b*.—After fracture.

Fig. 8.—Bismuth Single Crystal (B.1A). Diagram showing recorded values of the slopes of twin bands observed within the primary structure of the crystal. *Full circles* denote twin bands produced during the alternating torsional tests. *Open circles* denote " original " twin bands.

The ratios of these normal stresses to the nominal maximum shear stresses have been plotted against λ in Figs. 6 and 7.

Traces of Planes.—The slopes of the traces of the principal planes were calculated, and the angles of slope, at any point of either specimen, of the traces of the 111 and the twinning planes are shown in Figs. 8 and 9; the usual convention as to sign has been retained.

Details of Tests.—Both specimens were subjected to a small number of reversals of a range ± 0·25 tons/in.^{2} nominal maximum shear stress (B.1A, 26,900 reversals; B.2A, 25,600 reversals). The twist occurring during this preliminary run was negligible in both cases. The specimens were then carefully examined and photographed. In the case of specimen B.1A some doubt arose as to the nature of some of the surface markings produced by the test. This specimen was therefore polished and etched and, after examination of the etched surface, was finally repolished in preparation for the next test. The specimen B.2A was also repolished prior to the next test.

Both specimens failed by complete cleavage while loading up to a range of ± 0·5 tons/in.^{2} nominal maximum shear stress, the actual stress range attained immediately prior to fracture in each case being about ± 0·4 tons/in.^{2}.

MICROSTRUCTURE OF THE SPECIMEN B.1A.

Owing, presumably, to the effect of the machining and polishing operations, the surface of the specimen B.1A before test was covered with numbers of small twin bands; a survey of these bands was made and their distribution was recorded. In general, these bands were short and rather irregular, and were easily distinguishable from the long, straight bands formed by mechanical action. One or two of these " original " bands, however, were similar in general shape to the bands subsequently produced under alternating stresses; but no confusion between the two types of twin bands arose, owing to the distinct difference in their general appearance (see photomicrographs). The distribution of these " original " twin bands was quite irregular.

In the process of placing the specimen B.1A in the testing machine (Stromeyer), a small bending strain was accidentally imposed. The specimen was removed from the machine, and the surface was examined. It was found that one broad twin band had been formed (on the M plane (see Fig. 8)) extending from $\lambda = 280°$ to $\lambda = 60°$, the maximum width of the band being about 0·03 mm. The specimen was then replaced in the testing machine and subjected to the test run of 26,900 reversals of ± 0·25 tons/in.^{2}.

After this test the only new feature apparent on the surface of the specimen was a series of bands almost parallel to the axis of the specimen, and extending the whole length of the polished surface. These bands were everywhere parallel to the trace of the twinning plane N, and their distribution is shown diagrammatically in Fig. 8 (*a*). Unfortunately, it is not possible in this diagram to give any idea of the actual disposition of the bands, which were disposed in groups covering sectors of about 5° (λ), the centres of adjacent groups being about 15° apart. The distribution of the bands on the opposite side of the specimen was of an exactly similar type.

Fig. 9a.

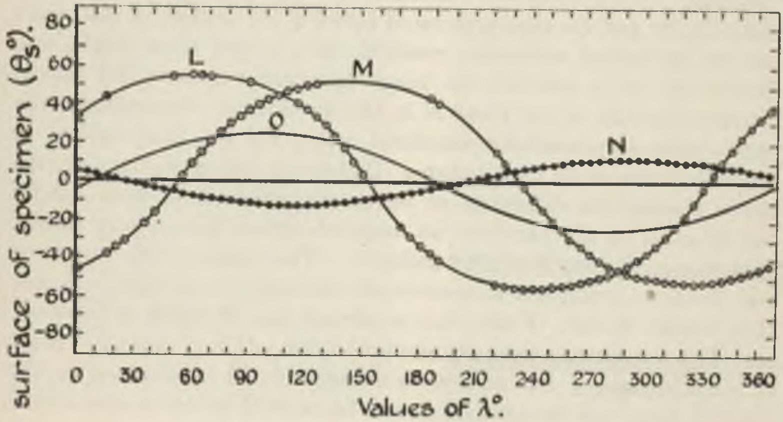


Fig. 9b.

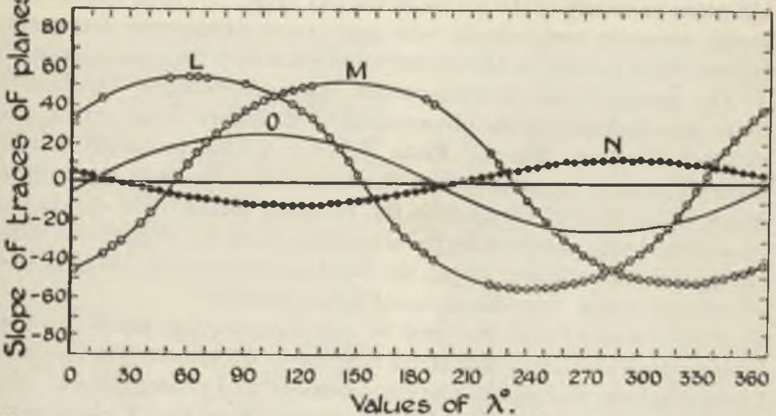


Fig. 9.—Bismuth Single Crystal (B.2A). Diagram showing values of the slopes of twin bands observed within the primary structure of the crystal. *Full circles* denote twin bands produced during the alternating torsional tests. *Open circles* denote "original" twin bands.

By reference to Figs. 8 (*a*) and 4 (*b*), it will be seen that the bands observed occurred at the values of λ at which the shear stress *Nc* is a maximum, and that this maximum value was considerably higher than the maximum of any of the other resolved shear stresses.

Since the bands observed were everywhere parallel to the trace of the twinning plane, *N*, it was natural to assume that the bands were twins; but their appearance, as shown in Fig. 11 (Plate XXIV), was not that of ordinary twins, as illustrated by the one large and numerous small "original" twins shown in the same photograph. In view of this dissimilarity and the close agreement between the position of the bands and the points of maximum resolved shear stress, some doubt was entertained as to whether the bands observed were not slip bands, produced by slip on the plane *N* in the direction *c*. Accordingly, the bands were very carefully examined, using oblique illumination, in order to decide as to their nature. Under this system of lighting, the bands showed the difference of lustre characteristic of twin bands; but in so far as slip bands on an *unetched* surface have a very similar appearance, the test was not conclusive. The surface of the specimen was therefore repolished to remove all the surface markings, and was then lightly etched. Under this treatment the *N* bands reappeared, and their appearance was very similar to that of the "original" twins at the same stage; but no *definite* evidence could be obtained on the point at issue, and no conclusions can be reached as to the true nature of the observed bands.

A very careful search was made for any traces of slip parallel to the 111 plane or to any of the planes of the $01\bar{1}$ type. No such traces were found, however, nor, indeed, were any traces whatsoever discovered beyond those parallel to the primary and secondary twinning planes.

The nature of the structure within some of the larger "original" twins was disclosed by the observations of secondary bands within the twinned structure (Fig. 11, Plate XXIV); all the secondary bands observed were in accordance with the definition of the twin as a mirror image of the original structure in the twinning plane. Unfortunately, none of the bands produced by the alternating torsional stresses was wide enough for the structure within the band to be resolvable, so that the orientation within these bands could not be decided.

After fracture (which occurred by complete cleavage parallel to the *O* plane while loading up to a stress range of ± 0·5 tons/in.^{2}) the surface of the specimen was again carefully examined and photographed. No new features were observed. The bands parallel to the *N* plane were more numerous than after the first test (Fig. 8 (*b*)), and the "grouping" effect was a little less pronounced; but their general appearance was unchanged.

MICROSTRUCTURE OF THE SPECIMEN B.2A

In order to avoid as far as possible the formation of twin bands on the surface of the specimen before test, the specimen B.2A was not

PLATE XXIV.

FIG. 11.—Specimen B.1A. $\lambda = 120{\cdot}6°$.
× 330.

FIG. 12.—Specimen B.2A. $\lambda = 198°$.
× 100.

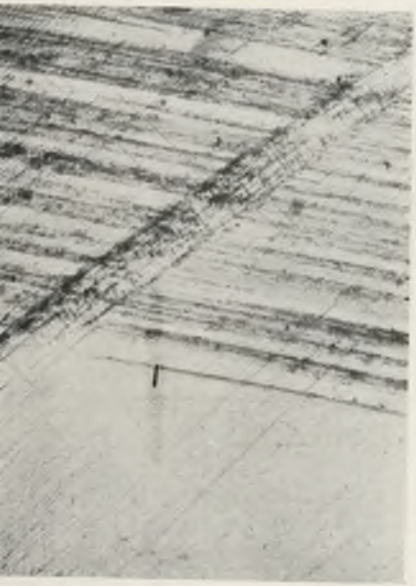


FIG. 13.—Specimen B.2A. $\lambda = 90°$.
× 100.

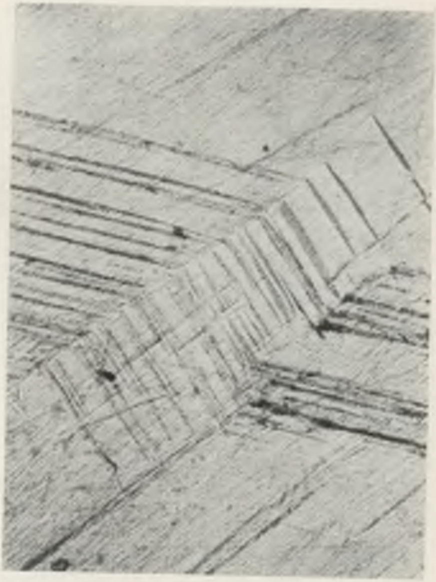


FIG. 14.—Specimen B.2A. $\lambda = 116{\cdot}5°$.
× 180.

All figures reduced by $\frac{1}{4}$ in reproduction.

[*To face p.* 240.

FIG. 15.—Specimen B.2A. λ = 125·3°. × 180.

FIG. 16.—Specimen B.2A. λ = 156°. × 100.

FIG. 17.—Specimen B.2A. λ = 105°. × 180.

FIG. 18.—Specimen B.2A. λ = 99°. × 180.

All figures reduced by $\frac{1}{4}$ in reproduction.

machined, but merely polished prior to test. Although this procedure was successful in eliminating the numerous small twin bands (such as were apparent on the surface of B.1A before test), nevertheless a number of fairly large twins and one very broad twin were present in the surface before the first test. As in the case of the specimen B.1A, however, these " original " bands were easily distinguishable from the bands formed under alternating torsional couples, and no confusion arose in the subsequent examinations.

After the first test (25,600 reversals of ± 0·25 tons/in.^{2}) the only new markings apparent on the surface of the specimen were bands everywhere parallel to the trace of the twinning plane N. These bands completely encircled the specimen (Fig. 9 (*a*)), and were disposed in groups in a manner similar to the grouping observed in the case of the specimen B.1A. The appearance of the bands was not uniform round the specimen. From about $\lambda = 65°$ to about $\lambda = 165°$, and over a corresponding range on the other side of the specimen, the bands were similar in appearance to those observed on the surface of the specimen B.1A, whilst in between these ranges the bands had definitely the appearance of twins. The change-over from one type of marking to the other was very ill-defined, and the change was to some extent masked by the presence of the " original " twins; but that the typical appearance of the bands varied with λ is well illustrated by a comparison of Figs. 12 and 13 (Plate XXIV).

A partial explanation of the change in appearance of the N bands is to be found in the curves of shear stress plotted in Fig. 5 (*b*). Considering shear stresses on the plane N, it will be seen that from $\lambda = 62°$ to $\lambda = 147°$ and from $\lambda = 242°$ to $\lambda = 327°$ the shear stress resolved in the direction c is greater than that resolved in the direction r, whilst in the intervening ranges the reverse is the case. Now it is in the range over which the shear stress Nc is a maximum that the bands are similar in appearance to those observed on the surface of the specimen B.1A, and it must be concluded that bands of this type are produced by movement due to shear stress on the plane N in the direction c. The atomic densities on this plane and in this direction are so low that it is difficult to imagine that this movement can be anything in the nature of pure slip; as a working hypothesis, it may be suggested that the process may be one of twinning initiated by partial slip on the twinning plane.

Reverting to the particular case of the specimen B.2A, it has already been remarked that over the ranges of λ for which the shear stress Nr is greater than the shear stress Nc, the N bands formed have definitely the appearance of twins; but whether this twinning is due to the high value of Nr, or to the low value of Nc, or even to some entirely different factor, there is at present no evidence to show. Although there is no experimental evidence as to the atomic movements occurring during twinning, consideration of the initial (untwinned) and final (twinned) disposition of the constituent atoms of the lattice makes it appear probable that these movements are largely confined to the planes of the type $1\bar{1}0$, which are of course severally perpendicular to the directions of the type $x\bar{y}$ (r) contained by the twinning planes. It might be assumed, therefore, that shear stresses of the type Nr should have very little, if any, effect on the process of twinning. In the case of the specimen B.1A the shear stresses Nr, Mq, and Lp were everywhere very low (Fig. 4), so that the failure to observe *definite* twins anywhere on the surface of this specimen is, in a negative manner, consistent with the view that the shear stress Nr *has* some effect on twinning; but definite evidence could be obtained only by further tests on a specimen for which the stress Nr is everywhere large compared with the stress Nc.

As in the case of the specimen B.1A, attempts were made, using oblique illumination, to decide as to the exact nature of the bands parallel to the N plane. In the regions ($\lambda = 65°$ to $\lambda = 165°$ and $\lambda = 245°$ to $\lambda = 325°$ approximately) over which the bands were similar to the bands observed on the surface of the specimen B.1A the results were again inconclusive; but in the intervening regions ($\lambda = 165°$ to $\lambda = 245°$ and $\lambda = 325°$ to $\lambda = 65°$ approximately) the bands had quite definitely the typical appearance of twins.

Careful examination of the whole surface of the specimen failed to reveal any markings parallel to the traces of the 111 plane or of the planes of the type $01\bar{1}$; nor were any markings whatsoever observed other than those parallel to the traces of the primary and secondary twinning planes.

In some of the broader "original" twin bands, secondary bands were formed during the torsion test. These bands were everywhere parallel to the traces of the secondary twinning planes of the structure within the primary twin, the orientations of these secondary planes being calculated on the assumption that the structure within the twin was a mirror image of the primary structure in the (primary) twinning plane. Unfortunately, in none of the bands formed during the torsion test, that were broad enough for the structure within them to be resolvable, could any secondary bands be observed. Fig. 14 (Plate XXIV) and Fig. 15 (Plate XXV) show the typical appearance of the secondary bands within the large "original" twins.

In some places, particularly in the regions where the N bands were most irregular (*i.e.*, in the regions $\lambda = 65°$ to $165°$ and $\lambda = 245°$ to $325°$

approximately), there were definite signs of what appeared to be recrystallization occurring in bands along the traces of the "original" twins and of the twins formed during the torsion test. One such field is shown in Fig. 16 (Plate XXV), which shows the effect occurring along the *N* bands.

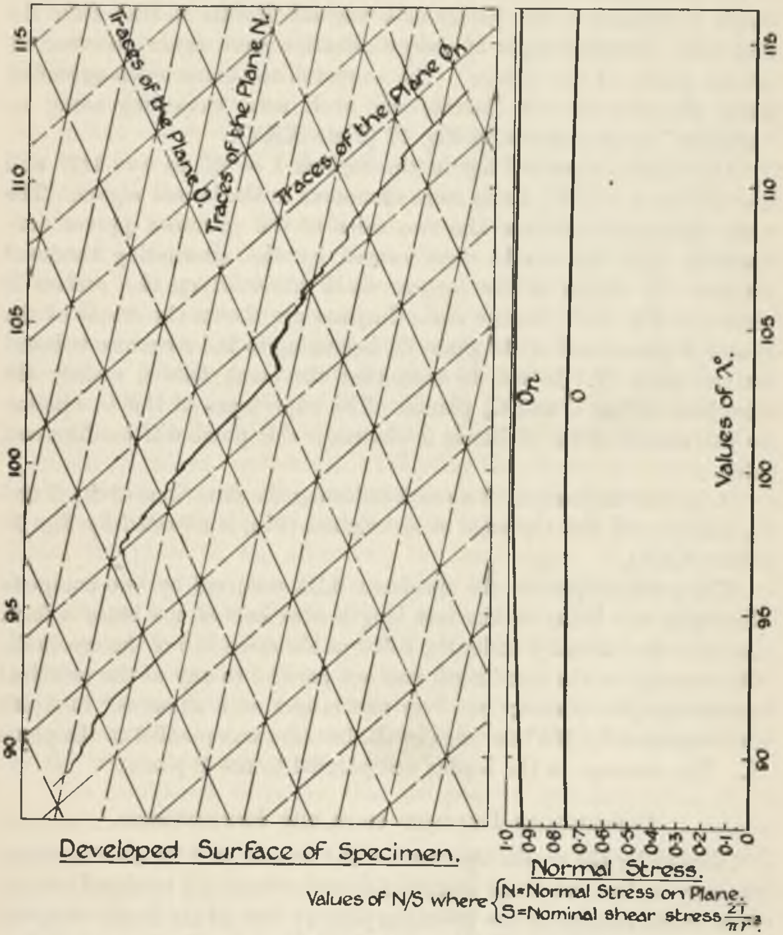


Fig. 10.—Bismuth Single Crystal (B.2A). Diagram of the largest crack on the surface of specimen B.2A showing tendency of crack to follow cleavage planes of the original structure and of the structure twinned on the plane N.

After fracture (which occurred while loading up to a stress range of ± 0·5 tons/in.^{2}) the only new features that were observed on the surface of the specimen were a number of fine cracks near one end of the test portion. Twins parallel to the plane N were again recorded at every value of λ (Fig. 9 (*b*)), and they were again grouped in bands in the same manner as after the first test. The appearance of the twin bands in relation to the values of λ was also similar to that after the first test. Distinct signs of recrystallization were again observed at several points of the surface. The recrystallized areas again extended along the sites of twin bands, one such area extending along an "original" twin is shown in Fig. 17 (Plate XXV).

The cracks observed lay in the regions $\lambda = 89°$ to $\lambda = 117°$ and $\lambda = 270°$ to $\lambda = 278°$, being more numerous in the former region. The close agreement between the two sides of the specimen proves conclusively that the cracks were caused by the alternating torsional stresses. A sketch of the longest crack observed on the surface is shown in Fig. 10.* In the same diagram are shown the traces of the O and N planes and of the plane O_n belonging to the structure twinned on the plane N. It will be seen that the crack follows mainly the directions of the O and O_n planes. The importance of this in relation to the nature of the N bands is obvious; this point will be discussed later.

A further illustration of a crack following the directions of the O and O_n planes, and also the edge of an original twin, is afforded by Fig. 18 (Plate XXV).

The actual failure of the specimen B.2A occurred by two complete cleavages, one being in the test length near one of the brass collars, and the other actually under the collar at the same end of the specimen. The cleavage in the test length was not parallel to any of the principal crystallographic planes; but over two ranges each about 50° in width and separated by 180° the edge of the fracture was parallel to the plane N. The cleavage in the holder was parallel to the O plane.

CONCLUSIONS REACHED FROM THE EXPERIMENTS.

Except for the cracks observed on the surface of B.2A after fracture, the only surface markings produced by the alternating torsional couples were bands parallel to the twinning planes; but all the bands observed on the surface of B.1A, and about half of those observed on the surface of B.2A, had not the appearance of ordinary twins. Microscopical and metallurgical examination of these bands failed to establish their identity as slip or twin bands. Whilst it is very significant that all the bands were produced on planes on which a high shear stress was developed, and that no bands were produced on similar crystallographic

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* This diagram was prepared from a panoramic photograph of the crack.

planes on which the shear stresses were low, yet it is extremely unlikely that anything in the nature of actual slip should occur on planes of such relatively low atomic density. None of the bands, the nature of which was uncertain, was wide enough for the structure within the band to be resolvable; nor, indeed, could any structure be observed within the relatively wide bands (on the surface of the specimen B.2A) which were regarded as definite twins.

The only real evidence as to the nature of the more irregular bands lies in the observed tendency of the cracks formed on the surface of the specimen B.2A to follow the calculated trace of the 111 plane belonging to the structure twinned on the plane, parallel to which these bands were formed. Over the two small areas in which cracks were observed this plane O_n has a slope that is very nearly 45°. There is therefore a danger that cracks that are considered to be following the plane O_n may, in reality, merely be following the direction of actual maximum normal stress. Two arguments may be advanced against this view. Firstly, in a material such as bismuth, which possesses well-pronounced cleavage planes, it would not be expected that any large part of a crack should be independent of crystallographic orientation. Secondly, if indeed the fracture is following the maximum normal stress plane, then it is a surprising coincidence that the small areas over which the cracks extend should correspond so exactly with the positions in which the plane O_n has effectively the same slope. If, on the other hand, the cleavage plane O_n existed in the specimen (by virtue of *twinning* on the plane N), then it is to be expected that cracks would be propagated along the trace of this plane at the points at which the normal stress across the plane is a maximum, and it should be remarked that this maximum normal stress is effectively equal to the *nominal* maximum normal stress and considerably greater than the normal stress on the original cleavage plane O (Fig. 7).

It is considered, therefore, that the position and orientation of the cracks observed on the surface of the specimen B.2A afford definite evidence of the existence of a cleavage plane O_n in these regions, and, since the plane O_n can be brought into existence only by twinning on the plane N, that the identity of the N bands as twins is thus established.

It remains only to add that, although the portions of the cracks that were parallel to the trace of the plane O_n extended over relatively large areas that were certainly not composed *entirely* of structure twinned on the plane N, yet this objection is of little importance, in that cracks once started at 45° would certainly be propagated for *short* distances through the untwinned structure merely by the actual maximum normal stress acting in this direction. An example of this is shown in Fig. 18 (Plate XXV), where the crack penetrates for some distance into the upper* edge of the *L* twin before deviating into the direction M_l.

GENERAL CONCLUSIONS.

If the evidence described in the paper as to the nature and mode of formation of the observed bands be accepted, the bearing of the results on the general conception of deformation by slip and twinning, &c., has to be considered. The conclusion that twinning is directly attributable to shear stress on the twinning plane appears at first sight to be entirely at variance with the conception of twinning proposed in the case of zinc.†

On the other hand, in accordance with the ideas expressed in the introduction to the present paper, it is possible to regard the shear stress not as the direct cause, but rather as a symptom of a somewhat more fundamental criterion. Thus, although the initial and final positions of the atoms in the process of twinning are known, there is no information as to the paths of lowest energy by which the atoms change their positions. In particular, in a complex lattice, such as that of bismuth and antimony, these paths may be very different from the shortest geometrical paths, and it is quite conceivable that the path of lowest potential gradient may differ widely from the line joining the initial and final positions. Thus, the stress condition determining twinning may involve as primary factors stresses that bear no obvious relation to the assumed group-movement by which twinning is produced if this group-movement is based purely on the initial and final positions.

In discussing the occurrence of twins on the surface of B.2A in the regions where the shear stress *Nr* was a maximum, the opposite argument, based on consideration of terminal conditions, alone, has purposely been presented. Comparison of the two views shows that the simpler conception is no more rational than the more complex idea. It is certain that the initial (untwinned) and the final (twinned) positions of any one atom are positions of minimum potential energy; but there is no information as to the potentials in intermediate positions, and it is quite reasonable to suppose that the initial and final positions may be separated by a ridge of high potential, such that the easiest path of transition may be obliquely up this ridge and through a " pass " in its summit line.

In addition, in this view the raggedness of the bands in the region where the shear stress *Nc* is a maximum is at least partly explained, for if twinning be produced by stresses acting directly up the ridge,

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* As the photograph is orientated in the attached plate.

† *Loc. cit.*

the tendency of the atoms to follow the lines of lowest potential gradient will produce disordered movement, leading to an imperfect twin formation. Moreover, it is not unreasonable to claim that the recrystallization observed on the surface of B.2A was probably due to disordered movement during twinning.

In conclusion, it must be emphasized that all the applications of the lowest energy conception that have been made above and in the introduction are purely tentative, and must remain so until our knowledge of the interatomic forces is rendered much more complete. Nevertheless it must be recognized that the conception itself represents a universal physical principle. In other words, the gain in physical reality by the adoption of energy rather than stress criteria is at the expense of practical convenience in the abandonment of known stress coefficients in favour of unknown energy differences. Whether this change is advantageous is a matter for dispute; but at least it should serve to demonstrate that any simple stress criterion cannot be regarded as fundamental.

ACKNOWLEDGMENTS.

The experiment described forms part of a programme of research undertaken, at the National Physical Laboratory, for the Aeronautical Research Committee of the Air Ministry. The authors take this opportunity of expressing their indebtedness to various colleagues at the National Physical Laboratory for considerable assistance rendered: to Mr. I. Backhurst, B.Sc., for the X-ray analysis; to Mr. J. D. Grogan, B.A., for the metallographic polishing of the specimen; also to Mr. G. Forrest, B.Sc., for valuable assistance rendered in connection with the photomicrographs.

NATIONAL PHYSICAL LABORATORY,
TEDDINGTON.
October 16, 1931.

DISCUSSION.

DR. HUGH O'NEILL,[*] M.Met. (Member): I have been greatly interested in this paper, and the authors are to be congratulated on having added another brick to the Tower of Babel which is being built round single crystals. The results, I gather, are not quite so clear-cut as they were in previous studies of other metals, and I wonder whether the testing temperature, considered on the absolute scale, is playing a part in this. Bismuth is a metal with a lower melting point than any previously studied by the authors, and at room temperatures is relatively near to recrystallization and fusion. It is known that with some metals the behaviour of the ultimate deformation

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[*] Senior Lecturer, Department of Metallurgy, The University, Manchester.

depends on the testing temperature. Thus if ordinary iron is deformed at room temperatures with slow speeds of straining, only slip bands are obtained, but at liquid air temperatures I believe that mechanical twins are formed.* It is therefore *possible* that different results would be obtained if the bismuth were strained at liquid air temperatures, or it might be of advantage to test it at higher temperatures still.

The introduction of energy considerations into the study of deformation is important, and will have to be considered a great deal in the future. One still wonders why crystals of iron at room temperatures do not produce mechanical twins when deformed statically, although if 2 or 3 per cent. of silicon be added to iron, slow deformation will cause mechanical twinning. Phosphorus will produce the same sort of thing. Those results are not yet explained, and it may be that energy considerations will help in their elucidation.

Dr. C. H. DESCH,† F.R.S. (Member of Council): Under these conditions it appears that slip is not possible in the bismuth crystal. On the other hand, although bismuth is not a plastic metal in the ordinary sense, yet it is very easily extruded, if placed in a press and forced through a die, into a very flexible wire. That deformation takes place presumably by slip. On what planes does that slip occur?

Also, taking the crystal structure in this form, how would the authors account for the fact that, whilst there is no definite slip on a plane, yet there is a remarkably perfect cleavage on one set of planes—the (111).

Colonel N. T. BELAIEW,‡ C.B. (Member): I should like to ask one question. I have been very interested in the illustrations in this paper, and especially in Fig. 15, where the authors show the primary twins and the secondary twins. I am interested to know whether the authors have observed any relation between the mean dimensions of the one and of the others. In one case in my work I have found a certain relationship between these, and I wondered whether such a ratio could be also found to exist in the case dealt with by the authors, and if so whether there are any energy reasons for it.

Dr. C. F. ELAM,§ M.A. (Member): I intended to send a written communication on this paper,‖ but as several references have been made to the ductility of bismuth I think that it is only right to say that bismuth crystals can be obtained ductile. For instance, Professor Kapitza obtained some very pure crystals which are extremely ductile, and under static tensile tests the distortion of bismuth crystals has been worked out by Georgieff and Schmid and they have definitely found a slip-plane and slip-direction.

Dr. C. H. M. JENKINS ¶ (Member): The authors have stated that they have had difficulty in identifying whether movement is occurring by slip or by the formation of twin bands. It is difficult to make this distinction in the case of metals which do not crystallize in the cubic system.

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* F. Robin, *Rev. Mét.*, 1911, 8, 436; F. Osmond, *J. Iron Steel Inst.*, 1905, 67, 242.

† Superintendent, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

‡ Paris, France.

§ Cambridge.

‖ See this volume, p. 251.—ED.

¶ Senior Assistant, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

In the case of bismuth and of metals such as cadmium, the zone of deformation is commonly lens-shaped with slightly curved sides. One usually finds that slip lines are straight, and, similarly, the boundaries of twin bands are found to be straight sided. One is therefore led to suggest that the structure observed is not produced by slip or twinning in a single direction, but by repeated twinning and slip in more than one direction in the crystal, such as is indicated in Fig. A.

I would like to confirm that bismuth is more ductile than is commonly supposed, and in some circumstances it is relatively easy to deform it. A piece of cast bismuth containing an aggregate of crystals can be deformed under a power hammer, but is relatively difficult to roll.

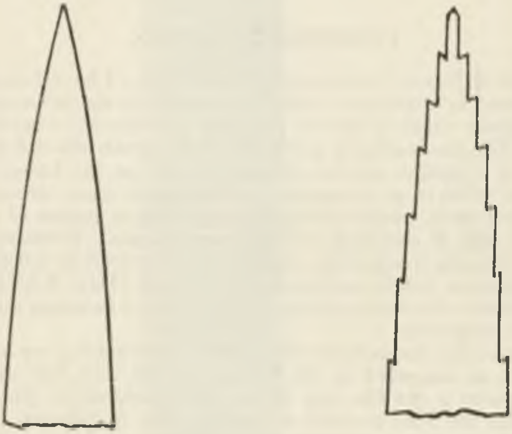

Fig. A.

Mr. Cox (*in reply*): With regard to the temperature effect, we have considered that throughout, not only in connection with bismuth, but also with antimony and zinc. We realize that we ought to test crystals at some fixed ratio of their melting points, but it is so much easier to test at air temperature that we did that first. We have definitely in view the possibility of making experiments on bismuth, either at very low temperatures or at relatively high ones; but with regard to slip one does not expect that lowering the temperature will facilitate slip. Normally, lowering the temperature tends to inhibit slip; bismuth at air temperature seems to be fairly near its melting temperature, so that higher temperatures do not seem likely to lead to slip.

With regard to the question of the ductility, there are one or two points which ought to be considered. For instance, on p. 238 there is a note about placing one of the specimens in the testing machine, where we imposed a small bending strain. That small bending strain was entirely due to the formation of a twin band; we could find no other deformation on the surface at all. We did not measure it, but it must have been of the order of nearly 1° between the two ends. Also, the crystals that were grown by the Bridgman method from the fine capillary tube have, of course, a tapered end, and those tapered ends could be bent up without fracture quite easily; but whether that is due to slip or twinning we have no evidence. On the other hand, we carried out *one* rough tensile test on a large crystal, ⅝ in. in diameter, and obtained some deformation, which was probably slip deformation, but not sufficient to be quite definite about it; distinct "cracking" noises accompanied the deformation. The crystal fractured quite quickly, after only about 5 per cent. extension.

Colonel Belaiew raised the point of the relative sizes of the primary and secondary twins. I am afraid that we have not studied that at all, but I have examined the photographs which are reproduced in this paper, and on comparison of Figs. 14 and 15 the relative width of the secondary bands does seem to bear some relation to the width of the main bands.

CORRESPONDENCE.

Professor E. N. da C. Andrade,* D.Sc., Ph.D.: I have found this paper of great interest in connection with some work on the behaviour of single crystals of metals which is now in progress, and nearing completion, in my laboratory. We are dealing in particular with metals which crystallize in a system having a unique axis of symmetry, such as the hexagonal system. Single crystal wires of such metals, *e.g.* cadmium, when stretched collapse into a flattened band, owing to slipping on a unique system of glide planes, which in the case of cadmium are the basal planes. When extension due to such pure slipping is complete, an increase of the load by a definite amount leads to twinning in bands, as illustrated in Fig. B (Plate XXVI). This use of tension instead of torsion enables the processes of twinning and of slipping to be studied separately.

Leaving aside for the moment the question of twinning, we have obtained evidence that, as suggested by Dr. Gough and Mr. Cox, the shearing stress in the glide plane is not the only factor which determines glide. We have been measuring the load required to initiate glide in different single crystal wires for which the hexagonal axis makes various angles χ with the axis of the wire. If the shearing stress were the only criterion, the curve showing load against χ should, of course, be symmetrical for values of χ to either side of 45°. We find, however, marked asymmetry, which suggests the influence of the normal tension.

That our twinning bands are true twins is borne out by the fact that in cadmium, which is hexagonal, the bands make angles of 60° with one another, as is evident from the photograph. The crystals in which the twinning takes place have already been so much extended by glide that the hexagonal axis is nearly normal to the plane containing the axis of the wire and the major axis of the ellipse to which the originally circular cross section has collapsed. If twinning takes place at the $(10\bar{1}2)$ plane, as shown by C. H. Mathewson and A. I. Phillips for zinc, the twinning bands on equivalent planes should actually make angles of 60° with one another on the plane normal to the hexagonal axis. In confirmation of this with tin, which is tetragonal, the twinning bands are at right angles to one another.

Dr. Bruce Chalmers, who has been engaged on this work with me, has recently made some rough preliminary measurements on the heat liberated † on twinning in cadmium, and finds it to be of the order of 0·1 cal. per gram, while less than one tenth of this amount is produced during the whole extension accompanying gliding, although this extension is very much greater than that due to twinning. This makes it appear that the present authors'

* Quain Professor of Physics, University of London.

† See *Nature*, 1932, **129**, 650.

FIG. B.

[To face p. 250.

conclusion that the energies involved in glide and twinning are of the same order is certainly not true in all cases, twinning representing a sudden change from one stable position to another which requires a comparatively large energy to effect it, much or all of which energy is subsequently liberated as heat, probably in consequence of heavily damped vibrations of the molecules or molecular units about the new position of equilibrium. In this connection another observation of Dr. Chalmer's is of interest—namely, that the well-known " cry of tin " is due to the twinning of tin crystals, and does not take place when glide is in progress, a conclusion which he has verified with cadmium. The cry can also be obtained from zinc, which twins readily. No cry can be detected with lead or copper crystals deformed by any treatment, which is in agreement with Dr. Gough's statement that no twinning can be produced by purely mechanical action with metals crystallizing in the face-centred cubic lattice.

Dr. C. F. Elam,* M.A. (Member): The authors' observations on the deformation of bismuth, following on their previous experiments on zinc and antimony, have thrown considerable light on the formation of twins in these metals. Under the particular conditions of this form of testing, all these metals deform more readily by the formation of twins than by slip. This is not so surprising when one considers that they have not the same choice of slip-plane as have metals of cubic crystal symmetry. Whereas in a tensile test a single plane can and does function as the slip-plane, in an alternating torsion test this is impossible without breaking up the crystal structure. Twinning leads to a re-orientation which enables slip to take place on the usual slip-plane for the type of lattice, as it is now in a more favourable position to do. It is all the more surprising that no evidence of slip in the case of bismuth and antimony has been observed.

Georgieff and Schmid † investigated the distortion of bismuth crystals in tension and, as in the case of zinc, divided them into ductile and brittle crystals, according to the inclination of the slip-plane to the axis. Ductile wires could be extended 100 per cent. The slip-plane was the (111) plane and the direction of slip $[10\bar{1}]$ referred to the rhombohedral edges of the distorted cube.

Some very interesting observations were made by Kapitza.‡ If bismuth crystal rods were grown under uniform temperature conditions, they were usually brittle, but if a temperature gradient was carefully controlled, they were ductile. Kapitza attributed this difference to the formation of cracks along the cleavage planes. It seems quite probable that the authors' bismuth crystals were brittle before testing. The large size would tend to accentuate any non-uniformities due to unequal shrinkage along certain planes on cooling.

Professor Dr.-phil Adolf Smekal § (Member): I should like to amplify the authors' interesting conclusions on the energy character of the condition necessary for twin formation by a note on the question as to whether the existence of such a condition should be expected in the sense of the macroscopic or in the sense of the molecular theory of elasticity.

This decision is influenced in favour of the necessity of molecular theory conditions for the slip process as well as for the development of cleavage planes. In the case of deformation by slip, it has already been emphasized by many authorities that the " macroscopic " internal stresses of plastically deformed substances, as determined directly or from röntgeno-

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* Cambridge.

† M. Georgieff and E. Schmid, *Z. Physik*, 1926, **36**, 759–774.

‡ P. Kapitza, *Proc. Roy. Soc.*, 1928, [A], **119**, 358–443.

§ Professor of Physics, The University, Halle (Saale), Germany.

grams, are considerably too small to explain the large amount of energy absorbed in the deformation. On the other hand, I showed some time ago by photoelectric tests on salt crystals that during deformation by slip, energy changes are taking place in a definite fraction of the crystal atoms and that the magnitude of these changes corresponds with the amount of energy which should be necessary for the temporary separation of the crystal units from the crystal structure; this energy is many times greater (about 1000 times) than the *mean* energy of elastic deformation on a single crystal atom. The molecular theoretical experiment therefore proves that the true elastic stress distribution is locally very uneven in the deformed crystal, though it is in a state of homogeneous mean stress. It is clear that the first permanent effects of deformation arise from stresses limited to microscopic parts of the material, so that actually no general macroscopic stress or energy condition is possible for the starting of slip. It is impossible to explain more fully here how from this fact it follows that the existence of statistically marked definite *directions* of slip can determine the occurrence of slip, as this has been proved correct by the beautiful researches of Dr. Gough on α-iron and, according to our observations, may also be realized with salt crystals; moreover high external pressures remarkably facilitate slip, which is then no longer determined only by shear stresses in the direction of slip. It need only be mentioned here that the spatial inhomogeneity of the molecular stress distribution is caused by faults in the crystal structure in which the presence of foreign atoms of impurities plays an important part, as can be shown directly by special photochemical tests.

As Dr. Gough has shown and emphasized, slip and twin formation can be caused by macroscopic stress systems which are quantitatively comparable; what has been said in regard to the beginning of slip can therefore be accepted with respect to twin formation; in the case of non-metallic crystals there already exists a number of indications on this point, and we hope in the near future to be able to give experimentally an exact decision.

In the meantime, it appears that a local–molecular energy condition must be considered to cause twin formation to begin, and that it is therefore hopeless to look for definite macroscopic stress criteria. Nevertheless I think that it is not only important to continue these tests but also to extend them to cover as many different materials as possible with the same lattice structure. By this means, the question of whether and how the transformation process for twin formation is to be interpreted on the basis of lattice geometry would lose its importance; on the other hand, it should also be possible, from the quantitative differences found in the tests, to characterize the primary process by reason of the known differences in the materials tested and in their crystal units.

The Authors (*in reply*): We are very gratified by the interest that has been taken in our paper and by the valuable contributions that members have made to the discussion. Since the presentation of the paper, we have carried out a test on a third single crystal of bismuth under alternating *direct* stresses. Much of the substance of our reply to the discussion arises directly out of the results of this test. Accordingly we propose briefly to describe the experiment and to base the greater part of our remarks upon the conclusions suggested by the results of this test. There are, however, one or two points raised in the discussion that require separate reply.

Professor Andrade's observations with regard to the behaviour of metals crystallizing in the hexagonal systems appear to be in general accordance with the results of previous work on such metals, including our own on the behaviour of zinc under alternating torsional stresses.

In these materials twinning appears to occur as a direct consequence of slip, but our observations of the behaviour of antimony and bismuth do not indicate that this conclusion is true for the latter metals. Twinning, in bismuth particularly, appears to be quite independent of slip and to be controlled primarily by the shear stress acting on the twinning plane.

We are particularly interested in the measurements of the energies involved in mechanical deformation in which Dr. Chalmers is engaged and shall look forward to the full publication of the results: we do not feel, however, that the results of these measurements can be held to be directly applicable to our suggestion, unless some estimate can be made of the proportion of the material actually concerned in these energy changes.

That the " cry " of tin and other metals when plastically deformed is due to the production of twin bands has long been known to metallurgists; but we should not regard the absence of such cry as sufficient evidence of the non-formation of twin bands.

Dr. Elam remarks that twinning may occur in order to produce new slip planes favourably orientated for slip under the applied stress system. This suggestion had occurred to us in relation to our work on zinc, and for that material it appears to be reasonably satisfactory, but in the case of antimony and bismuth, even this partial explanation of twinning is not admissible, for twin bands are formed without previous slip, do not in general result in slip planes more favourably orientated for slip deformation, and no slip has been observed within such bands. There appears to be no escape from the conclusion that twinning is *in itself* a mode of deformation the occurrence of which is governed entirely by stress considerations.

We find Professor Smekal's remarks on the localization of the energy in the process of slip and twinning particularly interesting. We are fully aware of the difficulty of accounting for the behaviour of materials without reference to some stress concentration effect, and our reference to the energies involved in twinning and in slip was intended to apply only to the localized energies and not to the average energies. Nevertheless, if the cause of energy concentration is the same for slip as for twinning, the ratio of the *average* energies in the two modes of deformation might be expected to be effectively the same as the ratio of the *localized* energies, when, for the consideration of such ratios, distinction between the two methods of computation would be unnecessary.

With regard to the photo-electric tests on salt crystals to which Professor Smekal refers, we are surprised to learn that he has observed energy changes comparable in magnitude to that required to rupture atom bonds. In our view, on the basis of both experimental evidence and theoretical argument, the normal process of slip must be accomplished with very much smaller change of energy, and larger changes can only be due to actual rupture of atom bonds. If these large energy changes are extremely localized, they may indeed be evidence of the " damage " (*e.g.* the production of submicroscopic cracks) that slip is known eventually to produce, but any association of these large changes with the process of perfect shear deformation on the slip plane would represent to us an entirely new viewpoint.

Professor Smekal suggests that the concentration of energy in restricted areas may be ascribed to the presence of impurity atoms. Other workers have postulated the presence initially of submicroscopic flaws, whilst Zwicky and Goetz have suggested the existence of a secondary lattice by which the true symmetry of the lattice is destroyed. None of these suggestions appeals to us as being entirely acceptable, although our objections cannot be elaborated in the present reply. It must suffice for us to state that we do not accept the view that the force or energy theoretically required to produce perfect plane *slip* is many times greater than the value determined by experiment. In the process of pure slip, no atom bonds (except those at the front and rear edges of the slip planes) need to be broken, so that analyses based on theories of rupture energies appear to us to be inapplicable. In the absence of definite evidence to the contrary, we prefer to believe that the theoretical values of the force or energy associated with either slip or twinning or even cleavage parallel to a cleavage plane may prove to be of the same order as the experimental values, and we suggest that the occurrence of twinning or slip in definite bands does not in itself necessitate the existence of actual flaws in the material, but may be due entirely to statistical causes.

Since the presentation of the paper, a third test on a single crystal of bismuth under alternating direct stresses has been carried out. The orientation of this crystal was such that the normal and shear stresses on the cleavage plane were approximately equal. According to the rule suggested by Georgieff and Schmid, general slip deformation will occur before cleavage if the ratio of the shear stress to the normal stress on the cleavage plane is at least 0·7; therefore, according to this law, our specimen should have deformed by slip. Actually, no appreciable deformation resulted under alternating stresses, and after fracture by cleavage, only a few markings parallel to the cleavage plane were observed (in the neighbourhood of the failure) and even these had not the appearance usually associated with slip bands. Thus the experiment yielded a result generally dissimilar in nature from that obtained by Georgieff and Schmid, but it is impossible to say whether this difference can be attributed to differences in the materials or to the type of applied stressing actions.

Our experiment also possesses interest with regard to further observations made of the production of twin bands and of the influence of twinning on the ductility of the specimen. In the actual test of the specimen under alternating direct stresses, failure by cleavage occurred before any general deformation of the specimen had taken place. After fracture, however, it was found that the specimen was covered by a system of twin bands, the majority of which must have been produced immediately prior to failure. By far the greater number of these bands were formed on the twinning plane that was subjected to maximum shear, whilst the distribution of secondary twins proved that many of the twins on the other planes were formed before the main set of twin bands and may, therefore, have been present initially. In this respect, therefore, the result of the test confirms our conclusion that the formation of twins is determined by the shear stress on the twinning plane, and proves that the process is not primarily the result of restriction imposed on slip by the impressed strain conditions. As reported above, some faint traces of slip parallel to and close to the plane of cleavage were observed; but no trace of slip within any of the twin bands could be found, and it was quite obvious that the process of slip had been entirely subsidiary to the main mode of deformation by twinning.

In the process of fitting the specimen into the machine used for applying the alternating stresses, it was found that the specimen had been slightly bent, and it was necessary to straighten it. This straightening was accomplished by light pressure with the fingers and, for bending in the required plane, the specimen appeared to be quite plastic. Very careful examination of the specimen proved that the plastic bending was accomplished entirely by the formation of twin bands, and no trace of slip could be detected.

It appears, therefore, that the single crystals used were not in a brittle state before test, but that, at least for bending in certain planes, they were essentially ductile. This observation is in general agreement with our previous experience of bismuth and we suggest that the plasticity of this material may often be due to deformation by twinning rather than by slip.

ON THE INFLUENCE OF TEMPERATURE ON THE ELASTIC BEHAVIOUR OF VARIOUS WROUGHT LIGHT METAL ALLOYS *

By FRANZ BOLLENRATH,† Dr.-Ing.

SYNOPSIS.

Details are given on the experimental determination of the modulus of elasticity and elastic limit of various wrought aluminium and magnesium alloys at temperatures between − 190° and + 180° C. The testing apparatus is described. Particular attention has been paid to the uniformity of temperature on the test length of the specimen. A description is given of the alloys tested. The results are communicated and discussed. The elastic properties are found to increase with decreasing temperature, except in the case of two aluminium alloys with a high silicon content.

INTRODUCTION.

THE conditions under which the light metals aluminium and magnesium, or alloys containing them in appreciable quantities, are now used in the chemical industry, and in the construction of internal-combustion engines and aircraft which are liable to be subjected to extreme climatic conditions, make it necessary, for economical construction and safety in use, to study carefully the behaviour of these materials under the influence of conditions to which they may be subjected.

In particular the strength of these materials is appreciably affected by elevated and abnormally low temperatures, and the influence of these on the elastic properties is determined by the experiments described in this paper. Although numerous papers already published deal with the influence of temperature on strength, insufficient attention appears to have been paid to the measurement of the small strains and stresses which are so important for the development of economically and safely designed engineering structures and for structural theory based on the assumption of perfect elasticity in the materials. In actual service, however, small plastic deformations must be permitted. For this reason, and because in many cases the so-called elastic limit is regarded as a measure of the essential quality of materials, this

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Aluminium Alloys.

Alloy.	Composition, per cent.									Heat-Treatment.
	Cu.	Mg.	Mn.	Si.	Fe.	Zn.	Li.	Ti.	Al.	
(*a*) Duralumin 681B	3·64	0·47	0·57	0·23	0·23	...	...	...	remainder	Annealed for 1 hr. at 525° C. Quenched in water. Aged at room temperature.
(*b*) Duralumin 681BZ	4·21	0·73	0·63	0·39	0·25	...	...	...	remainder	As above.
(*c*) Lautal	4·21	...	...	2·12	0·26	...	...	...	remainder	Annealed for 45 minutes at 525° C. Quenched in water of room temperature. Aged for 60 hrs. at 140° C.
(*d*) Silumin	...	...	...	13·1	0·38	...	...	...	remainder	Annealed at 380° C.
(*e*) Scleron	3·0	...	0·6	0·25	0·27	12·0	0·1	...	remainder	Annealed for 45 minutes at 480° C. Quenched in water. Aged at room temperature.
(*f*) Constructal 2	1·2	0·92	0·5	0·56	0·26	...	...	0·5	remainder	Annealed for 1 hr. at 540° C. Quenched in water. Aged for 25 hrs. at 145° C.
(*g*) Constructal 87	...	1·62	1·24	0·29	0·28	6·87	...	...	remainder	Annealed at 500° C. Quenched in water. Aged for 30 hrs. at 75° C.

Magnesium Alloys.

Alloy.	Si.	Cu.	Al.	Fe.	Mn.	Zn.	Mg.	Heat-Treatment.
(*a*) Elektron AZM	0·08	trace	6·02	0·01	0·41	0·90	remainder	None.
(*b*) Elektron V1w	0·05	trace	10·09	0·04	0·40	...	remainder	Hardened by artificial ageing.

investigation includes the determination of small permanent elongations. With regard to the elastic properties, tensile tests were made at different temperatures between + 180° and −190° C., the temperature of boiling air. The higher of these was selected because the resistance of aluminium alloys which have been improved by natural or artificial ageing is, in many cases, impaired by subjection to temperatures of this order, and because tests made at this or rather lower temperature serve to show how the improvement which has been effected by the ageing process may be lost again in regard to the elastic behaviour.

MATERIALS TESTED.

The tests were made on the main types of the best strong wrought aluminium and magnesium alloys, most of which can be greatly improved by natural or artificial age-hardening, and are much used in all branches of industry for structures in which lightness is an advantage. The alloys examined fall into two groups, containing respectively seven aluminium alloys and two magnesium alloys.

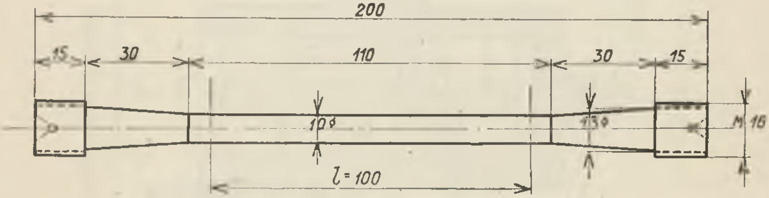

FIG. 1.—Dimensions of Specimens.

All materials were intensively wrought after casting and were delivered in the form of bars of circular cross-section of 18 mm. diameter.

DIMENSIONS OF SPECIMENS. APPARATUS AND METHOD OF TESTING.

All *specimens* for the series of tests of each alloy were taken from one single bar if perfect uniformity of the mechanical properties throughout the bar had been proved by special tensile tests and hardness tests, and were then machined to the dimensions shown in Fig. 1. The dimensions correspond with German Industry Standards (D.I.N. = Deutsche Industrie-Normen; it is the so-called Standard Long Proportional Specimen characterized by the $11{\cdot}3\sqrt{F}$ ratio, where F is the cross-sectional area), and the diameter of the central portion was 10 mm. The test length was 110 mm. and the distance between the gauge points 100 mm.

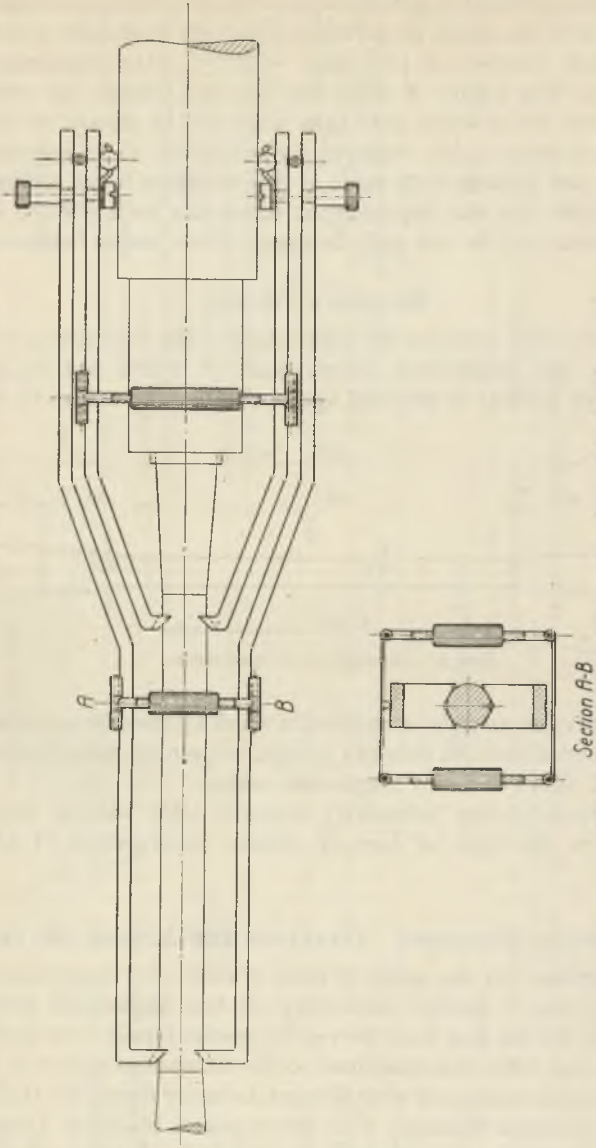

FIG. 2.—Martens Extensometer clamped to Specimen.

The *testing machine* was of the well-known Losenhausen type universal testing machine, of 10,000 kg. capacity and equipped with one manometer calibrated for 10,000 kg., and another for 1000 kg.

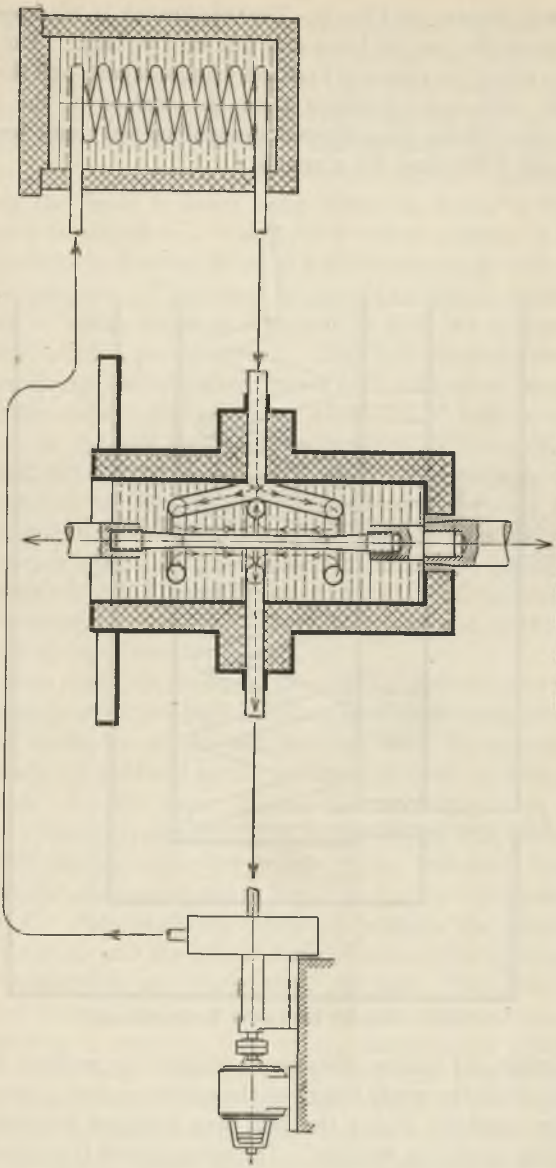

FIG. 3.—Cooling Equipment.

The latter was used for the investigations dealt with in this paper, as it allowed the loads to be determined with greater accuracy.

The *measurement of deformation* was made with a Martens optical extensometer, shown in Fig. 2. The apparatus is clamped to the specimen in couple, one in front and one on the back. The edges of the prism to which the mirror is fixed are 4·5 mm. apart, and the distance of the scale with mm. divisions from the surface of the mirror is 1125 mm., whereby the elongations are magnified 500 times for a single apparatus and 1000 times for a couple.

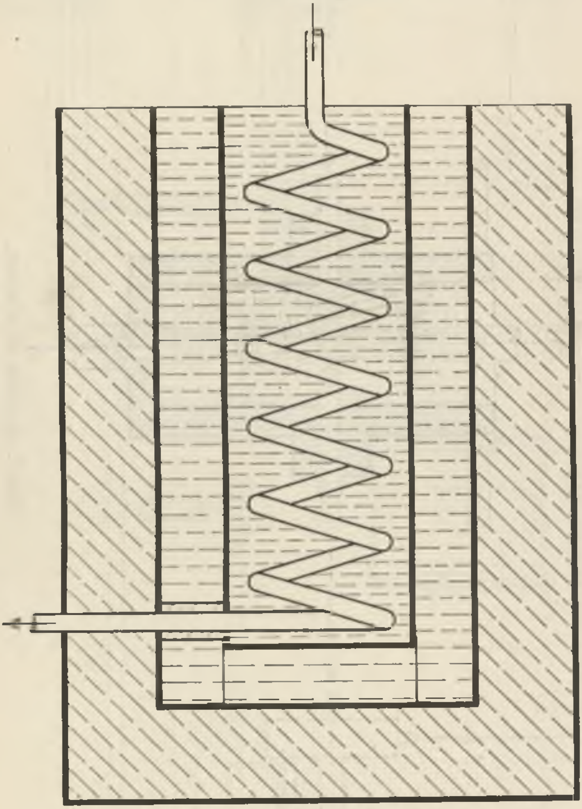

Fig. 4.—Cooler for Lower Temperatures.

The heating and cooling equipment, designed to produce a uniform temperature over the gauge length of the specimen and to maintain the temperature constant during the test, was arranged for the use of a liquid heating or cooling medium. The arrangement is shown in Fig. 3. The test-piece, screwed into two extension holders and with two extensometers clamped to it, is placed in the well-insulated vessel filled with the fluid,—oil for hot tests, and petrol, pentane, or methyl alcohol for tests at low temperatures. The bath medium circulates during the whole test in the direction indicated by the arrows, and its path is as follows: impelled by a motor-driven centrifugal pump, the fluid first passes through a helical copper tube in a cooling box, which is filled with a mixture of salt and ice, or of acetone and CO_2 in snow form for tests at medium low temperatures down to — 79° C. The arrangement for cooling the liquid to lower temperatures is shown in Fig. 4. The copper helix is placed in a vessel filled with a mixture of petrol and methyl alcohol, the freezing point of which corresponds with the desired testing temperature. This vessel is placed in another, containing such a quantity of boiling air as is necessary to keep the mixture of petrol and methyl alcohol partly frozen. The bath medium, entering the vessel containing the specimen, passes into perforated annular tubes encircling the ends of the specimen, where loss of heat or cold occurs by conduction through the extension holders. Flowing thence along the test-bar, the fluid is drawn off through a ring tube in the middle, and commences its circuit afresh. For heating purposes the copper coil is arranged in an electrically heated oil-bath. Thus the temperature of the specimen can be adjusted and kept uniform by regulation of the velocity with which the heating or cooling medium is circulated, having regard to the temperature of the secondary bath and to the value and fluctuations of room temperature.

In order to *determine the temperature* of the specimen and its relation to the temperature of the bath medium, nine thermocouples were used. They were made up of the test-bar itself and Constantan wires of 0·5 mm. diameter, soldered to the specimen in small annular grooves of cross-section 0·5 × 0·5 mm. All the thermocouples were calibrated before use. The temperature of the bath medium was measured with calibrated thermometers in the middle of the test-bar. Some of the results thus obtained are shown in Fig. 5 for bath temperatures of 85·5° and 161·5° C. The maximum difference between the temperature of the bath medium and the lowest temperature of the specimen within the gauge length was not more than 1 per cent. The same good distribution of temperature was obtained at low temperatures.

In preparing a specimen for testing, identification numbers were stencilled on the ends. The specimens were then kept in an oil-bath electrically heated, or in a bath of methyl alcohol at low temperatures, for a period of 110 hrs. at the test temperature, which time should have been long enough to render the condition of the specimen practically stable, so that no further change of structure would take place during the test. After placing the specimen, with the extensometer clamped to it, in the testing machine, and after the proper temperature had been reached and had remained absolutely constant for 1 hr., stress–strain data were obtained, starting from an initial stress of 1 kg./mm.^{2}, by applying increments of load corresponding with an increase of stress of 1 kg./mm.^{2}. When the deformation was seen to have become practically constant—sometimes after a period of 2 hrs. at the higher temperatures—the readings of deformation were made, the load being taken off, and the permanent deformation determined under only the initial load of 1 kg./mm.^{2}.

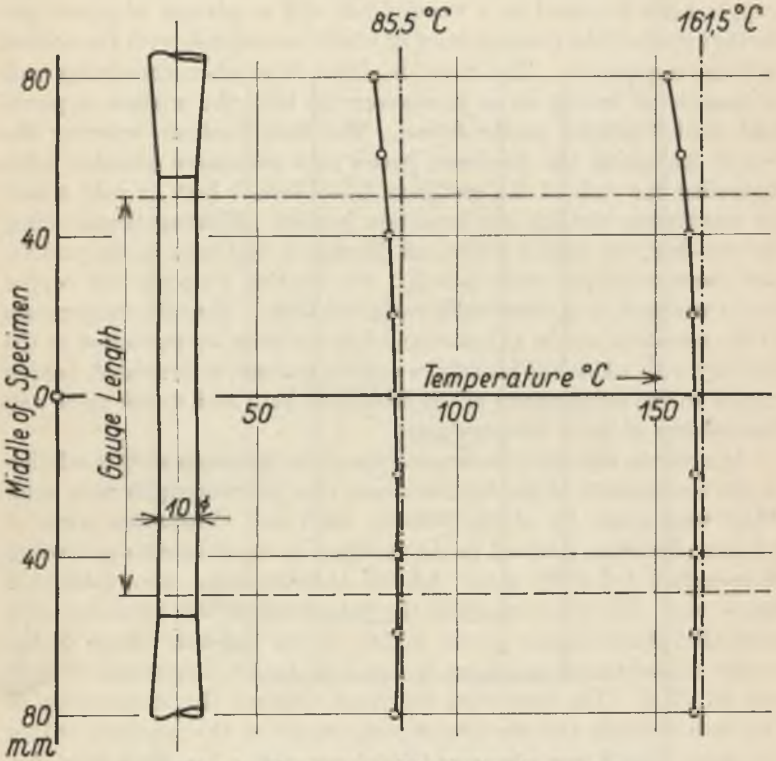

Fig. 5.—Temperature Distribution Curves.

Results and Discussion.

Looking over the data already published on the influence of temperature on the modulus of elasticity, we find only a small number of experiments made on pure metals, and only a few of these on single crystals. The latter are scarcely applicable to polycrystalline quasiisotropic specimens without further transformation. The results given for polycrystalline specimens show no uniform behaviour of the different materials. Three main types of formula are given by several authors, by which the relation between temperature and modulus of elasticity should be expressed. First, a logarithmic law as assumed by W. Widder,[1] or in another form proposed by J. P. Andrews.[2] Secondly, an exponential law, given by H. M. Dadurian [3] and in a similar form by Perret.[4] Thirdly, a linear function, as published by R. L. Templin, C. Braglio, and K. Marsh.[5] None of them has general validity. They agree very well in many cases, but show remarkable differences for other materials. Apart from this, the results obtained with pure metals cannot, in any case, be applied to alloys. It therefore appeared necessary to make individual determinations of the influence of temperature on the modulus of elasticity for the various alloys.

The results obtained in the experiments dealt with in this paper are shown graphically in Fig. 6. The elongations caused by the various increments of stress were plotted against the stresses. From the average value of the measurements, when the stress–strain curve was first observed to be a perfectly straight line, Young's modulus was calculated. The curves drawn through the points thus obtained show very clearly that the change of the modulus of elasticity varies greatly for the different alloys. In general, it increases with decreasing temperature, but not regularly, especially in the higher range of temperatures. Most of the alloys show a remarkable downward turn above a critical temperature, which is much lower than the temperature at which noticeable loss of strength or hardness is determined by common methods of testing. In consequence of a disturbance of the equilibrium between the respective phases, a relatively small elevation of temperature causes a loss of strength and of resistance to deformation. This is particularly the case in alloys in which, as a consequence of quenching, there is an unstable equilibrium between many of the phases.

Especial attention should be given to the magnesium alloys Elektron, and to the aluminium alloys Silumin and Scleron. There are only narrow limits of temperature between which a regular change of Young's modulus occurs. But within these the author believes an exponential formula to represent the actual conditions at least as well as the logarithmic equation mentioned above. Examining the average curve given by Templin in the paper [5] cited, we might be inclined to regard the results as being better represented by a smoothly curved line than by a straight line. Hence the following formula was assumed to be applicable, and the factors were determined:

$$E_t = E_{20}[1 - \alpha(t - 20) - \beta(t - 20)^2]$$

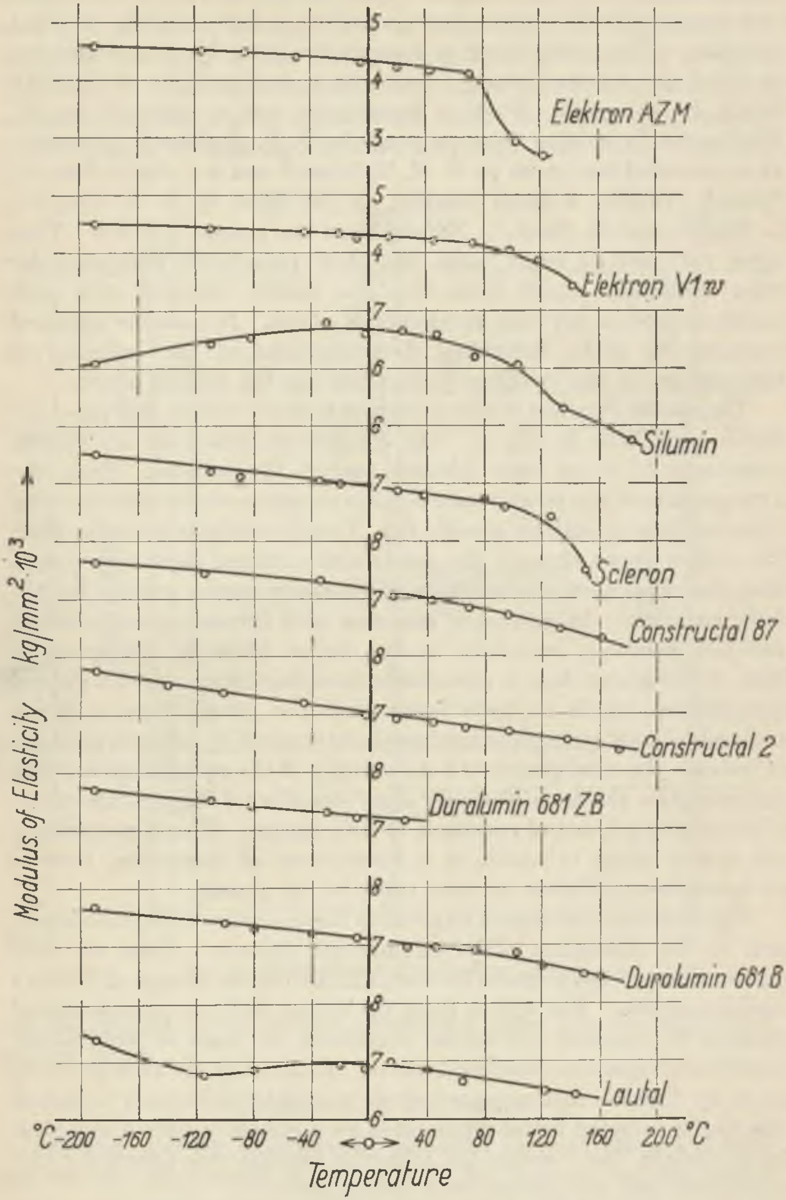

FIG. 6.—Influence of Temperature on Modulus of Elasticity.

where E is Young's modulus of elasticity in kg./mm². (E_t at the temperature $t°$ C. and E_{20} at 20° C.)
t is the temperature of the test, in ° C.
α and β are factors to be determined by experiment for each alloy individually.

The values for E_{20} and α and β are given in Table I. For several alloys the curve is practically a straight line, and in this case the factor β becomes zero. As remarked and explained above, the formula cannot be applied generally, and the limits of temperature are noted in the last column of Table I.

TABLE I.

Alloy.	Modulus of Elasticity. E_{20} kg./mm².	Coefficients of Temperature.		Applicable between the Temperatures.	
		$\alpha \cdot 10^{-4}$.	$\beta \cdot 10^{-7}$.	+ °C.	− °C.
Duralumin 681B	7050	4·05	...	110	190†
Duralumin 681ZB	7180	3·62	...	25*	190
Scleron	6880	4·42	...	85	190
Silumin	6650	4·11	41·5	80	190
Constructal 2	6950	5·55	...	140	190
Constructal 87	7100	5·61	9·47	100	190
Elektron AZM	4270	6·18	1·45	75	190
Elektron V1w	4280	4·19	8·45	80	190

* Not investigated at higher temperatures.
† Lowest temperature applied.

Special reference may be made to the lines for the alloys Silumin and Lautal, for which a clear maximum value exists at a temperature of about −20° C. Both lower and higher temperatures cause a decrease of Young's modulus. There is little doubt that the behaviour of these two alloys is caused by the content of silicon. The re-increase for Lautal at yet lower temperatures is probably a consequence of alloyed copper. Microscopic examination shows no alteration of structure.

Since no generally acknowledged definition exists for the elastic limit, there is some difficulty in justifying the selection of permanent elongation in determining the elastic limit. Hence, for the elastic limit the stresses corresponding with three values of permanent elongation, 0·001, 0·01, and 0·03 per cent., were determined. Using as abbreviation for stress σ kg./mm.² the elastic limit in the next figures is written thus: σ 0·001, σ 0·01, and σ 0·03. Very small elongations of the order of magnitude of 0·001 per cent. can be determined with sufficient accuracy only if the temperature can be maintained absolutely constant during the whole time of the test. This was possible at elevated temperatures, but not with the same accuracy at low temperatures, and here the elastic limit as given by permanent elongations of 0·01 and 0·03 per cent. was determined. It is believed that the shape of the curves cannot in any case be attributed to errors of temperature, and no test data were adopted which could not be determined with an accuracy of 1 per cent.

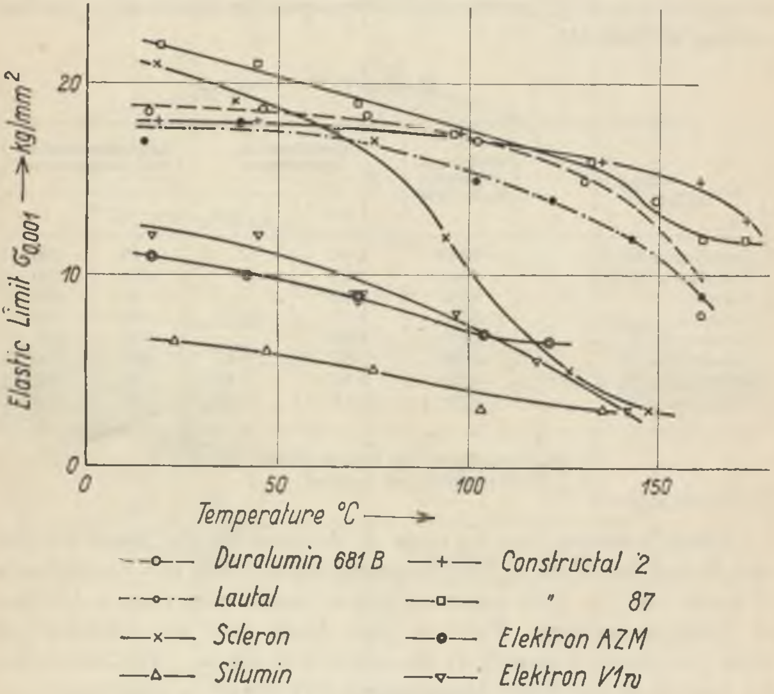

FIG. 7.—Elastic Limit σ 0·001 at Elevated Temperatures.

The results are plotted in Figs. 7 and 8. These curves indicate a behaviour of the elastic limit, similar to that of the modulus of elasticity, and some materials are found to be very sensitive at elevated temperatures.

In two earlier papers [6, 7] the effect of temperature has been determined on the mechanical properties which are characterized by a larger permanent deformation, viz. yield point, ultimate stress, and reduction in area. With elongations, which lie considerably above the elastic limit, no further decrease in the accompanying stresses was observed at low temperatures, as, for example, is the case with the elastic limit

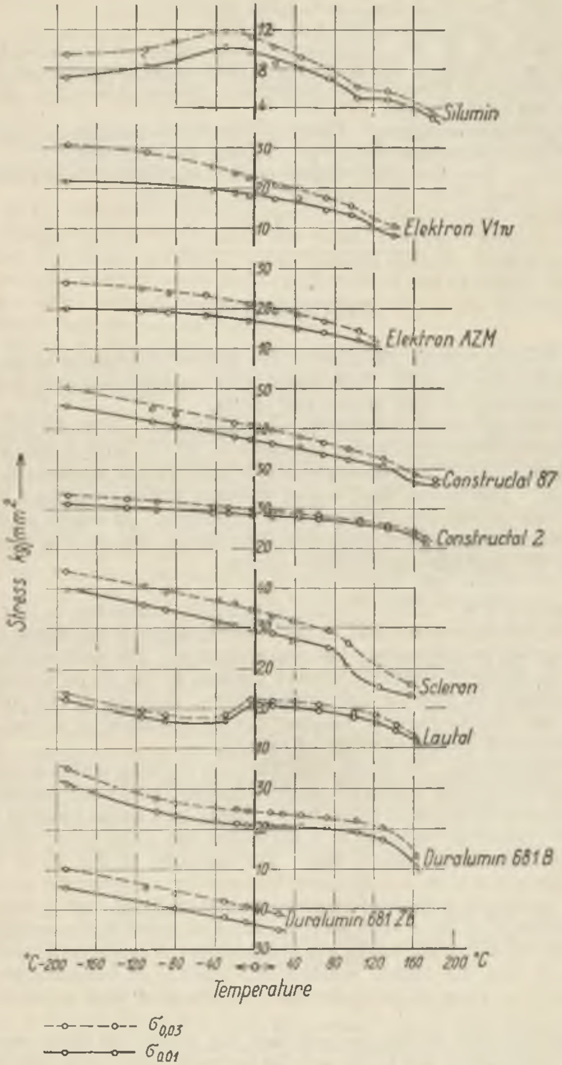

FIG. 8.—Elastic Limit σ 0·01 and σ 0·03 at Various Temperatures.

and modulus of elasticity of Lautal and Silumin owing to the increased hardness produced by falling temperature.

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[6] F. Bollenrath and Joan Nemes, "Über das Verhalten verschiedener Leichtmetalle in der Kälte," *Metallwirtschaft*, 1931, **10**, 609–613, 625–630.

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DISCUSSION.

Mr. H. Sutton,* M.Sc. (Member): We are very fortunate as an Institute to receive this paper from Dr. Bollenrath, who has made a special study of the modulus of elasticity of light metals and alloys.

Fig. 6 is of particular interest to me personally. A slight maximum is shown on the curves for Silumin at about − 20° C., and a similar one for Lautal at about −20° C., and those two alloys both contain appreciable amounts of free silicon. The Lautal used was of the type which contains a little more than 4 per cent. of copper and 2 per cent. of silicon. It would be of interest to know whether other alloys containing free silicon also show a maximum at − 20° C. on the modulus–temperature curves.

Dr. J. McKeown,† M.Sc.: I am particularly interested in this paper as I am engaged, at the present time, in the determination of the elastic properties of some materials at moderately low temperatures. The accurate determination of the modulus of elasticity always appears to me to be a very difficult matter, especially at high or low temperatures, because of the difficulty in controlling the temperature or keeping the temperature of a test-specimen absolutely constant during the time of testing.

In this investigation, Dr. Bollenrath has been working with materials which have comparatively low limits of proportionality, and such materials often have very high coefficients of expansion. Hence any slight gradual change of temperature—either an increase or a decrease—can have a very considerable effect on the slope of the elastic line. For instance, in Fig. 6, in the curve for Lautal there is a kink, a maximum followed by an apparent minimum, at − 110° C. Assuming a limit of proportionality of 10 kg./mm.^{2}, and a coefficient of expansion of 25×10^{-6} per ° C., the low point in the curve could be accounted for by a gradual fall in the temperature of between 2° and 3° C. I should like to ask the author whether his control of temperature at, say, − 110° C. was so close as to make him certain that that point was a low point.

I should also like to inquire whether the points in those curves were verified by duplicating the tests, or whether each point is simply the result obtained from one test-specimen.

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

Dr. C. H. Desch,* F.R.S. (Member of Council): There is a question of terminology which I should like to raise. On p. 265 the author remarks that "Since no generally acknowledged definition exists for the elastic limit, there is some difficulty in justifying the selection of permanent elongation in determining the elastic limit." The term "elastic limit" has an important theoretical significance. It means the stress at which the first non-elastic deformation occurs. Whether it is ever possible to measure that stress is another question, but in tests of this kind I think that it would be better to abandon the term "elastic limit" altogether, and to speak definitely of a "proof stress." It is a proof stress which is actually measured, and the use for it of the technical term "elastic limit" causes a great deal of confusion when discussing the theory of elastic deformation.

Dr. A. G. C. Gwyer † (Vice-President): Dr. Bollenrath's paper bears the impress at every turn of very careful and valuable work. I had a doubt when I heard what Dr. McKeown said. I had thought that the details for the temperature control generally were rather well worked out to avoid differences in temperature, but I had not realized that such a very small difference in temperature would have such a very large effect.

There are one or two questions which it would be interesting if the author could deal with in his reply. I think that in all work of this kind the details of the hot- and cold-work to which the bars have been subjected should be placed on record. It is not quite clear what was done in this particular case.

Another small point concerns the method of fastening the Constantan couples to the wire so as to avoid local overheating. The author says that they were soldered. If he has any figures for the tensile strength of the alloys throughout the temperature range, it would add to the interest of the paper if they were included. The only point about which I am a little doubtful concerns the higher temperatures, and is in connection with the question of creep. I do not think that due allowance has been made for that. It seems that every care was taken to bring the alloys up to the desired temperature before the test was carried out, but the question of creep is of great importance, and appears to have been ignored.

With regard to the temperature range, Dr. Bollenrath states that he took his highest temperature as 180° C. because the resistance of aluminium alloys which have been improved by natural or artificial ageing is in many cases impaired by subjection to temperatures of this order, and, presumably, higher. I would like to point out that in internal combustion engines—and I am thinking in particular of the piston and connecting rods—the average working temperature would be 250°–300° C., and it is well known that aluminium alloys stand up everlastingly at those temperatures. It would be wrong to have the idea that 180° C. is about the highest temperature at which these alloys can safely be used.

Professor Dr. G. Sachs (Member): May I ask what are the words in German which correspond with the English term "proof stress"? We have a term for "critical stress." Is that the same?

Dr. W. Rosenhain,‡ F.Inst.Met., F.R.S. (Past-President): That is not the same thing. I do not think that there is an exactly equivalent term in German for "proof stress." The German usage is to speak of it as the "0·1 Streckgrenze."

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‡ London.

CORRESPONDENCE.

The Author (*in reply*): I am very much indebted to Mr. H. Sutton for his remarks. I am at present engaged in experiments with aluminium–silicon alloys to find the cause of the peculiar behaviour in the cold of these alloys containing free silicon. I hope that dilatometric study will afford an explanation.

Referring to the remarks of Dr. McKeown, I agree that there are many difficulties in controlling the temperature and keeping it constant to such a degree of accuracy that measurements can be made of the small deformations involved in the determination of the modulus of elasticity; but I think that by the arrangement used these difficulties have been overcome. For the determination of the elastic limit—and here I refer also to the remarks of Dr. Desch respecting the definition of the elastic limit—I consider that the accuracy obtainable with the Martens extensometer should be acceptable, unless measurements could be made to a higher degree of accuracy with some new and improved apparatus. This limit of accuracy is 0·001 mm. for a gauge-length of 100 mm. For an assumed variation of temperature of 1° C. an aluminium bar 100 mm. long would alter in length by about 0·0024 mm. The accuracy with which the temperature could be controlled was 0·1° C. at a test temperature of 100° C., hence the degree of accuracy is given, with which the permanent elongation of 0·001 mm. has been determined. The points plotted in Fig. 7 do not show such smooth curves as in the results obtained for greater permanent elongations, where the deviation caused by an uncontrollable change of temperature was about 1 per cent. of the average value. Not all the points given in the curves are average values of several tests, but many of the experiments, particularly those with alloys which show a peculiar behaviour, have been carried out three or four times, and one may therefore assume that none of the effects shown is due to irregularities in the structure of the alloys.

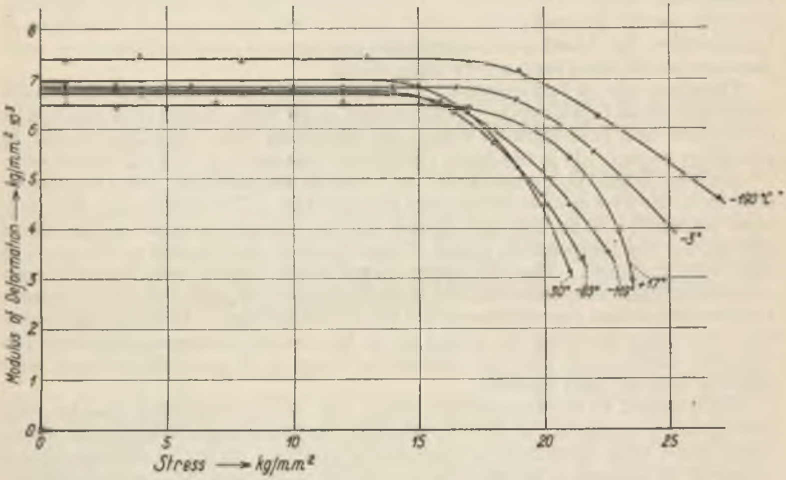

Fig. A.—Modulus of Deformation–Stress at Various Temperatures for Lautal.

The extensions, which were produced by a change of temperature during an experiment were added to or subtracted from the elongations due to the stresses.

In this way the influence of variations of temperature should have been compensated.

Figs. A shows the relation between stresses and modulus of deformation and Fig. B that between permanent elongations and stresses for the aluminium-alloy Lautal. The modulus of elasticity is identical with the constant part of the modulus of deformation. This curve proves the usefulness of the results found.

If, during the test, a loss of temperature of 2° or 3°, as assumed by Dr. McKeown, had taken place, smooth curves could not have been drawn through the plotted points. Owing to the large thermal capacity of the apparatus the temperature could not alter rapidly enough between consecutive readings to give a difference of 2° or 3°.

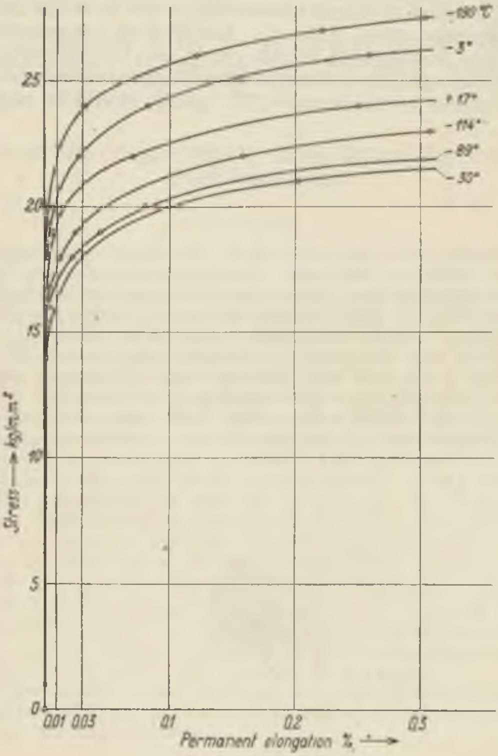

FIG. B.—Stress–Permanent Elongation at Various Temperatures for Lautal.

I agree with Dr. Desch that the term "proof stress" is preferable to "elastic limit" as an indication of the stress by which an elongation of 0·01 or 0·02 per cent. is produced.

To Dr. Gwyer I may reply that the nine thermocouples mentioned in the paper were used only for investigating the distribution of temperature on the test-pieces and its relation to the temperature of the bath medium. After the conditions for correct distribution of temperature had been found, thermocouples were fixed at the conical ends of the specimen only. During this operation the rest of the specimen was well cooled. Owing to the good thermal conductivity of the materials investigated, overheating of the specimen within the gauge-length could not well occur. Subsequently, in the later experiments, the temperature of the end of the specimen and of the bath medium was observed and regulated so that no greater difference than 1 per cent. occurred.

Finally, I do not think that age-hardened alloys, for which thermo-dilatometric phenomena indicate a rapid precipitation of the hardening components from supersaturated mixed crystals between 190° and 220° C., and for which nearly the whole effect of thermal hardening is lost again at 250° C., can be used advantageously above 180° C. Above that temperature unrefined alloys of the type investigated in this paper, or other alloys in the cast or wrought condition, especially developed with a higher resistance to deformation at high temperatures, as for example " Y "-alloy, should be used.

THE TESTING OF CASTINGS

OPENING ADDRESS FOR A GENERAL DISCUSSION HELD AT THE ANNUAL MEETING OF THE INSTITUTE OF METALS, MARCH 10TH, 1932

By WALTER ROSENHAIN, D.Sc., F.Inst.Met., F.R.S.,
Past-President.

Synopsis.

The paper summarizes some of the principal points under discussion in regard to the testing of castings. Attention is confined to what is termed specification testing and control testing, leaving aside investigatory testing. Ideal methods of non-destructive testing being as yet unavailable, the application of the usual mechanical tests to castings is considered. The use of actual castings, or pieces cut from them for such tests, or the alternative use of specially cast test-bars, is considered in view of the fact that the properties of castings frequently vary from place to place in the same piece. The author favours the adoption of a separately cast test-piece, the use of small samples cut from actual castings being reserved for investigatory purposes. The use of chill-cast and sand-cast test-bars is discussed with special reference to the forthcoming adoption of a standardized sand-cast test-bar for the light alloys of aluminium. Reference is also made to the difficulty of determining small percentage elongations; and the author's suggestion that the practice followed in cast-iron testing of using bending tests in which deflection is measured as a means of testing ductility, is described. Reference is also made to the discussion on the Testing of Cast Iron which took place at the Zurich Congress of the New International Association for Testing Materials; and the author's summary of that discussion—prepared by him as Chairman—is given as an appendix to the paper.

In conclusion, the author discusses the value of tensile testing and the desirability of improving methods of testing in the interests both of the user and the manufacturer.

The testing of castings presents many difficult problems which are of importance both to the founder and to the engineer. At the present time the whole question is of particular interest because it has been the subject of much discussion both in connection with the proposed revision of certain British Standard Specifications and also in relation to the testing of cast iron. The latter question formed the subject of a particularly active discussion at the Zurich Congress of the International Association for Testing Materials. No apology is required for including the subject of cast iron in the present discussion on the testing of castings, since the problems are, in many respects, identical. A general discussion of the subject at a meeting of the Institute of Metals should prove helpful to all concerned with these questions, since the manufacturer of castings, the user of castings, the scientific investigator, and those engaged professionally in testing are all interested, and there is probably no gathering where all these groups can meet on more even or more friendly terms than at the present meeting.

Before we consider the various possible methods of testing, it is desirable to define the purposes for which tests are to be carried out. Of these purposes probably the widest and most important is that of ascertaining whether a given delivery of castings meets the requirements of a specification. This may be called reception or *specification testing.* In addition, we have a type of testing, also for immediately practical ends, which is applied for the purpose of enabling the makers of castings to maintain the requisite quality. This type of testing, where it is employed, may be described as *control testing.* Finally, there is a third type of test which is made for the purpose of investigation, most frequently in order to ascertain the qualities of new materials or the effects of new processes or methods of production or treatment. In addition, there is also the occasional necessity to investigate the causes of failures which may occur either during manufacture or in service. This type of testing may be described as *investigatory.*

In the present discussion attention may well be concentrated upon the first two types of testing, since for investigatory purposes many special methods may become applicable which are not of such general interest and importance as those which have to be employed day by day in manufacture and reception.

The requirements of reception and control testing are very similar, and the possibilities of the methods which can reasonably be employed are limited by the need for simplicity, cheapness, and speed. The tests specified and the methods used for carrying them out must not add unduly either to the cost of the material or to the time required for delivery. On the other hand, the tests should be, if possible, such that they give an adequate insight into the quality of the castings and assure to the user the necessary degree of strength, ductility, and other properties which he may require. It is the difficulty of reconciling these two types of requirements which gives rise to the divergence of opinion and widely differing methods which we have to consider in the present discussion.

An ideal test should be capable of being quickly applied to every casting without injuring it in any way. At the same time, it should give full data in regard to the strength and quality of the material.

Obviously no such method of testing is yet available, but it must not be supposed that the development of some such test is entirely outside the bounds of possibility. In the case of magnetic materials such as heat-treated steel forgings or stampings, it has now become possible to apply rapidly and certainly to every piece produced a test which will readily reject those with properties which fall outside certain narrow limits. Some attempts have been made to develop magnetic methods of testing non-ferrous alloys, but although some promising results have been obtained, the development has not yet been carried far enough for practical application. It would not be surprising, however, if in the future some means of investigating the quality of a piece of metal, even of non-magnetic non-ferrous metal, could be found which would make it possible to examine every individual casting in a very short time. In this connection brief mention may be made of the use of X-rays in examining castings. Two methods of utilizing X-rays are available. One consists in passing a sufficiently powerful beam through the casting with a view to discovering cavities or unsoundness. This is much too slow and expensive a process to be used in routine practice, and its application must therefore be confined either to the examination of very important castings or particularly important places in special cases, or to the study of methods of casting directed to the end of eliminating the occurrence of serious internal defects. X-rays have been successfully used for both purposes, but cannot be regarded as suitable for routine commercial use at the present time. The second method of using X-rays which has found such wide application in the scientific study of the crystal structure of metals and alloys makes it possible to form estimates of the size and predominating direction of crystals in a given piece of metal. Again the application is not of a nature which could be used for routine purposes, and must still be regarded as limited to investigatory work.

Another method which may be mentioned in this connection consists in determining the density of an entire casting, as, for instance, by weighing first in air and then in water or other liquid. By this method the occurrence of unsoundness can readily be detected, and it might be possible to develop means for making tests of this kind which would render them applicable in practice to castings of moderate weight. In cases where the absence of unsoundness is of sufficient importance, this method of testing, which, it should be noted, is non-destructive, might well be applied. It is in use to a limited extent in certain industries at the present time.

Turning now to the more familiar types of testing which are concerned with what we describe as the mechanical properties of a casting or of the material of which it is made, there are broadly two questions that have to be answered. The first is what type of sample are we to use? and the second what type of test is to be applied? Since the type of test necessarily depends on the type of sample, we may perhaps consider the question of the sample in the first place.

Since the engineer naturally desires to know the properties of the casting which he actually uses, it would at first sight appear rational that we should test one or more actual castings out of those which are to be supplied. There are, however, difficulties in the way of carrying out this apparently simple and rational method. Where the castings are small and supplied in considerable numbers, the sacrifice of a certain percentage of individual castings for testing purposes is quite feasible. On the other hand, where the castings are large and supplied either singly or in small numbers, such a procedure is out of the question. Further, the shape and size of castings, in many cases, render them unsuitable for use for mechanical testing unless sample pieces are cut from them. This is frequently a laborious process, and, in order to avoid it, the practice has been adopted in many industries of casting special test-pieces either attached to one of the castings under production or cast separately.

The use of a separately cast test-piece, whether attached to the main casting or not, has been severely attacked in certain quarters, especially in France, on the ground that the engineer user is not really interested in the properties of a specially cast test-piece, but only in the properties of his actual casting. Whilst this is, at first sight, a logical attitude, it is largely untenable, and for this reason—the castings as such cannot really be said to have mechanical properties, since such mechanical properties as tensile strength, hardness, elongation, &c., may differ widely from one part of a casting to another. Every founder is familiar with the fact that in the great majority of materials those parts of a casting which have a thin section, and therefore cool more rapidly in the mould, are harder and stronger than parts having a thick section which undergo more gradual solidification. Further, unless a casting is particularly designed and very skilfully made, there is a risk that, owing to "drawing," one part of a casting may become sound and strong at the expense of a neighbouring part, which is left porous and weak. There is also the fact that, owing to variations of detail in melting or casting temperatures and other factors, the properties of one casting may differ appreciably from those of another of the same type and series.

In view of these facts, it must be realized that even if a sample is cut from one of a series of similar castings, or even if an entire casting could be tested, the test still remains that of a sample, and to that extent does not differ appreciably from the testing of a specially cast sample, provided that the latter has a cross-section which may be regarded as reasonably representative of that of the casting itself. It is this consideration which appears to weigh conclusively against the demand for tests made on the casting itself or on samples cut from it, so far as reception testing is concerned.

In reply to this view it may be said that the engineer requires to know the strength of the material which he uses as it actually exists in various parts of his casting. This is, no doubt, true, but the information cannot and need not be obtained afresh every time a batch of castings is supplied and accepted. If the engineer has before him data of the strength and other properties of different parts of a typical casting of the kind he is considering, properly correlated with tests made on separately cast test-pieces of suitable size from the same metal as the casting in question, he has all the information which can reasonably be demanded. Given satisfactory foundry practice and supervision, the strength and other properties of the casting will be reasonably proportional to the strength and other properties as found in the separately cast test-pieces of the same metal.

This correspondence can, if desired, be further checked by the use of an indentation hardness test on any desired number of castings and almost any desired number of points. If the casting shows hardness or indentation numbers which are satisfactorily close to some previously determined standard values, and are also in proper relation to the hardness numbers of the separate test-pieces, it will be safe to conclude that the properties of the casting will bear the normal and previously ascertained ratio to those of the separate test-piece. Such a method of using indentation hardness tests for closely correlating the casting to the test-bar has been extensively investigated by Dubi in Switzerland, who has found it useful and reliable. Some fairly obvious precautions are required. It must be realized that a few hardness tests can give no guarantee of soundness and good quality of the casting as a whole. For assurance on that vital point, good foundry practice and careful inspection are the best safeguards. Care must also be taken that the hardness of the casting is not locally affected—at the points where it is to be tested—by the use of chills or other means. Finally, in making indentation tests, it should also be borne in mind that in some castings the crystal structure is apt to be coarse, so that very small indentations may give irregular results.

Where the engineer is concerned in detail with the strength of his casting in regard to any particular system of stresses, that is a matter for investigation, the results of which can be readily correlated with the results of tests on appropriate separately cast test-pieces. It would seem to be entirely a mistake from the practical and economic point of view to require tests on a number of pieces cut from actual castings in connection with each delivery when the necessary information can be obtained by the methods outlined above. For the purpose of obtaining such information in the first instance, however, and also for investigating the properties of a casting which has failed, the cutting of test-pieces from an actual casting is essential. Where a case of failure has to be investigated it will not as a rule be possible to obtain separately cast test-pieces. For many such cases, however, the test-pieces which can be obtained from different parts of the casting will necessarily be of very small size. For testing these very small specimens, the French investigators who have occupied themselves with this question, including Portevin and Guillery, have done very valuable work in perfecting special testing machines, notably for the application of the shear test. For a time they advocated the general use of these small samples for the reception testing of castings. A full discussion of the subject at the Congress of Zürich, to which reference has already been made, clearly showed, however, that the consensus of opinion among the testing engineers and metallurgists of the world was strongly against the use of these small test-pieces cut from the castings themselves, and definitely in favour of the use of specially cast test-bars. The author had the privilege of presiding over this discussion and was called upon to summarize its result. This summary is reprinted as an appendix to the present paper.

If we accept the use of specially cast test-pieces we have to decide how they should be made. The first question is the old one, whether the test-pieces should be " cast-on " or separately cast. In favour of the " cast-on " test-pieces there is, it seems, only one serious argument—that the casting itself affords a guarantee that the material of the test-piece is derived from the same cast of molten metal as the casting itself. This identity of origin, however, is sometimes interpreted as meaning " identity of quality," but such identity is by no means certain. Where the " cast-on " test-piece is merely a relatively small projection on the surface of a large mass of metal in the casting, identity, or at all events close similarity with the material of the adjacent portions of the casting, is no doubt secured, but the instances where this condition can be fulfilled are relatively few. In the great majority of cases where castings of small or moderate size are concerned, the test-piece constitutes a very considerable projection from the surface of the casting, and may be attached to it only by a thin runner or gate. In such cases the rate at which the test-piece cools may be very different from that of the casting, although one will be influenced by the other—so that anything like a standard rate of cooling of the test-piece cannot be secured. Further, it is quite possible, by the use of chills or other moulding and casting devices, to secure accelerated cooling of the test-piece. There is also the further consideration that by skilful location of the test-piece, and the use of suitable gates and feeders, it is possible to make the test-piece sounder and denser than the casting to which it is attached—indeed, in extreme cases the casting may act as a feeder for the test-piece. It is, of course, clear that practices of this kind would not be contemplated by founders of good repute; also, adequate inspection should make their use impossible. They are, however, automatically eliminated to a great extent by the use of separately cast test-pieces, and if the latter are suitably standardized, then even the unauthorized use of chills can be entirely prevented. It would not, perhaps, have been necessary to refer to this aspect of the question were it not that the principal argument in favour of the " cast-on " test-piece turns upon a similar point—that of automatically securing the identity of the metal in the test-piece with that of the casting. If the honesty of the founder and the thoroughness of inspection can be relied on to prevent abuse with the " cast-on " test-piece, the same applies to the separately cast bar.

If the separately cast test-bar is adopted, we have to decide on the manner in which it is to be produced. Here I would like to suggest that the facility of standardization is most important. Every founder knows that in the majority of metals and alloys different results can be obtained from the same heat by casting test-bars vertically or horizontally and under different conditions as regards head of metal and sizes of gates and risers. At the present time, widely different methods in these respects are used by different founders, even when working with identical or similar alloys, and the real meaning of the requirements of a given specification therefore differs with different makers—a highly undesirable state of affairs. It is for this reason and for the purpose of securing test-bars which should produce identical results wherever made, that a chill-cast test-bar has been specified for many non-ferrous alloys. There are, of course, certain materials in which the use of a chill-cast test-bar could never be contemplated. Cast iron is obviously one of these. Even in other alloys—such as the light alloys of aluminium—where the chill-cast bar has been in use for many years, its employment has been severely criticized.

The main grounds of this criticism are that the chill-cast test-pieces give test figures which are very different from those of the sand castings for which they stand, and that these figures—and especially the statement of them in the specifications—are misleading to the engineer who requires to know the strength of his actual castings. The answer to these contentions is that the intelligent engineer-designer will surely know a great deal more about the material he proposes to adopt for a given purpose than the bare data which are included in a specification. If he does not, the fact—already mentioned above—that the properties of a casting, unless it is of the simplest shape, vary widely from one part to another—would invalidate any inferences he might draw even if the specification tests were made from test-pieces cut out of the casting itself. On the contrary, the correlation of the properties of various typical parts of a given type of casting with the test results obtained from the same alloy when cast into a standard test-bar, whether sand or chill, is a perfectly practicable and necessary thing if the casting is to be intelligently designed and used. It may, however, be pointed out that in many castings of complex shape it is extremely difficult even for the most skilful engineer to calculate the working stresses with any accuracy, nor is it usually necessary or desirable to cut down the dimensions of stressed castings to an excessive extent unless extensive experience indicates that a valuable saving of weight is possible. Even when this is done, however, the really essential point in accepting any given casting or batch of castings is to be sure that the quality of the metal or alloy used for making them does not fall below a certain well-established standard of quality. If this is secured, then good foundry practice and good inspection will ensure that the castings also do not fall below the previously accepted standard of quality. From this point of view—and I suggest that it is the most rational view of the whole question—the object of the test-piece for reception testing purposes is to determine the quality of the metal that has been used for pouring the casting. For this purpose, in a great many alloys, the readily standardized chill-cast bar affords the simplest and best means.

It has already been pointed out, however, that there are a certain number of alloys to which the chill-cast test-bar is not applicable, and recent progress in our knowledge of alloys has led to a recognition of the fact that exceptional conditions of this kind are found in a much larger range of materials than had previously been suspected. At the present time this development has taken place mainly in the light alloys of aluminium in which two distinct types of difficulty have arisen in the use of the chill-cast test-bar. The first and most general of these relates to the greater attention which is now rightly given to the gas-content of light alloy castings. In sand-castings cooled at ordinary rates the presence of gas makes itself felt—as is now well known—by the occurrence of pin-holes or other types of small cavities, accompanied by a very appreciable loss of strength and other undesirable features, such as difficulty in securing a good finish on machining. When an alloy containing sufficient gas to produce defects of this kind in a sand-casting is cast into a chill mould, however, the gas appears to be retained in solution or, at all events, it does not make its presence visible in the chill-casting and does not appreciably affect the tensile test results obtained. The consequence is that a chill-cast test-piece can no longer be regarded as affording a true index of the quality of the alloy, and the abandonment of the chill-cast test-bar in favour of a standardized sand-cast bar becomes inevitable.

A second factor of the same kind, although as yet of more limited application, arises from the phenomena of " modification " which occur mainly in the aluminium–silicon alloys. In these materials it is of primary importance that the test-piece should definitely show whether the alloy as poured into the castings was properly " modified." In a chill-cast test-piece, however, a properly modified material and one which is quite unsatisfactory from this point of view may give very similar results, whilst a suitable sand-cast test-bar distinguishes clearly between them. Here again the adoption of a sand-cast test-bar is necessary.

The principal difficulty which has hitherto weighed against the adoption of sand-cast test-bars has been that of securing standardization. Recently, however, investigations which were begun in the first instance at my own suggestion in the Metallurgy Department of the National Physical Laboratory, and have since been extended by the co-operation of manufacturers and of other Institutions, have shown that a simple form of sand-mould could be specified which can be reproduced easily in any foundry and which gives reproducible results. The details of these investigations will, it is to be hoped, be published in due course by those who have carried them out, so that I will say no more about them here than to indicate that the standard mould which has been suggested is a cylindrical bar with a conical " feeder-head " at the top, rammed in sand in a cylindrical steel tube of specified size, the bar being poured with the mould standing freely in air and inclined at a specified angle. Although intended in the first instance to meet the needs of aluminium alloys, it may prove possible to adopt a standard sand-cast test-bar of this type for a very wide range of alloys. The round test-bar can, of course, be specified of various diameters, if desired, to accord with the section of the castings under production.

The question of the testing of castings is not, however, settled when we have decided—if we do so decide—to adopt a separately-cast standardized sand-cast test-bar, since it still remains to be agreed what tests are to be applied in order to ascertain the "quality" of the metal. In non-ferrous alloys, it is conventional practice to specify as a rule a simple tensile test in which ultimate stress, proof stress, and elongation per cent. on 2 in. are determined. In the case of cast iron, whilst tensile tests are widely used, some form of bending test is also specified, with a measurement not only of the "modulus of rupture," but also of the deflection. In the case of the highly ductile non-ferrous alloys of the brass and bronze and similar types, the measurement of elongation is a sufficient measure of one kind of "ductility," and the use of a bend-test is scarcely required. It is a different matter, however, with many of the casting alloys of aluminium, in which the elongation is rarely as much as 3 per cent. I have long considered that the measurement of these small elongations on fractured test-pieces, where an error of the order of 2 per cent. is quite easily made, is unsatisfactory. None the less, the fact that an alloy does show a small degree of ductility is important in these alloys just as it is in the case of cast iron, and I have therefore recently suggested the adoption of the bend-test with a deflection measurement for ascertaining the ductility of certain cast aluminium alloys in place of the specification of any elongations lower than 5 per cent. The method of applying the bend-test to test bars of light alloys requires some investigation, which has, I believe, been begun, and I very much hope that in the near future this more satisfactory way of testing cast light alloys for a small degree of ductility may be adopted. It is, I think, a case where the non-ferrous industries have something to learn from the practice of the ferrous, and I have no doubt that there are instances of the converse.

I do not propose to enter here into the much wider question whether tensile tests, supplemented by bending tests or otherwise, furnish the best possible data as to the "quality" of a casting alloy. Since the stresses under which castings are used are frequently other than tensile, tests of this type can be regarded only as more or less conventional "tokens," but the fact that they have been in use for a very long time, and that, in consequence, the data which they have given have become correlated with lengthy experience, gives to these tests a weight which they would not intrinsically possess. On the other hand, we shall be wise if we recollect that a few tensile tests do not constitute an exhaustive examination of the properties or qualities of any material, whether cast or wrought. The argument is sometimes used that, provided that his product possesses the required mechanical properties, a manufacturer should be left entirely free as to the raw materials used, the chemical composition adopted, or the method of manufacture employed. If we could really measure, in every case, the "mechanical properties" which we actually require, this argument might hold, but in fact we do not and cannot do this. We test a few samples and rely on the uniformity of the material—and here we are entitled to require the manufacturer to use such methods and such materials as are known to favour uniformity of product. Again, in the small number of samples we examine, we test a certain few physical properties—usually tensile strength and elongation. Experience has taught us how far we can go in relying on these as a guide to the "strength" of the material for the uses to which we put it, but this correlation is limited, and we can rely upon it only where the materials are closely similar—any serious variation of composition or method of manufacture, or even of raw materials used, might introduce factors which we are unable to estimate. Considerations of this kind have frequently stood in the way of anything but the most cautious adoption of promising new alloys; they would stand in the way of the use of materials corresponding with existing specifications so far as tensile tests are concerned, but freed from all other restrictions.

These considerations, which have sometimes been lost sight of when specifications have been discussed or criticized, suggest that in order to improve our specifications, and thereby allow of the improvement of our materials, while at the same time permitting more economical methods of production, much further knowledge is needed. The improvement of our methods of testing is of first-rate importance both to the manufacturer and the user. If we can render our methods of testing more completely reliable from the user's point of view, we shall be more readily able to admit quicker and cheaper methods of production or the use of more economical raw materials by the manufacturer. At present, apart from the methods of mechanical testing which have been discussed above, we have little but chemical analysis and the determination of density that can be readily applied. Other methods of testing have yet to be developed. The use of magnetic and X-ray methods has already been mentioned, and systematic microscopic examination is also coming into use in some cases, although its possibilities have not been fully exploited in this country. The measurement of electrical conductivity is a possibility of the future; as yet it is used mainly in the scientific study of alloy constitution, but the scientific method of to-day frequently becomes the workshop method of to-morrow. This possibility also applies to other methods, such as the measurement of the velocity and intensity of transmission of sound which is being developed in our physical laboratories. Nor need the maker of castings fear these things. If they teach engineers to test his products more thoroughly, they will not necessarily lead them to make higher demands. After all, the products which industry now supplies in the great majority of cases meet the demands of service. Those demands will, doubtless, continue to rise as both our engineering and our metallurgical practice continue to improve. Progress in methods of testing, however, is likely to give the manufacturer greater freedom, since it is often found that some of the conditions on which users insist are unnecessary restrictions on the manufacturer. The close interdependence of engineer and manufacturer is nowhere more apparent than in this field of testing, and especially the testing of castings. The economic production of good castings is of importance to both, and the improvement of methods of testing is therefore a matter of common interest.

APPENDIX.

THE NEW INTERNATIONAL ASSOCIATION FOR TESTING MATERIALS.

ZÜRICH CONGRESS, SEPTEMBER, 1931.

Section A (Metals).

The Testing of Cast Iron.

The following statement has been prepared by the President of Section A, in accordance with the procedure approved by the Permanent Committee of the Association. It is intended to represent not the personal views of the President, but the best estimate which he has been able to form of the general conclusions to be reached from the Reports submitted and the discussion which took place at the Zürich Meeting. In formulating this statement, the President has had the great advantage of having before him reports, prepared at his request immediately after the conclusion of the discussion, by Messrs. Benedicks, Dubi, Pearce, and Portevin.

President's Summary.

In the Reports submitted and in the discussion upon them, two somewhat different view-points emerged. On the one hand, the use of separately cast test-bars to be tested either in tension or bending or both was advocated. This was the view of the great majority of those present, and it corresponds with present practice in Belgium, Czechoslovakia, Germany, Great Britain, Holland, Switzerland, and the United States of America. On the other hand, the use of very small test-pieces, trepanned from the actual casting and tested in shear, with a supplementary bending test also on a very small bar, was advocated by the French representatives, and this method of testing is favoured also in Italy and Spain.

Whilst these divergent opinions have not, perhaps, been entirely reconciled as the result of the discussion, a considerable measure of agreement has emerged. It has been recognized that the separately cast test-bar is the only practical means for controlling the quality of the liquid iron which is used in the production of castings. By many, it is further considered that this control is sufficient for the acceptance of the castings themselves, and that it is possible by establishing a relation, based on Brinell or other hardness tests, between the properties of the test-bar and of the casting itself, to arrive at a sufficient knowledge of the properties of the casting. With regard to the claim that the properties of the casting can be tested only by testing portions taken from the casting itself, it was pointed out that these properties vary widely in different parts of the same casting and may even vary, to a considerable extent, between one casting and another made from the same metal and to the same pattern. In these circumstances, the test-piece, whether large or small, cut from one casting out of a series, does not differ in principle from a separately cast test-piece. The only difference is that in the one case the test-piece is cut from a casting made to the same pattern as those to be accepted, whilst in the other, a simplified form of casting (test-bar) is employed. Where the dimensions of the separately cast test-bar are adjusted so as to correspond approximately with the wall thickness of the casting under test, this difference may be regarded as negligible.

On the other hand, where only a small number of similar castings are made, and it is possible to take samples from each of them, so that the uniformity of the material from one casting to another can be investigated in this way, or where it is desirable to explore the properties of different portions of the same casting, or where it is important to obtain a specially close correlation between the properties of a particular part of a casting and the results of a separately cast test-bar, the use of small test-pieces, suitable for shear testing, as advocated by the French representatives, is recognized as having very great value.

The position may be summed up briefly by saying that, in the opinions of the great majority of those who took part in the discussion at Zürich, the use of a separately cast test-bar, to be tested in tension and bending, is to be regarded as satisfactory and sufficient for the majority of industrial purposes, but that for the exploration of the properties of various parts of castings, and for the study of variations from one casting to another of the same type, and also for the investigation of castings which have failed in service, the small test-piece, cut from the casting itself, should be adopted.

GENERAL DISCUSSION *

Mr. J. B. Hoblyn, † A.R.C.S. (Member): I very much appreciate the introductory address. Dr. Rosenhain has, however, omitted the important factor of the time effect introduced by the testing of castings. The time required for density determination is not justified, and I think that the best tests are those made at the works by the men working on the castings. (The speaker showed slides illustrating gross defects in castings, and expressed the view that X-ray examination would impose too high a standard of quality for regular attainment in foundries.)

Professor Dr.-Ing. **G. Sachs** ‡ (Member) and Dr. **E. Scheuer** ‡: For the acceptance testing of castings Dr. Rosenhain recommends separately-cast pieces, emphasizing that, in consequence, only the quality of the metal as used for the casting is tested, and that for the faults originating in the actual foundry practice and the construction of the mould a suitable test is lacking. For general foundry practice this method, in itself unsatisfactory, is employed, because it is the cheapest and simplest. It has also the advantage of permitting comparison with a standard figure (strength of standard test-piece) for every alloy.

Table A.—*Comparison of the Strengths of Different Kinds of Test-Bars.*

Type of Test-piece.	Number of Samples.	Strength, kg./mm.^{2}.		
		Range.	Mean Value.	Deviation. % of Mean.
Round bar cast-on . .	43	16·0–22·8	19·9	34
Attached the whole length .	24	9·65–20·2	13·7	77
Sample from casting . .	10	9·9–19·3	14·1	65

Where, however, high demands on the quality of castings are imposed, one can and does go somewhat farther, and seeks, in some way, to test samples taken from the casting itself. True, the cast-on test-piece which is commonly joined to the casting by one or two thin runners, has little advantage over the separately cast bar. It can be almost quite as strong, and surreptitiously doctored, as the latter but projections on a suitable part of the casting, attached for their whole length and afterwards sawn off, the position of which on the casting, dimensions and method of running (position in relation to the gate, chills, &c.) are definitely fixed, give average values and limits of variation which agree approximately with those of the casting (Table A). These projections will be placed as near as possible to the most highly stressed part of the casting.

This test certainly involves more expense, and its evaluation more consideration than the separately cast test-piece; nor can it be directly related to a number of castings in the same alloy without further consideration, but it must be adjusted by the mean value derived by experience and determined for the particular casting, or similar ones. Also, one must either cast on a

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* *Note:* Some condensation of the verbatim report of the discussion has been effected but nothing essential of the speakers' arguments has been omitted.

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‡ Metall-Laboratoriums der Metallgesellschaft A.G., Frankfurt-am-Main, Germany.

single casting a number of such projections, or content oneself with the average of a number of castings as a basis for judging the whole batch. The acquiring of the data for such an acceptance test is a preliminary task for the foundry and the user to accomplish in co-operation. Instead of a definite acceptance specification, there will be obtained guiding indications, which are of importance apart from the acceptance of a single consignment and lead to improvement in the quality of the castings. It is emphasized by Dr. Rosenhain that it is not possible to rely on the properties of simple test-pieces in the case of unknown alloys. We may therefore consider more closely the relation between casting and test-piece.

From the little reliable information which exists in literature concerning the distribution of strength in castings we find that the maximum and minimum strength values of different casting alloys show a variation of the order of 1 : 1·5 to 1 : 3.* These differences are not distributed regularly, but may be found in immediately adjacent parts of the casting. Even in tensile test-bars, cast under only slightly varying conditions but without rigid standardization, variation up to 1 : 2 may be found, although by more careful work appreciably narrower limits could be preserved. It cannot, therefore, be sufficiently emphasized that, for cast even more than for wrought metal, a single test-piece is useless as evidence.

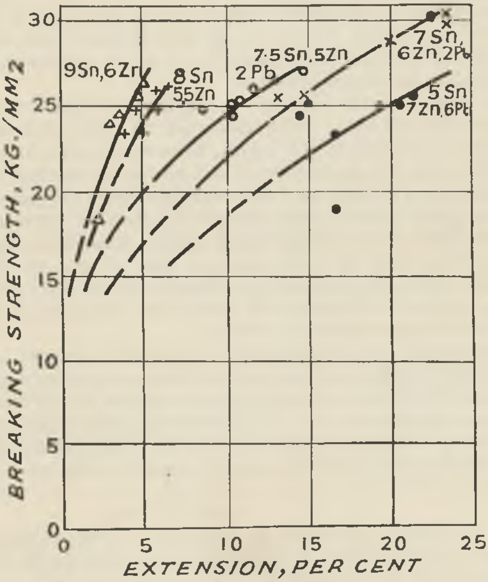

Fig. A.—Strength of Test-Bars of Red Brass (Sand-cast, with varying tin content).

The great variations in properties depend, in castings to a greater extent than in wrought metal, on local faults in the cohesion and on structural defects (draws, blowholes, fissures, slag inclusions). The tensile test, distinct from many others, is very sensitive to these defects, and, especially in the test-piece

* G. Schreiber, *Z. Metallkunde*, 1927, **19**, 456–458 ; J. Dornauf, *Metallwirtschaft*, 1929, **8**, 255.

cut from the casting, discloses the existence of defects rather than the properties of the metal itself. An illustration of this experience is shown in Fig. A, giving a summary of a series of tensile tests on bronzes. In the graph of strength as a function of elongation, apart from some exceptions, the values found for different samples of the same alloy arrange themselves about a line which corresponds with the load-extension curve. The true quality of the *material, which is expressed by the course of the load-extension curve*, is practically the same for all samples. According to the extent to which the cross-section of the test-piece is weakened by structural defects, the load-extension curve breaks earlier or later.

An evaluation of testing results on cast bars on this basis would perhaps make it possible to acquire an insight into the extent to which variations in strength are due on the one hand to defects and on the other to the true properties of the material.

The observation that structural defects play a great part in the variability of the strength of castings is in agreement with the fact that, occasionally, in quite thick sections, strength values are found which approach the properties of good samples cast in thinner sections.

In general, however, the average strengths decrease considerably with increasing cross-sectional area. The reason for this may be found, in the first place, in the rate of solidification.* This, however, is not adequate to explain the difference between the properties of test-piece and casting.

The examination of slices from large castings allows extremely small draws and pores to be made visible, more completely than by examining machined surfaces.† It is found that castings which appear dense from the examination of the surface are equally or more unsound than others, on the surfaces of which pores are distinctly noticeable. Minute fissure-like pores which are invisible on the polished surface are of much more influence on the properties of the casting than larger rounded cavities.

It has been found, by investigations on special samples approximately similar geometrically to the castings, that the influence of chemical composition, casting procedure, and heat-treatment is very similar in the model and in the actual casting (see Figs. B and C). The acceptance test in this case is the story of the whole casting. This test could, in our case, be carried out on a laboratory scale with a model casting, and the results applied, with good agreement, to actual practice.

Mr. A. H. Mundey ‡ (Member of Council): I believe that most manufacturers would not desire to have a test-piece attached to their castings, but it is often insisted on by inspectors. It is a question of a choice between the types of testing. I feel that the investigatory test must be carried out in the early stages for the information of the designer and the manufacturer. Then the acceptance test may be on the material itself as material, and not as part of the casting. I think that will be the only practical working method. On taking tests from various parts of large castings I have obtained altogether different results from the various parts. Therefore those tests were not truly indicative of the quality or the properties of the material as material, but of the strength of those particular parts. The problem as a whole requires more co-operation between the designer and the metallurgist.

Reference has been made in the paper to the weighing of castings. In the manufacture of die-castings we weigh every casting of a certain type as it comes off the machine, and we find it an extraordinarily fine method. Certain

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* See also W. Claus, *Giesserei-Zeit.*, 1928, **25**, 529.

† O. Bauer and O. Vogel, *Mitt. Material.*, *Sonderheft* **18**, 1931, 51; O. Bauer and G. Sachs, *Metall u. Erz*, 1927, **24**, 154.

‡ Technical Director, Fry's Metal Foundries, Ltd., London.

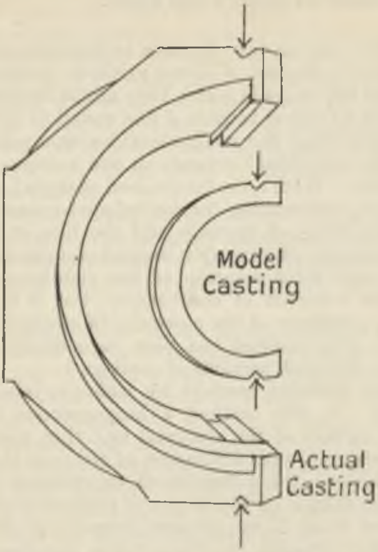

Fig. B.—Actual casting and model casting.

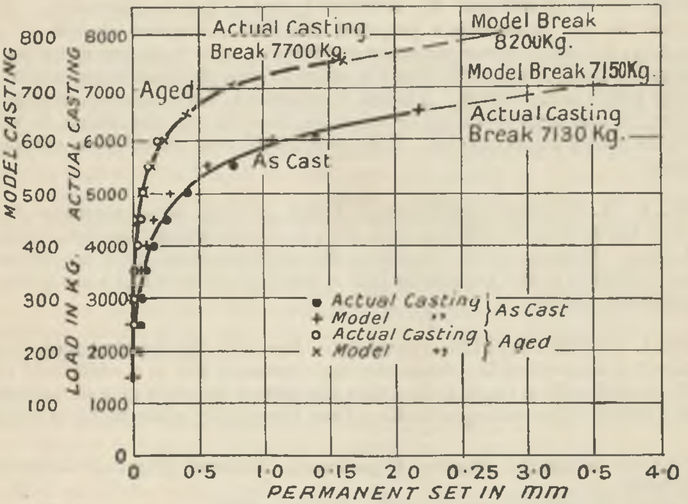

Fig. C.—Mechanical testing of castings and model castings of bronze (tin 8, nickel 2, silicon 0·5%, copper remainder).

other die-castings which we make also have to be perfectly sound, and are tested with high-pressure air under warm water.

Dr. G. SHEARER [*]: In his introduction to this discussion, Dr. Rosenhain made a brief reference to the use of X-ray methods in the testing of castings, and he mentioned the two ways in which they might be employed.

The usual method has been to pass a fine pencil of heterogeneous X-rays through the material so that the resultant diffraction pattern consists of the Laue patterns of the individual crystals in the volume bombarded, superimposed on each other. With a coarse-grained material, the pattern consists of a collection of spots surrounding the central spot caused by the undeflected X-ray beam. In the study of castings and the like, it is often found that radial streaks appear on the photographs instead of, or in addition to, the usual Laue spots. The exact interpretation of the significance of this so-called "asterism" has been a matter of controversy, but it is generally accepted that such asterism is evidence of the existence of strain and distortion in the individual crystals. This method has been successfully used to study the variation of strain in different portions of castings.[†]

There is a rather different method by which crystal distortion can be detected by X-rays. In this method a homogeneous beam of X-rays is diffracted from the surface of the material and that part of the pattern is recorded which corresponds with diffraction of the rays through a large angle (say, 140°–180°). Just as the definition of an ordinary light line spectrum depends, among other things, on the degree of perfection of the grating, so the definition of the lines in an X-ray pattern depends on the perfection of the crystals. With perfect crystals, free from strain, the lines will be sharp and well-defined, whilst the lines will broaden and become diffuse if the crystals are imperfect and under varying degrees of strain.

Engineer Rear-Admiral M. RUNDLE [‡] (ret.), D.S.O. (Member): With reference to Dr. Rosenhain's proposal that the test-piece should be cast separately, it would appear necessary for the inspector to be present when the castings are turned out of the sand in order to identify the test-piece with the castings which it represents. I think it important, when possible, to apply to a casting a test corresponding in some degree with the conditions to which it is to be subjected in service. The mechanical test should be a test of the material.

Mr. R. H. STANGER [§] (Member): I may perhaps direct attention to the fact that the testing of cast-iron, as a rule, is on specimens " as cast," without machining. If the material is tested in the machined state, there is a difference in the deflection in the transverse test. Non-ferrous specimens are generally machined for testing.

Mr. A. J. MURPHY,[||] M.Sc. (Member): Few will dispute the views on this matter of testing which Dr. Rosenhain has expressed, but in a wider field there is still undoubtedly a vague feeling that the cast-on bar does give an indication of the quality of the casting as distinct from the quality of the metal of which it

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[*] Senior Assistant, Physics Department, National Physical Laboratory, Teddington.

[†] Clark " Applied X-rays," p. 231. London: 1927.

[‡] Development Section, British Non-Ferrous Metals Research Association, London.

[§] London.

[||] Chief Metallurgist, J. Stone and Co., Ltd., London.

is made. I do not think that the cast-on bar is advocated simply because its use identifies the metal tested with the main casting.

Another aspect of this question is that it is often not possible to locate a cast-on bar in a position which will ensure that the metal there is adequately fed during solidification. Further, there is sometimes a real danger of the test-bar cavity, which was never provided for in the design of the original casting, acting as an effective dirt trap during the pouring operation. These are factors which suggest that the test results from the cast-on bar are often inferior to those which would reasonably be expected from a sample cut from the main body of the casting.

A second consideration is the possible effect of these projections, which are made by the cast-on bars, in introducing undesirable stresses in the casting by their action in restricting contraction after solidification. This may become a very important factor in certain materials, and one suspects that this feature is rarely considered.

With regard to the question of the standardization of the sand-cast test bar for light alloys, there are indications that we are now approaching a phase in metallurgical control in which it will not be sufficient simply to concentrate on entirely eliminating gas from light alloys, but I think that we shall have to face the problem of *controlling* the amount of gas in the metal. From an aluminium alloy containing an accurately controlled small quantity of gas a perfectly satisfactory chill-casting can be produced, complying in mechanical properties with the most rigid specification for that metal, and yet that same material, if tested as a loose sand bar would be rejected every time. I would suggest, therefore, that the indiscriminate application of the sand-cast bar at this stage to chill-cast work may not only debar from use material which would produce satisfactory die-castings, but may also impede progress by deterring investigators from following this line of research, namely the control of the gas content of metal to be used for complicated die-castings, in which promising results have already been obtained.

Mr. R. B. Deeley,* B.Sc., A.R.S.M. (Member): I would like to support Dr. Rosenhain's remarks with regard to the separately sand-cast test-piece, particularly in respect to the aluminium–silicon alloys. With these alloys, a certain amount of modification is obtained by casting unmodified alloy in a chill mould, and the chill-cast test-piece made from unmodified alloy would give relatively high results, whilst the casting would consist of extremely weak and brittle alloy. For specification purposes, therefore, it is absolutely essential that a sand-cast test-piece should be employed in order to eliminate the possibility of unmodified alloy being used in castings.

In connection with the relation between the strength of a cast-on test-piece to the properties of the casting itself, and to those of a separately-cast test-piece, I have found that the mechanical properties of a casting in modified aluminium–silicon alloy vary over a much smaller range than is the case with other aluminium alloys.

Mr. A. Wragg,† B.Sc. (Member): The question of the test-pieces on castings is possibly being regarded in too strong a light, in view of the fact that many castings are not the result of a calculated design, but have more or less been evolved, especially in cases where they are required in fairly large numbers, as in the motor trade. However, there must be some acceptance test, and I do not think that there is much difference between a test-piece that is cast-on and one that is cast separately, having in mind gun-metal and

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† Metallurgist, Vickers-Armstrong, Ltd., Newcastle-on-Tyne.

manganese–brass castings. There are certain objections to a cast-on test-piece with regard to location, height of feeder, method of running, question of chilling, and so on, but the same applies to a separately-cast test-piece. There are several methods which the moulder can use to vary the quality of a casting. If a separately-cast test-piece is adopted, different foundries will still produce castings of varying quality, not due to any difference in the quality of metal in the ladle, but to variations in the technique of casting.

One serious objection to a test-piece cast separately, from the production viewpoint, is the question of identification. There is also the question whether, in the manufacture of a number of small castings from a single ladle, the separately-cast test-piece is to be cast at the beginning or end of the series.

The application of X-rays, or density determination, is at the moment scarcely a practical proposition.

Dr. D. H. INGALL * (Member): With reference to unsoundness testing, and in particular "porosity" tests, there are one or two which have not been mentioned. The dye-penetration test is employed to a certain extent in America particularly for aluminium castings, where petrol containing a dye such as methyl blue is painted or spread on the side of a casting, and the other side of the casting examined for signs of penetration. In a similar test alcohol suitably coloured with picric acid, or other bright dye, is placed on the surface of a casting. The surface is then wiped dry and the casting put in a warm place, examination being made for exudation.

With regard to pressure tests, a quantitative pneumatic test has been developed by Bezzenberger and Wilkins.† A cast hollow cylinder open at one end is subjected to compressed air of specified pressure for a specified time and the amount of air permeating the casting is collected and measured.

Another hydraulic test of special application was used by Goeke and Claus ‡ in work on bronzes. This test is applicable only to the special case of a hollow cylinder. Successive thin layers are removed from the cylinder, either from the outside by turning, or from the inside by drilling, and between each layer removal the cylinder is subjected to hydraulic pressure of a specified amount. The layers are removed until leakage occurs, and the soundness of the casting is determined by the quantity of material which has to be removed prior to leakage.

There is a further interesting test, carried out by Tammann and Bredemeier,§ where coloured water was applied to castings under pressures as high as 2500 kg./cm.^{2}. Sections of the castings were then removed in a fine state by filing or turning and the amount of penetration of the dye was ascertained by quantitative determination.

Mr. GEORGE MORTIMER || (Member): The first step towards obtaining good castings is to ensure that the metal being poured into the mould is of high quality and the same quality all the time. That is precisely why we in this country tend to use a test-bar which checks the quality of the metal rather than the properties of the casting. Dr. Rosenhain has given the reasons why we have adopted, for aluminium castings, a bar cast in sand. I have nothing to add to that, but Professor Sachs' comments show how widely at variance

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* Assistant Director and Research Manager, British Non-Ferrous Metals Research Association, London.

† F. K. Bezzenberger and R. A. Wilkins, *Chem. and Met. Eng.*, 1920, **22**, 1031.

‡ Hans Goeke and Willi Claus, *Giesserei*, 1929, **16**, 153.

§ G. Tammann and H. Bredemeier, *Z. anorg. Chem.*, 1925, **142**, 54.

|| The British Aluminium Co., Ltd., London.

we are in this country with other lines of thought in different parts of the world. We particularly need international agreement on this and many other points. I myself have found, on a Committee working in Paris on an attempt to standardize test-bars for aluminium practice, the same measure of disagreement, as to whether a test-bar shall be cast integral or separate, in chill moulds or sand, and if the latter, whether cast to size or machined to size. I am emphatically for the separately-cast bar, and in the case of aluminium this should be cast in sand. Dr. Rosenhain indicated that perhaps the only advantage of the integrally cast bar lay in the question of identity of material. On that point I would suggest that it is not impossible to ram up a heat-treated "Y" alloy test-bar in a mould intended for a cheaper and weaker alloy, and so to run the casting that the bar is welded neatly to the job. I do not suggest that this would be done, but the possibility disposes of the main advantage of the integral cast bar.

As Mr. Hoblyn pointed out, the chief difficulty the founder has to compete with is the great time lag, between the time the first casting of a contract is delivered and the time the founder first hears of some small but vital defect, uncovered, it may be, at the very last stage in a long series of costly machining operations.

There are several tests employed in routine foundry practice which have not been mentioned. Sand-blasting reveals at the surface the existence of porous, open-grained material beneath, which might otherwise escape observation. Testing a casting under air pressure and immersing it in hot water is more stringent than the usual hydraulic test, where such tests are feasible. Methyl blue is more stringent still: it is only necessary to paint it lavishly on the inside of a thin-walled sump, and in a very brief time, if the metal is porous, a patch of blue appears on the outside. None of these tests will indicate the presence of the persistent blow-hole at some vital spot, and in this connection I associate myself with the references made by Dr. Rosenhain concerning X-rays. It is necessary to know the extent, the location, and the nature of the unsoundness, before one can take steps to cure it, and neither X-rays nor density measurements will give this information. Where one is dealing with a large number of small, simple parts, the X-ray apparatus can be a very useful adjunct to the foundry, but with a large aeroplane engine crank-case the position is different. Yet this is the chief field in which a reliable test would be most valuable to the founder. In practice it would pay to make a series of such crank-cases and section them for examination, rather than instal the X-ray plant and take the number of exposures necessary to locate the defect and its nature. The control tests at present devised do not prevent castings going forward which the founder would gladly scrap if he knew of their defects.

(*Communicated later.*) There is a need nowadays for a quick test for the efficacy of certain heat-treatments. Usually the Brinell hardness test on the actual casting has been enough, as a routine check, but nowadays a casting is subjected to different heat-treatments, according to the properties desired. A Brinell test may therefore be passed with ease at the expense of a vital measure of ductility.

Mr. R. Genders,* M.B.E., M.Met. (Member): There is probably wide agreement on most of the matters dealt with in the opening address; the point referring to the difficulty of testing ductility, however, appears open to criticism. The measurement of small elongations on tensile test-pieces is admittedly unsatisfactory, but it is questionable whether the information to be gained from bend tests would be much more valuable. With relatively

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* Research Department, Woolwich.

brittle materials the total deflection of the bend test-pieces before fracture is small and represents the sum of the elastic deflection (which may be about 0·2-in. for a bar of aluminium alloy, 12 in. long and 0·5 in. square), and the small amount of permanent deformation undergone between the elastic limit and fracture. This permanent deformation, representing the measure of ductility in the test, is mainly localized, owing to the concentration of stress at the point of flexure, and is probably comparable with the local elongation which occurs in the immediate region of a tensile fracture. The general elongation measured in the tensile test as a part of the total would not be reflected to the same extent in the bend test. Thus the bend test, although apparently more sensitive, gives a measure which includes elastic deformation, whilst neglecting some proportion of the ductility measurement given by the tensile test. The bend test may also be affected by local defects in the material, similarly to the tensile test. From these considerations, therefore, it is thought desirable that the addition of the bend test to those already in use should be made only when full investigation has provided proof of its value. On the other hand, the bend test has the advantages that the test can be made on the material as cast without machining, and that difficulties caused by test-pieces fracturing at inconvenient positions are avoided.

With regard to the general problem, it seems inevitable that any methods which may be found capable of determining the serviceability of castings will involve some elaboration of testing, in view of variations from one design of casting to another in the nature and extent of any unsoundness present. It appears essential, therefore, that each particular design of casting must to some extent be treated individually, apart from the mechanical tests on separately cast bars which govern the quality of the liquid metal. Density determinations are practicable with comparatively large masses, and measure the total volume of any internal cavities. For information as to the number and disposition of the cavities there is no more certain method than the use of radiography, which is much superior to that of taking numerous sections, and can now deal with castings of large size. It should be practicable, for each design of casting, to take trial castings for density and X-ray tests and to arrive, without undue expense, at a pattern complete with runners, &c., that would produce the best result under certain casting conditions, which would ultimately be specified. Apart from the immediate benefit, much useful knowledge would accrue from the correlation of accumulated results. With properly organized co-operation in the different branches of the foundry industry such a plan for the improvement of the product would appear reasonable, and the present mechanical tests could be relied on for the final reception testing.

Mr. H. W. G. Hignett,* B.Sc. (Member): We can obtain, from test-bars of a given alloy, four sets of quality figures for any one particular foundry: (1) the maximum figure which can be obtained for the alloy when cast under laboratory conditions (this will be a constant); (2) the maximum figure which this particular foundry can obtain using its ordinary equipment. In some cases this would be obtained with a chill-cast test-bar; (3) the figure obtained on such a standard test-piece as that suggested by Dr. Rosenhain; (4) a whole range of figures to be found in the casting itself. This last will vary very considerably with differences in foundry practice which are adjusted by the skilful foundryman to produce the best results. For efficient foundries the average quality of a given casting in a given alloy should approximate to a constant.

In the standard sand-cast test-bar, however, where certain of these details are definitely fixed, there is no opportunity for adjustment, although this may

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* Metallurgist, The Aluminium Plant and Vessel Co., Ltd., London.

be rendered advisable by variation in factors which it would be impossible or impracticable to standardize. For example, the heads and runners which give the best results with a gun-metal melted in a coke-fired furnace will not do so when an oil-fired furnace is employed. Although it may not be possible to remove the difference completely, it is certainly possible to reduce it very considerably and raise the lower value by an alteration in casting procedure.

It thus seems that the test-bar in which the casting conditions are left to the discretion of the founder to obtain the best possible figure for the particular alloy, will give results which are more constant and, therefore, more suitable for correlation with the properties of the casting than a sand-cast bar where certain of the conditions of casting are standardized.

As regards the modified aluminium silicon alloy, I do not think that any mechanical test is suitable for determining the extent of modification. The discrepancy between the test-bar giving maximum figures and the casting is due to defects in the latter. I would suggest that until that fundamental knowledge is available it is not advisable to standardize the casting conditions of a test-bar.

Mr. A. R. GREATBATCH *: X-rays are not particularly suitable for a general acceptance test except in the case of aluminium and light alloy castings where visual methods can be employed. For all other castings the time taken and the expense involved are rather too heavy except in very special cases, but we have found at Woolwich that in a series of castings of the same type the flaws always appear in the same region. This would suggest that X-rays could be employed as an investigatory test for improvement in the design and method of manufacture of castings.

One speaker stated that sound castings are never obtained, but our experience at the Research Department, Woolwich, has shown that it is possible to get sound castings.

(Slides were shown illustrating a casting free from unsoundness, porosity in die-castings and brass ingots, and comparative radiographs obtained by using radium and X-rays.)

The PRESIDENT: Engineers require knowledge of the strength of the various parts of the casting itself. That is essential from their point of view. The ideal method would be to break up and test one trial casting, and consider the design in the light of the results. I would then suggest the addition of a cast-on test-piece, another break-up test with this test-piece on, and, if necessary, reconsideration of its position on the casting. I feel that this can be done, and is done in certain cases where many repetition castings are required.

Dr. ROSENHAIN: I feel in a sense that I am scarcely called upon to reply at all, because I have deliberately put forward questions on which I knew perfectly well there were considerable differences of opinion.

I would remind Mr. Hoblyn that the subject on which we were intending to have a discussion was the testing of castings and not the inspection of castings. To hear Mr. Hoblyn say that he has no use for a testing machine rather astonishes me. I hear it with sorrow.

Professor Sachs' remarks were very interesting, particularly the account he gives of the care which is taken in certain German foundries to secure good castings. It is very similar to what the President suggests. The only thing in which I differ from the President is that I would like that correlation not with a cast-on test-piece, but with the separately-cast test-piece. Professor Sachs gave us some very interesting figures, but I think that they prove

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* Research Department, Woolwich.

exactly the opposite of what he was trying to show, because of the immense range of values obtained. I cannot understand why Professor Sachs thinks it worth while comparing averages taken from such highly divergent values. On the other hand, the figures which he gives seem to me to prove conclusively that one cannot correlate the results in that particular way; the variations are altogether too wide.

Several other points have been raised, but I think that the whole issue has been confused a little by not separating questions of foundry technique and inspection from that of the mechanical testing of castings, which was the aspect I principally intended to deal with. Consequently I disregard all the criticisms, implied or explicit, which suggest that I did not mention certain points.

There is only one speaker with whom I feel I must cordially disagree, and that is Mr. Hignett. I think that he has misunderstood the whole question at issue. When he suggests that the founder should be allowed to adjust his test-bar so as to get the best results, he is suggesting that we should allow the man who makes inferior metal to get sufficiently good tests out of it by any device he can use. I do not consider that reasonable, and yet that is how his proposals would be interpreted in practice. Standardization is essential, and if A can make good metal with a particular standard mould, then B is, or should be similarly capable, and if not he probably is at fault in the matter, provided that the standardization is arrived at after sufficiently careful investigation as to the proper kind of mould for a particular metal. The mould to which I referred has been standardized with a view to use with light alloys only. Whether or not it is suitable for bronzes and brasses I do not yet know, because it has not been sufficiently tried.

There is only one other point to which I want to refer, and that is Mr. Genders' interesting criticism of the suggested use of the bending test. I do not think that he is right, because although there is something in the fact that the elastic deformation of a light alloy beam will be greater than that of a cast-iron beam, I think that the actual deflection—the permanent deflection—will still be very much easier to measure than the small extension of a tensile test-piece. But there is one thing which arises out of his remarks which I think it will be possible to incorporate when we come to carry out this test after further investigation, and that is not to bend by the application of a single load, but by loads giving a uniform bending moment over the part of the beam under test, and in that way obtain the elongation (deflection) over a larger length of the test-piece than by bending under a single load. That merely requires a double head on the bending press instead of a single one, and will probably overcome the difficulty if in actual fact it proves to be as serious as Mr. Genders suggests.

CORRESPONDENCE.

M. Albert M. Portevin * (Member): I am glad to see the Institute of Metals approach the problem of the testing of castings, because this question is not only topical, but is primordial for the foundry, since it affects the progress hoped for in regard to quality and the development of the use of castings. Needless to say, the problem should be approached with scientific method, unbiased by any preference expressed by a majority opinion. It is evident that the view of the majority will be in favour of the retention of the existing methods, because of inertia. Further, opinions are influenced by considerations quite foreign to reason and scientific method; the commercial

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point of view and the possibility of influencing the results of tests are sometimes not without effect on opinion.

To determine the quality of a particular form of casting, or more generally a single casting, is to obtain by a test defined in all its conditions, a numerical coefficient classifying the strength of the casting and its behaviour in service. The reception test should fulfil these conditions. It is by the study of articles broken or rejected in service, compared with others having a good life, that the limits of the specification should be fixed. The study of the casting after use dominates therefore the whole problem of the test of the materials, and this examination after or during service can only be carried out by tests on the actual castings.

Two methods are at present advocated :—

1. The old school which considers that the properties of the casting can be determined by the testing of another piece, cast separately (casting sample).
2. A more recent school which considers that the test-piece should be taken from the casting itself or from one of a series cast in identical manner in the same metal, the comparability of the castings being verified by a so-called test of uniformity.

Whatever the procedure adopted, neither of these methods takes account of defects and internal stresses in castings. The separately-cast test-piece contains stresses and defects different from those in the casting, since it has neither the same shape and size nor the same mode of feeding, whilst in a test-piece cut from a casting, the existing internal stresses are in part released, and the defects existing elsewhere than in the test-piece are neglected. From this point of view the two methods are both open to criticism, and it will consequently be necessary, whatever be the method of testing adopted, to provide a special and individual means for dealing with defects and internal stresses, a problem that may be put aside for the time being.

The only serious objection to the method of cutting small test-pieces from the casting, is that the castings are not uniform, and that consequently the results obtained on the test-piece are not applicable to all parts of the casting, but in this respect it seems still more difficult to deduce the strength of a heterogeneous casting from that of another heterogeneous casting of different dimensions and shape, *viz.*, the separately-cast test-piece.

The heterogeneity of castings, on which these objections are based, is variable from one casting to another, and arises from the effects of factors which govern the cooling of the casting and its different parts, known as "general foundry factors." These factors are enumerated in the list below.

General Foundry Factors.

1. *Factors introduced by the metal.* Nature of the metal or alloy, the main properties concerned being the specific heat, density, thermal conductivity, freezing point, and latent heat of solidification and transformation. Changes occurring in the melt and between successive melts by loss of volatile elements (zinc in the brasses), by absorption of gas, by inclusion of oxide (Al_2O_3 in aluminium alloys) or by loss of oxidizable elements.
2. *Factors introduced by the casting conditions.* Casting temperature and speed of pouring. Mode of feeding, such as position, section (shape and dimensions), position, and number of runners. Circulation of metal within the mould. Natural or artificial agitation of the liquid metal.
3. *Factors introduced by the mould.* Initial temperature and nature of mould (heat conductivity, density, and specific heat). Porosity of mould

(liberation of gases). Thickness of mould and method of external cooling. Conditions of discharging from mould.

4. *Factors introduced by the casting.* Weight and thickness of casting (including risers and feeding heads). Extent and curvature of external surface.

5. *Factors introduced by contact between casting and mould.* State of mould surfaces, facings, contact, oxidation, separations admitting an insulating gaseous layer (unless cast *in vacuo*).

The simple enumeration of these factors shows the impossibility of deducing from their values the properties of a casting, supposing that they can be numerically defined, which is not true for the majority. These factors which govern the conditions of solidification modify the mechanical properties by acting :—

1. In every case, on the grain size, *i.e.* structure.
2. In many cases, on the uniformity of concentration of solid solutions; this depends on the speed of diffusion, the speed of crystallization, the solidification range, and the speed of cooling through this range.
3. In certain cases, on the actual mode of solidification. This happens in the case of cast iron, where it is possible, according to the values of the foundry factors, to obtain two entirely different products, white cast-iron and grey cast-iron. Since it is impossible to connect by definite relations the cooling conditions with the result of solidification (structure, &c.), or to deduce the conditions of solidification from the foundry factors, it is totally impossible to predict the mechanical properties of a casting, of whatever form and size, made from an alloy of known composition and preparation.

It can be stated, further, that the mechanical properties of a casting cannot be deduced *a priori* from those of another casting such as the separately cast test-piece. All that we know is that if we maintain constant all the foundry factors, including the size and shape of the casting, as well as the conditions of pouring, we may assume within limits, that the castings will have equal properties and a similar distribution of heterogeneity, and that the properties obtained on a small test-piece, taken by cutting always from the same point of the casting, will classify the whole batch.

On the other hand, experience alone can show in what measure the problem, theoretically insoluble, of the estimation of the mechanical properties of a casting from those of another casting, has any value or significance. Firstly, the mechanical properties of a casting can be extremely different from those of the separately-cast test-piece which is used for its reception test. Without again taking examples among the cast-irons, where the differences are accentuated by the two modes of solidification, we select a relative example from the casting of a screw propeller in brass. The results of the tensile test-pieces cooled separately, and of those taken from the casting itself, are given below :—

	Tensile Strength. Kg./mm.^{2}.	Elongation. %.
Separately-cast test-piece	45	27
Test-piece taken from the casting . .	30	3

If it seems difficult to compare these breaking loads, it is quite impossible to connect the elongations by any general relation, and in this case, the separately-cast test-piece can only deceive the user as regards the properties of the casting. Further results, obtained by Isidre Sans Darnis on test-pieces fed in different ways with the same phosphor–bronze (tin 10, zinc 2 per cent.), are shown in Figs. D–K. These show that, without making use of specimens of

Influence of Foundry Factors (Mode of Feeding and Mould) on the Mechanical Properties of Bronze

(88% Cu; 10% Sn; 2% Zn; 0·006% P.)

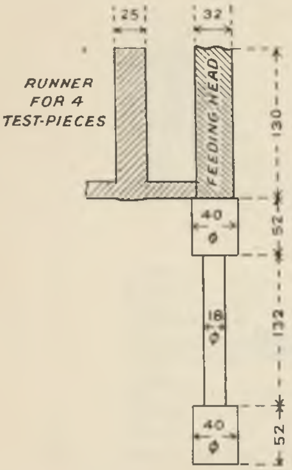

FIG. D.—Test-piece M1. Tensile strength, 17·7 kg./mm.^{2}; elongation, 4·5%.

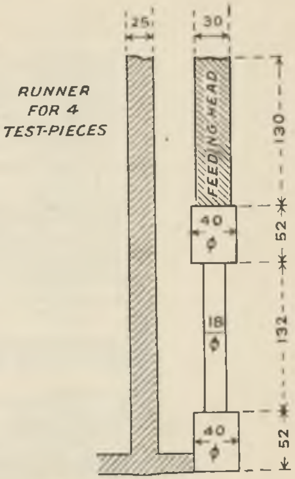

FIG. E.—Test-piece M3. Tensile strength, 20·4 kg./mm.^{2}; elongation, 8%.

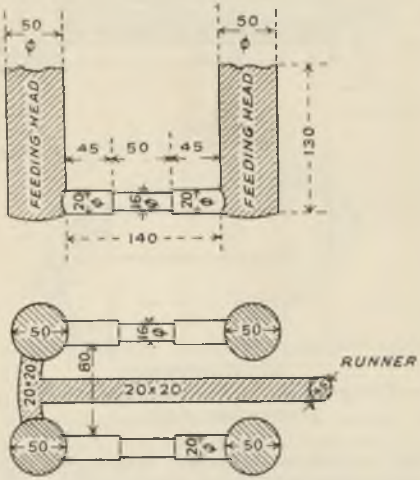

FIG. F.—Test-piece M9. Tensile strength, 25·6 kg./mm.^{2}; elongation, 15%.

very different dimensions, the tensile strength can vary from 17 to 30 kg./mm.^{2} and the elongation from 29 to 4 per cent.

These numerical results, of which the majority relate to castings, not only of the same thickness, but of the same section, show how untenable it is to define the strength of a piece by its section, and especially to relate strength to thickness, since it is not certain what is meant by the thickness of a casting. A cube, a square prism, and a slab of the same thickness have not in any way the same mode of cooling, and consequently have not the same mechanical

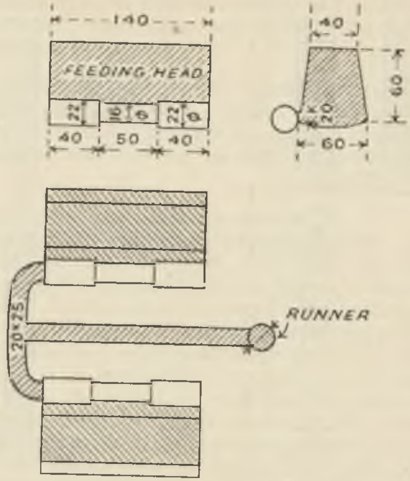

Fig. G.—Test-piece M4. Tensile strength, 23·7 kg./mm.^{2}; elongation, 19%.

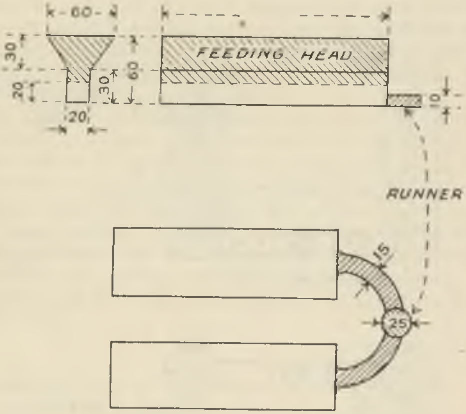

Fig. H.—Test-piece M5. Tensile strength, 19·4 kg./mm.^{2}; elongation, 6·5%.

properties; the case of two cast bars of the same thickness, one square and the other round, is still more difficult as regards comparison of the results.

I have referred intentionally to the results of personal experiments to demonstrate the impossibility of estimating the strength of a casting from

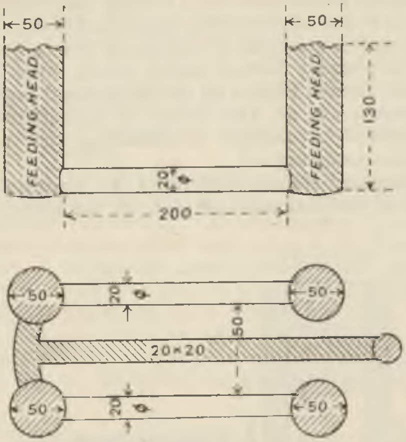

Fig. I.—Test-piece M8. Tensile strength, 24·7 kg./$mm.^2$; elongation, 15%.

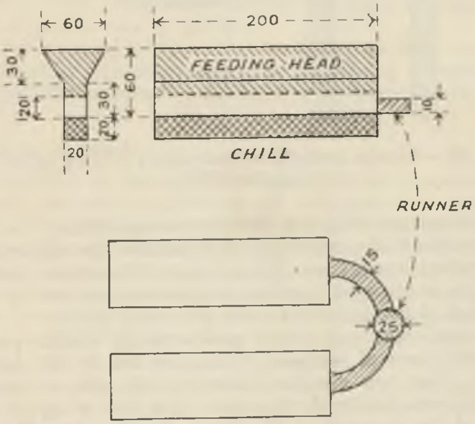

Fig. J.—Test-piece M7. Tensile strength, 30·6 kg./$mm.^2$; elongation, 29%.

results obtained on separate test-pieces. With equal intention I have selected results dealing with non-ferrous alloys, because I have already completely reviewed the important connected problem of the testing of cast-iron on two occasions, at the International Congress for Testing Materials at Amsterdam in 1927, and at Zürich in 1931; in the preparation of the reports presented to these Congresses I reviewed all the experimental work published during the last 20 years.

My conclusions are formally in favour of tests made on test-pieces cut from the casting, and the discussions of the Congress at Zürich have not in any way modified my views.

In the publications (more than sixty) which have been reviewed in these reports, there are to be found interesting experiments concerning the influence of various factors on the strength of cast-irons, but they are isolated results and the number of foundry factors shown above must not be overlooked. The influence of the various factors on the mechanical properties of cast-iron, and alloys in general, can be the object of systematic study leading to numerical or graphical expressions representing the influence of factors *capable of being numerically defined.*

Thus, in the proposed standardization of the separately-cast test-piece it would be possible, by maintaining constant all the foundry factors, to relate the mechanical properties with the chemical composition of the alloy and in particular, in the case of the cast-irons, to determine the influence of the principal elements carbon, manganese, silicon, &c.; if, however, one of the other foundry conditions is changed (casting temperature, nature of mould, shape and feeding of test-piece, &c.) the results are invalidated.

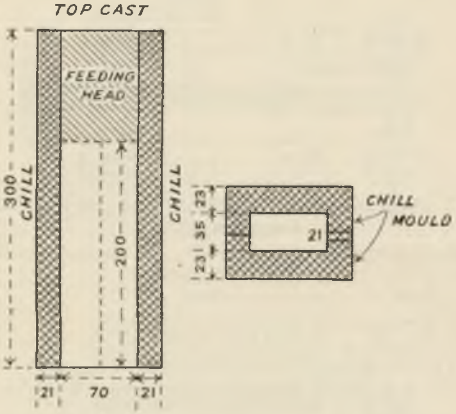

FIG. K.—Tensile strength of test-piece : 21·2 kg./mm.^{2}; elongation, 22%.

If, with the same cast-iron, simple geometrically similar pieces are cast, such as cylindrical bars of increasing diameter fed in the same way, the properties of the cast-iron can be related to the size of bar by a curve approximately represented by the formula : $\text{Log}\, R = a \log kd$; R being the tensile strength, d the diameter of the bar, and a and k coefficients. R can then be determined as a function of diameter, a and k being known, provided that the other foundry factors have been constant.

By casting simultaneously castings of a certain form and separate test-pieces, a relation can be found for a series of cast-irons of neighbouring compositions, between the mechanical properties of the test-piece and those of the casting determined on a test-piece cut from a definite position, but if foundry factors are varied, particularly the shape of the casting or the mode of feeding, the relation fails.

By making such experiments, the relations between certain properties and certain foundry factors can be found and utilized to guide the founder in obtaining the properties determined for the castings, but it is not clear how account can be taken of the influence of factors not measurable or definable, such as the shape of the casting and the nature of mould or facing.

Those who recommend the use of separately-cast bars, and criticize the small test-piece or the test made on the casting, propose to avoid these difficulties by taking the strength of the separately-cast bar (which is similar in hardness to the casting), and making a hardness test on the casting. It is thus conceded that a test of hardness at a certain position on the casting can characterize it, and consequently there is no reason against making a test on small test-pieces cut out of the casting, since the localization of the test is the sole objection to this method.

The separately-cast test-piece is unquestionably of great utility to the founder, and will continue to be used by him, as a control of the liquid metal, but not of the metal of the casting. It is necessary for him to be precisely informed as regards variations which may occur in the liquid metal (chemical composition, degree of oxidation, casting temperature, &c.) independent of the casting, and to maintain uniformity by means of a test-piece of definite dimensions cast always under the same conditions. But, as regards the use of this separately-cast test-piece to indicate the quality of castings of the same "alleged thickness," I should first be glad of a precise answer, not based on opinions but on numerical or graphical results, to the following questions:—

1. What is the thickness of a casting of whatever shape or section?
2. How can thickness, a single dimension, represent the variations in the three dimensions and in the shape of a casting?
3. Since it is affirmed that there are general relations between the castings and the separately-cast test-pieces, what are the relations, algebraic or graphic, connecting their mechanical properties?
4. How, in the comparison between the mechanical properties of the castings and those of the separately-cast test-pieces, is account taken of all the foundry factors enumerated above and notably the method of feeding the casting?

To sum up, in our view:—

1. If the opinion of founders is asked without requiring experimental proof in support, the majority, but not all, will prefer the separately-cast test-piece, since it would not involve any inconvenient change of custom.
2. If a procedure is sought which is simple and convenient, giving a numerical result characterizing the liquid metal without any definite connection with the mechanical properties of the casting or any guarantee of the quality of the latter, the separately-cast test-piece must again be chosen.
3. But if it is desired to know the real strength of the metal of the casting, it is necessary to test the casting itself by means of test-pieces cut from it or from an identical casting, besides confirming the representative character of the selected casting, by ball tests at similar positions.

Professor Dr.-Ing. E. PIWOWARSKY * (Member): For the manufacture of high-grade grey cast-iron the resistance to shock is, in my opinion, of such supreme importance that testing methods should be amplified by the inclusion of a determination of the so-called "wall thickness sensitiveness" (Wandstärkenempfindlichkeit). This can be best made either on box-shaped hollow castings, the side-walls of which are of different thicknesses

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(*e.g.* 20, 40, 60, and 80 mm.) or on cylindrical rods of varying diameters. In this connection Dübi's reference to the best relationship between volume and surface is of importance and should be taken into account in casting all test-pieces, especially those of cylindrical form. Round rods of 30 mm. and 50 mm. in diameter cool under approximately the same conditions as plate-shaped castings with walls 12–15 mm. and 30 mm. thick, respectively. The test for wall thickness sensitiveness affords information on the degree of homogeneity of the graphite distribution (by the tensile strength of short rods cut out of the middle portions of walls of the different thicknesses) as well as on the degree of uniformity of the metallic ground mass (Brinell hardness tests). In a paper in *Giesserei,* 1931, **18,** 533, I have shown the effect on wall thickness sensitiveness, of processes for producing high-grade castings and of the various elements which are added to cast-iron.

Mr. A. CROWTHER * (Member): I have for many years been in favour of the separately-cast test-piece, except in certain special cases, but Dr. Rosenhain's remarks seem to leave no doubt whatever on this point, and I hope that the discussion will be a step towards the standardized test-piece.

Dr. Rosenhain, on p. 277, directs attention to the necessity for careful foundry methods, and his remarks suggest that the only way to ensure this is by careful inspection. I would like, however, to direct attention to the testing of castings hydraulically. The test is used extensively for engineers' and plumbers' hollow castings, with pressures varying from 100 to 2000 lb./in.^{2}. Whilst giving little information regarding the quality of the metal, as the pressures employed are usually within safe limits, the test is yet extremely valuable in assessing the efficacy of the foundry and melting-shop technique. Faulty gating, improper sand preparation and incorrect pouring temperature are at once detected. Absorption of furnace gases by "stewing" in the furnace, is not, however, often revealed by it, as such "gassed" castings will frequently pass the test. The hydraulic test is being superseded to some extent by substituting air at a pressure of 60 to 100 lb./in.^{2}. In most cases, each individual casting is tested, and as the walls are frequently less than $\frac{1}{8}$ in. in thickness, one tiny inclusion is sufficient to cause rejection.

Because of the non-destructive character of hydraulic and air pressure testing, and in spite of the fact that the methods are applicable only to castings of certain types, it is probable that, in non-ferrous foundry work, these tests are more generally used than any other for control and reception purposes.

Dr. A. L. NORBURY † (Member): Attention might be directed to a test which is, at present, only of theoretical interest, namely that of determining the specific electrical conductivity or resistivity of a casting at various points on its surface. It is possible to do this without machining test-bars from the casting and without damaging it. The method consists in making a Brinell (or 90° steel cone) test on the surface of the casting, passing an electric current through a circuit containing the Brinell ball or cone and the casting during the test, and measuring the drop of potential between the equator of the Brinell ball (or the shoulder of the cone) and the neighbouring surface of the casting. From measurement of the diameter of the impression produced and calibration of the apparatus on metals and alloys of known specific electrical resistivity it is possible to calculate the specific electrical resistivity of the casting under test with an accuracy of the order of 1 per cent. It is necessary to etch and then dry the surface of the casting and the steel indentor before each test. The test is fully described in the *Phil. Mag.*, 1929, April, p. 668.

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Mr. VINCENT C. FAULKNER * (Member): Foundrymen are constantly expressing their indebtedness to Dr. Rosenhain for his help in clarifying the international situation as it affects the testing of castings. In order to prevent confusion in the minds of many members of the foundry industry, a better definition of Dr. Rosenhain's phrase " bend-test " would be welcomed. This term may relate to a method of evaluating the malleability of metal used in the making of castings (by firmly fixing a bar in a vertical position in a vice and bending by hammering or leverage so as to produce a maximum amount of deflection before fracture), or may indicate that the material should bend, without fracture, through 180°.

The object sought in asking for this definition is to establish whether it is always correct to translate the French word " flexion " (when used in connection with testing) as " transverse," and " pliage " as " bending." This also applies to the German equivalents.

Mr. H. A. TREADGOLD † (Member): I am inclined to the view that there is no need to consider either " control " or " investigatory " testing, because firstly, it is no part of the duty of a " user," or of any inspectional authority, to take responsibility for the internal control of a foundry, and secondly, in my own experience, it has always been possible fully to investigate cases of failure, &c., with the material available.

Taking this view, the main issue is whether the specified test-bars shall be actually attached to the castings represented, or cast separately. I am entirely opposed to Dr. Rosenhain's view, and the decisions of the Zürich conference of 1931 leave me " quite cold," and this for two reasons. Firstly, because with separate test-bars, as Dr. Rosenhain admits, the honesty of the founder must be one factor in the specification. I submit definitely that specifications should be prepared without this factor being considered. It was my daily duty for more than 30 years to deal with manufacturers, and I have the highest possible opinion of their integrity, but I have known firms of the first order ignominiously let down by some employee. I am aware that Dr. Rosenhain couples the honesty of the founder with thoroughness of inspection, and I should like to know what this " thoroughness " exactly means. I trust that it does not imply that the inspector must actually live on the founder's premises.

Secondly, for small castings a percentage of the moulding boxes may conveniently have test-bars attached to a chain of the castings represented. Further, with large castings, in most cases an additional piece of metal, to form the test-block, might be a solid part of the casting, *i.e.* without gate, &c. This block could be sawn off to provide suitable material for all the necessary tests, including tensile, bending, and indentation hardness. With the provision of a number of destruction tests, the situation would be met. As regards bending tests, I designed some time ago a simple test-bar, for malleable iron, attached to the casting, and see no reason why a similar bar should not be used for non-ferrous castings.

Mr. H. B. WEEKS ‡ (Member of Council): As was so well emphasized during the opening of the discussion, a very great deal depends on what the test is supposed to reveal. Those who have had a large experience in designing, in pattern-making, in moulding, melting, and casting, will know how impossible it is to make any mechanical tests that will satisfactorily reveal the properties which a casting—in some cases weighing several tons—will possess as a whole. Here it seems to me lies the crux of the situation.

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One cannot expect a designer to possess the knowledge or experience that is represented or would be required to master the whole of the above branches of engineering and foundry technique, each of which is important as contributing to the successful production of a large casting. A designer possessing the necessary knowledge of the behaviour of molten metals whilst cooling would not be expected to design a casting that could not be satisfactorily cast. Such a design should ensure the absence of shrinkage defects and " pulls " which might be caused by irregular cooling.

It may be thought that I am digressing somewhat from the title of the matter under discussion, but I am satisfied that if any test is to be specified that will reveal the mechanical properties obtainable from a casting, it must be pre-supposed that the latter has been made under as near ideal conditions as possible—both from metallurgical and founding points of view.

With regard to " cast on " or separately-cast test-bars, however much one might favour the one system or the other, I am afraid that a good deal of work of an educative nature will need to be done before the user or his inspector will be satisfied that the separately-cast bar best represents the metal of which the casting is made. Certainly, cast under such conditions as I have mentioned and cast in a standardized form, it would probably give as true an indication of the quality of the metal in the casting as could be obtained. This again would depend on the manner in which the alloy had been made; its suitability for the purpose required, such as the knowledge that segregation would not take place during cooling; that correct melting and pouring temperatures had been used, and a uniform rate of cooling were ensured.

On the other hand, I am afraid that the majority of engineers or their inspectors who have to use the castings are under the erroneous impression that a " cast on " test-bar is more likely to reveal the characteristics of the casting. This is where a knowledge of metallurgy would become a valuable asset to the engineer, and, as at the moment it is practically impossible to embody the whole of the necessary knowledge in one person, nothing would be lost and everything gained by the designer or engineer more frequently consulting the experienced, scientifically-trained metallurgist whose advice on the most suitable alloys for various purposes should be invaluable and whose business it is to know something of the behaviour of molten metal whilst cooling in the casting. Until this desirable combination is more frequently made use of, I do not think that there is any single mechanical test that can be devised that would be considered satisfactory to either the engineer or the founder, the designer or user.

While many of the photographs exhibited during the discussion did not throw much light upon the best means for the mechanical testing of castings, they did reveal foundry defects that it is hoped are not general, but for which I am sure there are suitable remedies. If such defects cannot be overcome locally, there are Research Associations and consulting metallurgists who possess the knowledge and means of overcoming such troubles as were indicated, and if those concerned in their production will put their difficulties before them, it is more than probable that they would be able to suggest suitable remedies.

Mr. J. G. PEARCE * (Member): These remarks refer primarily to the problem of testing cast-iron, although the principles involved apply equally to all the cast metals. Specification tests and testing procedure have such an important influence on practice that there is an inevitable tendency for the tests employed in specifications to be adopted for control testing. It is also economical to apply the specified test for control purposes.

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The limitations of any simple mechanical test are almost self-evident. For example, there is no direct relationship between the tensile or transverse test and resistance to abrasive wear or machinability, factors which often concern the user more than the mechanical properties. Care is, therefore, required in using and interpreting mechanical tests. Tests adopted are also very greatly influenced by tests already in use and the equipment available. For example, although cast-iron has no appreciable elongation in tensile stress the standard tensile pieces embody a 2-in. gauge length.

Before the adoption of British Standard Specification No. 321 (1928), many anomalies arose in cast-iron testing on account of the application of standard bars specified for particular castings to other castings of thicknesses outside the range for which the test bar was intended. Thus the 2 in. × 1 in. bar 42 in. long, originally specified for cast-iron pipes might be used for a casting so massive that the test-bar would be white; conversely, it might be specified for castings so small that a 2 in. × 1 in. bar would be soft and ferritic. In the past, in fact, the founder has often been forced into the position of having to decide whether to make a good test-bar or a good casting. These anomalies were corrected by British Standard Specification No. 321 (1928), the first British national specification to deal with iron castings in general. Its proposals were revolutionary for in it were adopted for the first time the separately-cast test-bar, cylindrical in shape, and having a section proportional to the thickness of the casting represented. The British Cast-Iron Research Association has shown that, other things being equal, the round bar is stronger per unit of area in transverse than the square bar. This is not due, as is popularly supposed, to a casting effect (the mode of orientation of the crystals), but to a testing effect, because the round bar is superior when machined from a bar originally cast square, and the square bar is inferior when machined from a bar originally cast round.

A test-bar cast integrally with the casting itself is called a "cast-on" bar, and the bar separately poured, of the same metal at the same time, is called the "cast-off" bar. From the metallurgical point of view there is everything to be said for the cast-off bar, for if cast-on its inherent cooling rate is upset by the presence of the cooling mass of the casting. The influence is not constant, for it will depend on the position of the cast-off bar in relation to the casting and on the length and section of the connecting runners. In cases of doubt as to the identity of cast-off bars, chemical analysis can be relied upon.

It is sometimes loosely stated that the cast-on bar tests the casting, whereas the cast-off bar tests the metal of the casting. This is not the case. As Dr. Rosenhain points out, the casting may vary in strength from section to section, and consequently no test-bar, which is a casting of uniform section, can truly represent it, whether it is cast-on or cast-off, or, indeed, when it is taken from the casting itself. If, however, the section of the test-bar is related to the section of the casting, as provided for in British Standard Specification No. 321 (1928), its strength approximates to that of the casting as closely as is commercially practicable. I have shown * that there is one diameter of cast bar which has the same strength as a similar section of the casting. Thicker sections in the casting will be slightly weaker; thinner ones will be slightly stronger. If the range of thickness of casting for which the test-bar is applicable be defined within sufficiently narrow limits the strength of the bar represents the strength of the casting within any desired margin, above or below. It was also shown that a separately-cast bar prepared under British Standards Institution conditions approximates more closely to the actual strength of the casting than a separate small bar trepanned from the casting. Such a piece must be taken from the point at which it can most conveniently

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* *Metallurgist* (Suppt. to *Engineer*), 1931, 7, 184.

be spared, usually the centre of the thickest section. The metal at the core of a thick section is lower in strength than that of the section as a whole, and consequently specifications based on trepanned pieces are lower than specifications based on test-bars. The figure obtained on a trepanned bar has no particular value to the designer.

The cast-off bar prepared under standard conditions enables comparisons to be made between foundry and foundry, and forms an automatic criterion of foundry progress from year to year. The medium size specified by the British Engineering Standards Association, 1·2 in. in diameter, serves at present for the majority of engineering castings, and is identical with the standard bars used in the United States of America and Germany.

I have always strongly advocated the more intelligent use and interpretation of the transverse test, a simple, cheap, and easily made test, which can be carried out on the full section of a bar of any size without the necessity for machining. The breaking load should be used for calculating the transverse rupture stress (modulus of rupture). This automatically compels the measurement of the dimensions of the fractured section. The method makes possible a rational comparison of the results on bars of differing size or tested on different spans, and also permits comparison with tensile and compression tests. Variation in strength with section is continuous for ordinary mechanical tests.

In many cases when the transverse strength on a bar is determined for a cast section slightly different from the standard the practice is adopted of converting the strength at the casting size to the strength at the specified size. I have shown * that the calculation involved is based on a fallacy, since rupture stress is not constant for varying sizes of bar.

The result of the Zürich discussion was highly encouraging to those who have consistently advocated the use of the standard cast-off bar, cylindrical in shape, and of a size related to the section of the casting. This matter was first taken up in this country in 1921 by a Committee of the Institute of British Foundrymen, under the chairmanship of Mr. John Shaw. Both investigation and experience have confirmed the conclusion mentioned. Further work is required, however, to determine the best size of large and small bars and the section of casting which they should represent, leaving the 1·2 in. bar as at present standardized.

Dr. Rosenhain (*in reply*): I am gratified to find that several gentlemen, and more particularly M. Portevin, have sent important contributions. I will endeavour to deal with M. Portevin's views in the first place, but a detailed reply will be impossible because of the large amount of space which it would require.

The views which M. Portevin expounds so clearly and ably are by no means new to me, since they had been put forward repeatedly at International Congresses and elsewhere. I learn, however, with regret that M. Portevin's views have not been influenced by the discussion on this subject which took place at the Congress of Zürich, since M. Portevin's own report on that discussion had suggested that he (M. Portevin) had gone some way towards coming into line with his colleagues from other countries in regard to this matter. It was certainly corrct, as M. Portevin said, that a numerical majority in favour of a particular idea or process cannot establish its validity, but, on the other hand, he and his French colleagues were not entitled to suggest that the engineers and metallurgists in the majority of other countries belong to an "old school" and are not willing to listen to reason. On the contrary, I think that M. Portevin would be better advised to realize that others are as well informed and

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* *J. Iron Steel Institute*, 1928, **118**, 73.

equally capable of logical reasoning as himself. It is a perfectly legitimate attitude to write and speak strongly of a favourite view, but it is a different matter to suggest that those who do not follow it do so because they are old-fashioned or unduly conservative.

In the present instance it appears to me, and I believe that a great many engineers and metallurgists agree with me in this view, that almost all the arguments advanced by M. Portevin against the separately or specially-cast test-bar can also be advanced against the small test-piece trepanned from the casting. It would be quite easy to cite figures which show a wide discrepancy between the results obtained from such a small test-piece and the material taken from other parts of the same casting. In itself the very necessity for taking a test-piece from a casting constitutes an undesirable limit to the size of test-piece that can be used and to its possible location in the casting. In the majority of castings only the thickest portions will allow of the cutting out of a test-piece without destroying the casting; if, on the other hand, the casting were destroyed, it would become a separately-cast test-piece, and logically would not differ from a simpler shape of casting prepared for the same purpose. If one were to carry M. Portevin's arguments to their logical limit, it would be necessary to test the casting as a whole by destruction under stresses proportional to those which it is intended to resist, since only in that way can the real "strength" of the casting be ascertained. Clearly such a procedure is not possible except in a few special cases.

M. Portevin lays great stress on what he calls "foundry conditions." With his analysis of these I am in full agreement, but I would point out that certain of these conditions are the very factors which it is necessary to determine by means of a reception test. The composition of the metal being regarded as constant or as determined by other means, such questions as casting temperature, condition of mould, speed of casting, gas content of the metal, &c., would affect, not precisely to the same extent but in a similar manner, the results obtained with a separately-cast test-piece and with a casting made from the metal at the same time. Broadly, the position may be put in this way: that if a founder could make a good separately-cast test-piece under definite standardized conditions in regard to the mould, he could probably also make a satisfactory casting at the same time. The actual strength values of the casting cannot, it is agreed, be deduced quantitatively from those of a test-piece, but this applies to any test-piece which does not constitute the entire casting. On the other hand, the quality of the metal used in the full sense of the word, which includes many of the foundry conditions of M. Portevin, can best be determined by means of a separately-cast test-piece cast into a suitable mould and fed in a suitable manner. The fact that in my opening remarks I referred to the need for using a standardized sand mould for separately-cast test-bars should, I think, have obviated the necessity for M. Portevin to cite figures showing the great variety of results which could be obtained by using moulds of various kinds. This information was well-known and had little bearing on the matter under discussion.

While, therefore, I do not think that M. Portevin has in any way strengthened the case in favour of small test-bars trepanned from actual castings, it is clear that the use of such test-pieces is highly important in the investigation of broken castings where separately-cast test-pieces are not available. The extensive work of French metallurgists on these small test-pieces, therefore, must be regarded as of very great value from the point of view both of makers and users of castings. Ultimately, no doubt, agreement will be reached as to the proper places in any consistent scheme of testing for these small trepanned bars and the larger separately-cast bars which are advocated by the great majority of metallurgists to-day.

The discussion relating to separately-cast test-bars leads next to the question whether a separately-cast bar is preferable to one that is "cast on." Throughout the discussion those engineers who have been good enough to take part have stressed the view that they require to know "the properties of the casting itself," and have suggested that they are not concerned with the properties of another piece of metal cast at the same time. Unfortunately, as I have tried to show in the opening paper, it is not possible to determine the "strength" of the casting except by the process of service trial and correlation of the results with the indications of some form of test-piece. Metallurgical considerations, to which I think engineers are not always ready to give due consideration, however, make it clear that more reliable and satisfactory data can be obtained from a separately-cast test-bar than from one which is cast on to the main casting. Mr. Treadgold emphasized the point that although the honesty of the foundry as a firm can be relied upon there are misgivings as to the possible action of undesirable individuals. In reply to this point, however, it might be mentioned that it is at least as easy to use dishonest means for securing a good result from a cast-on test-bar, as it is in the case of separately-cast pieces. It is quite possible, in fact, so to arrange the gating and feeding of a casting that the cast-on test-bar is fed at the expense of the casting itself, with the result that a good test-bar is obtained but a bad casting, or at least a casting with spongy places in it. The use of local chills and other well-known devices also makes it quite possible to produce spurious results in a cast-on test-bar. As suggested in the opening paper, therefore, the honesty of the foundry, which can be ensured to some extent by adequate inspection, must be relied upon whatever type of testing is used, so that this argument in favour of the cast-on bar in reality can have little weight.

A great many other points have been raised in the various verbal and written contributions, but I think that most of these have, in reality, been met either in the opening paper or in the present reply. There are, of course, many further details which lend themselves to fuller discussion, but in view of the extent which the discussion has already assumed these may be reserved for some future occasion.

BRITTLENESS IN COPPER *

By CLEMENT BLAZEY, M.Sc., Member.

Author's Reply to Correspondence.

Regarding Dr. Ramsay's criticism of the "loss-in-hydrogen" results, it would appear from his remarks that, at Swansea, the copper sample and combustion tube are weighed together, but at Port Kembla the sample is placed in a boat and heated in an electric tube furnace. The volatile impurities in this case are condensed mainly on the cooler portions of the furnace tube, and the "loss of weight" should be slightly greater than when sample and tube are weighed together.

I cannot explain why the results on HC15, HC17, and HC18 do not add up to 100 per cent., but feel sure that the discrepancy does not lie in low results for "loss-in-hydrogen." In my experience arsenic is not volatilized in hydrogen.

I agree that some oxygen might have been present in the brittle strips (see statements in the paper on pages 378 and 379), but with a 4 mm. objective and ordinary light I could not find any cuprous oxide particles. For this reason, in Table II, I recorded "none" for the AC strips, and for HC12, HC16, and HC18. I regret I am not able to make use of polarized light at the moment.

That oxygen and bismuth are important factors is further borne out by experiments which have been carried out in continuation of those recorded in the paper.

For instance, a charge of 12 lb. cathode copper was melted under charcoal and well stirred with a stick. A small billet (L15) was then cast as a check. A small amount of bismuth (about 0·006 per cent.) was then added and a second billet (L16) was cast. The charcoal cover was then skimmed off and a third billet cast (L17). The surface of the melt was again covered with charcoal, and well stirred, and a fourth billet cast (L18). The charcoal was again skimmed off (the surface of the copper was exposed to the air for not more than one minute) and a fifth billet cast (L19). The remaining metal, weighing about 1·5 lb., was also cast as a short billet (L20). It was poured without a charcoal cover.

Billets L15, L16, and L18, which had been well stirred (overpoled) and cast under charcoal, contained blowholes and were of low density. Billets L17, L19, and L20, which had been well poled, but poured without a charcoal cover, were almost free of holes and were of relatively high density.

The six billets were hot-forged, cold-drawn, and annealed in the manner described in the paper. Strips L15, L17, L19, and L20, were not susceptible to brittleness, but strips L16 and L18 were susceptible. Microscopic examination proved that L15, L16, and L18 contained practically no cuprous oxide inclusions, but that L17, L19, and L20 contained quite an appreciable amount.

In regard to Dr. Ramsay's reference to the magnification adopted for Figs. 2 and 3 (Plate XXVI), if Fig. 2 had been photographed at × 500 no particles of oxide would have been visible. A magnification of × 150 was adopted to make the photograph comparable with Fig. 6 given in Hanson and Ford's paper (*J. Inst. Metals*, 1927, **37**, Plate LVI), which illustrates the inclusions present in their alloy containing 0·006 per cent. bismuth and 0·016 per cent. oxygen. If Fig. 3 had *not* been photographed at × 500 the oxide particles would scarcely have been visible in reproduction. The magnifications, therefore, were chosen after careful consideration of all points of view.

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* For paper and correspondence, see *J. Inst. Metals*, 1931, **46**, 353–382.

PHYSICO-CHEMICAL STUDY OF THE GOLD-COPPER SOLID SOLUTIONS *

By Professor N. S. KURNAKOW, Member, and N. W. AGEEW, Met.Eng., Member.

Authors' Reply to Discussion.

Alloys of gold with copper present an interesting case for investigation : both from the purely practical point of view, since changes in mechanical properties, such as the appearance of brittleness on transition from solid solution to chemical compound, are profoundly important, and also from the aspect of pure theory, in that they show a complete analogy to crystallization from the liquid phase. The study of this typical example of the crystallization of a chemical compound out of solid solution is highly important as regards the elucidation of the general problem of the formation of definite chemical compounds. We are extremely grateful to Dr. Rosenhain, to Dr. Hume-Rothery, and to Professor Westgren for taking part in the discussion and for examining the questions touched on in our paper.

Dr. Hume-Rothery has raised two points which require some explanation on our part. The first of these is in connection with the degree of equilibrium in our alloys. The degree of equilibrium attained is usually judged by some property that remains constant for a definite period of time. The equilibrium attained in our alloys was determined (as stated in the paper (p. 486)) by the fact that, as the result of maintaining the alloys at a given temperature, the electrical resistance, as measured every five minutes, remained constant. Further, preliminary experiments showed that longer periods of annealing (up to 10 hrs.) left the resistance practically unaltered. (The experiments were carried out within the critical range.) The degree of equilibrium attained was thus not determined by the 10 days' maintenance at 350° C., as this treatment applied only to the initial state of our alloys, and not to their degree of equilibrium during the determination of the electrical resistance curve. In Dr. Haughton's and Mr. Payne's researches this initial condition was obtained by quenching the alloys from 600° C. and rolling. On the other hand, the degree of equilibrium of the alloys when the electrical resistance curves were taken was determined by the rate of heating and cooling, *i.e.*, 2°–7° C. per hour, as shown in the reproductions of the curves which Dr. Haughton has so kindly sent us, and for which we are very grateful. Similarly, in the recently published work of G. Grube, G. Schönmann, F. Vaupel, and W. Weber,† the initial condition of the alloys was obtained by alternate annealing above and below the critical region (300°–440° C.) and subsequent gradual cooling from 400° to 40° C. during 60 days. The degree of equilibrium in their alloys was determined by heating from 20° to 460° C. during 18 hrs. It is evident that in the course of our electrical resistance determinations the degree of equilibrium was thus the same as that usually attained in investigations of this type.

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* For paper and discussion, see *J. Inst. Metals*, 1931, **46**, 481–506.

† *Z. anorg. Chem.*, 1931, **201**, 41–74.

The deviation of isothermal resistance curves at concentrations of 22 and 40 per cent. may be due to two causes : the formation of new phases, or the fact that the degree of equilibrium attained by us was insufficient. The final resolution of this interesting problem will probably require the application of other methods of physico-chemical analysis, *e.g.*, hardness and extrusion pressure, which have in the past given extremely valuable information in the study of solid metallic systems. Our observations show that hardness is a more sensitive method than even electrical resistance.

The second point touched on in the discussion concerns the existence of chemical compounds. The constitutional diagram of gold–copper alloys presents an extremely interesting example of the possibility of giving absolutely accurate indications as to the existence of definite chemical compounds AuCu and $AuCu_3$ by means of the methods of physico-chemical analysis (*i.e.*, by the construction of " composition–property " diagrams).*

The method of physico-chemical analysis extensively employed by us for the study of the diagram of state of the alloys and the nature of intermetallic phases, affords a means of giving an absolutely accurate definition as to what may be considered a definite chemical compound, namely : " A chemical individual, belonging to a definite chemical compound, is represented by a phase which possesses singular or ' Daltonian ' points on its property curves. The composition corresponding to these points remains constant when the factors determining the equilibrium of the system are altered."†

The example afforded by the gold–copper alloys is not unique, and alloys obtained by the replacement of the gold and the copper by metals of the platinum and iron groups show the formation of definite chemical compounds of this type out of solid solutions. (Platinum–copper, N. S. Kurnakow and W. A. Nemilov; platinum–iron, W. A. Nemilov; platinum–nickel, N. S. Kurnakow and W. A. Nemilov.)

We are extremely grateful to Professor Westgren for his valuable comments and quotation of cases of deviation in certain intermetallic phases from his definition of a definite chemical compound. We are of the opinion, however, that such individually observed exceptions should not be regarded as invalidating the above definition, but merely as an indication of the possible existence of a whole series of intermediate stages between a definite chemical compound and a solid solution.

We are firmly convinced that a systematic study of the intermetallic phases will ensure the discovery of the most rational classification, which will be based on the nature of the interaction of the atoms constituting the phase, since there is every reason to believe that the type of crystalline space-lattice and the properties of a given phase are but the reflections of such interaction.

* *J. Inst. Metals*, 1916, **15**, 305.

† *Z. anorg. Chem.*, 1925, **146**, 69–102.

ANNUAL MAY LECTURE.

At a General Meeting of the Institute, held in the Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W.1, on the evening of Wednesday, May 11, 1932, Sir Henry Fowler, K.B.E., LL.D., D.Sc., President, in the Chair, Professor Dr. F. Körber delivered the Twenty-Second May Lecture (see pp. 317–342).

The Chairman proposed, Sir Harold Carpenter seconded, and there was carried with acclamation, a hearty vote of thanks to Professor Dr. Körber for his lecture.

The Minutes of the Annual General Meeting, held in London on March 9 and 10, 1932, were taken as read and signed by the Chairman.

Election of Members and Student Members.

The Secretary announced that the following members and student members had been elected on April 7 and May 11, 1932.

Members Elected on April 7, 1932.

Asher, Harry H., D.D.S.	Chicago, Ill., U.S.A.
Britton, Sidney Charles, B.A.	Cambridge.
Every-Clayton, Cecil Edward, M.A.	London.
Hunt, Leslie Bernard, M.Sc.	Luton.
Jennings, Judson T.	Seattle, Washington, U.S.A.
Liddiard, Edwin Andrew Guthrie, B.A.	London.
Littley, Howard	Stourton, Stourbridge.
Price, Frank Sidney	Walsall.
Sonnino, Dr. Carlo	Mori (Trento), Italy.
White, Richard Frederick, B.Sc.	Birmingham.

Student Members Elected on April 7, 1932.

Harrison, John Sidney, B.S.	Cleveland, Ohio, U.S.A.
Jenkins, Ivor	Swansea.
Knight, Harold	Neath, South Wales.
Ratcliffe, William James	Bushey, Hertfordshire.
Rowland, Edward Geoffrey	Lapworth, Warwickshire.

Members Elected on May 11, 1932.

Alexeewa, Elizabeth J.	Leningrad, U.S.S.R.
Densham, Alec Bramley, B.A.	London.
Drane, H. D. H., M.Sc., Ph.D.	Cawnpore, India.
Herbert, Thomas Martin, M.A.	London.
Juriew, Professor Konstantin	Leningrad, U.S.S.R.
Kastchenko, George A.	Leningrad, U.S.S.R.
Kookanow, Lucas	Leningrad, U.S.S.R.
McKeown, John, Ph.D., M.Sc.	London.
Omodei, Clifford Theodore, B.E.	London.
Lewis, Kenneth Glyn, M.Sc.	Cambridge.
Rabbitt, James A.	Tokyo, Japan.
Slater, Harry Oliver	Belvedere, Kent.

STUDENT MEMBERS ELECTED ON MAY 11, 1932.

CUTLER, William	Birmingham.
KENNEFORD, Arthur Spencer, B.Sc.	Manchester.
LENTON, Kenneth William	Coventry.
MEES, Eric Henry	Stourbridge.
MOSELEY, Norman Hurlstone	Birmingham.
PARSONS, Leonard Frederick	Birmingham.
PENDREY, Arthur L.	Birmingham.
WIESE, Kurt	Hannover, Germany.

The CHAIRMAN proposed, and there was carried unanimously, a vote of thanks to the Council of the Institution of Mechanical Engineers for permitting the use of their Hall on the occasion of the lecture.

The proceedings terminated at 9.30 *p.m.*

MAY LECTURE, 1932

THE PLASTIC DEFORMATION OF METALS

By Professor Dr. F. KÖRBER,* Member.

TWENTY-SECOND MAY LECTURE TO THE INSTITUTE OF METALS, DELIVERED MAY 11, 1932

The use of industrial metallic materials depends to a considerable extent on their ability to suffer changes of shape—on their capacity to endure severe plastic deformation without any loss of internal cohesion. In mechanical–technical shaping processes—the most important of which are rolling, forging, pressing, drawing—the temperature at which the work is carried out is of great importance, since the ability to change the form, as well as the resistance to such alteration, which is determined by the power used in the deformation, are greatly dependent on this factor. Almost without exception deformation is facilitated by a rise in temperature.

In this lecture only those questions will be considered that are of importance in establishing and continuing the plastic processes in manufacturing materials by industrial methods of working, and the essential object of which is the transformation of the materials into the form most appropriate for their use.

A comprehensive insight into the processes of plastic transformation, and the deduction of the laws governing the latter, will be possible only if we possess for each individual process a clear and distinct picture of the stress relations and the manner in which the material flows. A large number of researches have been made during recent years with this object in view. If I may present to you in the following discussion some advances in this direction, I should like to take as a basis in the first place my own investigations and those of my colleagues which have been conducted during recent years in the Kaiser-Wilhelm-Institut für Eisenforschung, Düsseldorf, over which I have the honour to preside. I am conscious, and would like explicitly to emphasize, that the survey which is given of the researches which have been made into the mechanism of plastic deformation must in

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* Director, Kaiser-Wilhelm-Institut für Eisenforschung, Düsseldorf, Germany.

many respects remain incomplete. I hope, however, to be able to show you how the methods of modern metal research, the advancement and useful application of which to practical problems are at the focus of the work of the Institute of Metals, provide valuable aids for obtaining an insight into the processes of plastic deformation.

A.—CONDITIONS FOR THE OCCURRENCE OF THE PLASTIC STATE.

For the characterization of the plastic processes those conditions are first of all of importance under which, with increasing stress, plastic deformations begin to occur in material primarily purely elastically stressed. For the proper understanding of these plasticity conditions those researches which have been carried out in this field of mechanical testing are of special significance. One important object of the latter is the determination of the limiting stresses which a test-piece may be able to endure without plastic deformation occurring. The methods of testing used in practice are intentionally selected so as to exert only a single type of stress; the test-piece is subjected as nearly as possible to pure tension, compression, or shear stress. Such simple and straightforward stress relationships are, however, never experienced in commercial shaping processes, hence systematic investigations into the deformations arising from the action of a combination of forces, by which we may become acquainted with the nature and the state of the stress in a body, are especially valuable. Such researches enlarge our knowledge of the determinative laws, and must be considered the most promising way of developing the fundamental laws of a modern theory of tenacity. They may, especially, lead to a decision between the different theories which have been advanced with reference to the establishment of the plastic state.

The original theories, according to which the exceeding of a maximum stress (theory of maximum stress) or of a maximum extension (theory of maximum strain) is essential for the appearance of fracture or of the plastic condition, have been replaced by the maximum shear stress hypothesis by reason mainly of the research results of English investigators.* According to this theory, in order that flow may commence, the condition that the greatest difference between the principal stresses should exceed a certain limit, which characterizes the resistance to deformation of the material, must be fulfilled. Judging from the observations of W. Lode,† with

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* J. J. Guest, *Phil. Mag.*, 1900, **50**, 67; W. Mason, *Proc. Inst. Mech. Eng.*, **1909**, (3–4), 1205; C. A. M. Smith, *ibid.*, **1909**, (3–4), 1237.

† *Z. Physik*, 1926, **36**, 913; *Forschungsarbeiten auf dem Gebiete des Ingenieurwesens*, 1928, Heft **303**.

progressive plastic deformation the influence of the mean principal stress on the process of flow is increasingly evident; for progress of flowing the condition of constant energy due to change in shape appears to become more and more determinative; according to this, the sum of the squares of the principal shear stresses is given by the square of the yield stress under pure tensile conditions.*

Owing to the extensive development of the theory of elasticity, we have been satisfactorily informed in many cases as to the state of stress under purely elastic influences. There is so far no similar complete and reliable mechanics for the plastic state, so that a corresponding mathematical treatment is, in general, not feasible. Certain deductions from the distribution of stress under purely elastic conditions are, however, applicable to those for flow, especially for the stress relations which determine the occurrence of plasticity, and these deductions are, in many cases, profitable.†

The examination of the slip which occurs in certain layers of a material at the beginning of flow has been shown to be a method of investigation which affords obvious results, particularly for the study of the first stages of deformation. It is the matter of those phenomena which appear on passing the yield-point in mild steel during tensile tests, and which are known under the name "flow lines" or "Lüders lines." Such lines on the polished surface of a rectangular test-piece are shown in Fig. 1 (Plate XXVIII). They are visible macroscopically, and no other assistance is needed.

If we examine these flow lines more closely, we notice that they are the intersections of the flow surfaces with the surface, and these are inclined at angles of about 45° to the axis of the specimen. They are surfaces of maximum shear stress along which the portions of the test-piece mutually move against one another. The evident formation of the flow lines in mild steel is attributable to the sharp demarcation of the flow range at the yield-point for this material which is clearly shown in the tensile stress diagram. In Fig. 2, diagrams *b* and *c* of this type are arranged side by side with the normal diagram *a*, which applies to copper, for example. Within the horizontal range of flow shown in the diagrams, and especially at the sudden decrease of stress from the upper yield-point S_0 in Fig. 2*c*, there appear on the test-piece, singly or in certain groups, the sharply defined flow lines, which gradually spread over the entire length with progressive extension within the same range.

* R. v. Mises, *Nachr. Ges. Wiss. Göttingen. Math-physikal. Klasse*, **1913**, 582; H. Hencky, *Z. angew. Math. Mech.*, 1924, **4**, 323; *Z.V.d.I.*, 1925, **69**, 695.

† F. Körber and E. Siebel, *Mitt. K.-W.-Inst. Eisenforschung*, 1928, **10**, 15.

The course of these flow lines is in close relationship with the distribution of stress in the metal. It could be shown by an extensive examination of the stretch and deformation of dished ends of boilers * that in more or less convex ends, which have, by internal pressure, been stressed far beyond the yield-point, a totally different course of the flow lines is obtained, *vide* Fig. 3 (Plate XXVIII). These lines run in directions corresponding with the state of stress derived from measurements of the change in shape of these two plates. This close connection between the course of the flow lines and the complicated stress distribution could be confirmed in many cases.† To do this it was necessary to follow up the course of the flow surfaces into the interior of the boiler end. In such instances we possess, in the etching process developed by A. Fry,‡ an excellent means of rendering the flow surfaces within the steel visible. Fig. 4 (Plate XXIX) shows a section through a boiler end, which has been stressed beyond the yield-point by internal pressure and then etched in this manner.

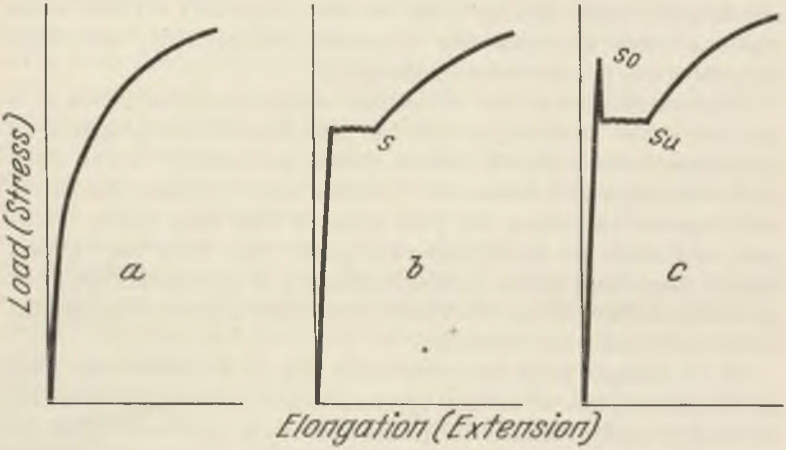

Fig. 2.—Types of Load–Elongation Diagrams of Metals.

The path of the flow surfaces in the metal corresponds to a great extent with that which is to be expected from our, hitherto still limited, knowledge of the laws of plastic deformation. This will be shown by a few examples which have been so selected as to permit inferences, derived from the results thus obtained, to be applied to the processes of forging and rolling.

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* E. Siebel and F. Körber, *Mitt. K.-W.-Inst. Eisenforschung*, 1925, **7**, 113.

† E. Siebel and A. Pomp, *ibid.*, 1926, **8**, 63.

‡ A. Fry, *Stahl u. Eisen*, 1921, **41**, 1093.

PROFESSOR DR. F. KÖRBER, MEMBER
May Lecturer, 1932.

[*To face p.* 320.

FIG. 1.—Flow Lines in Mild Steel.

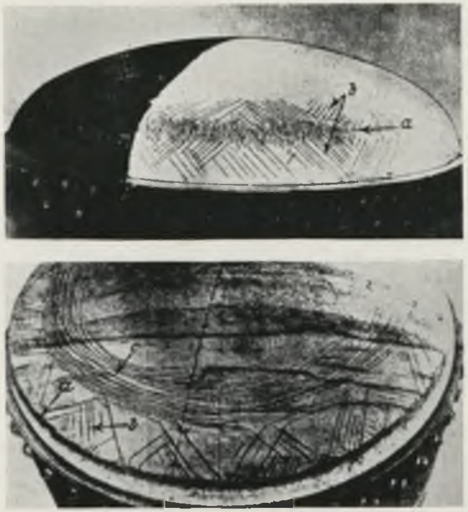

FIG. 3.—Flow Phenomena in Boiler End Plates.

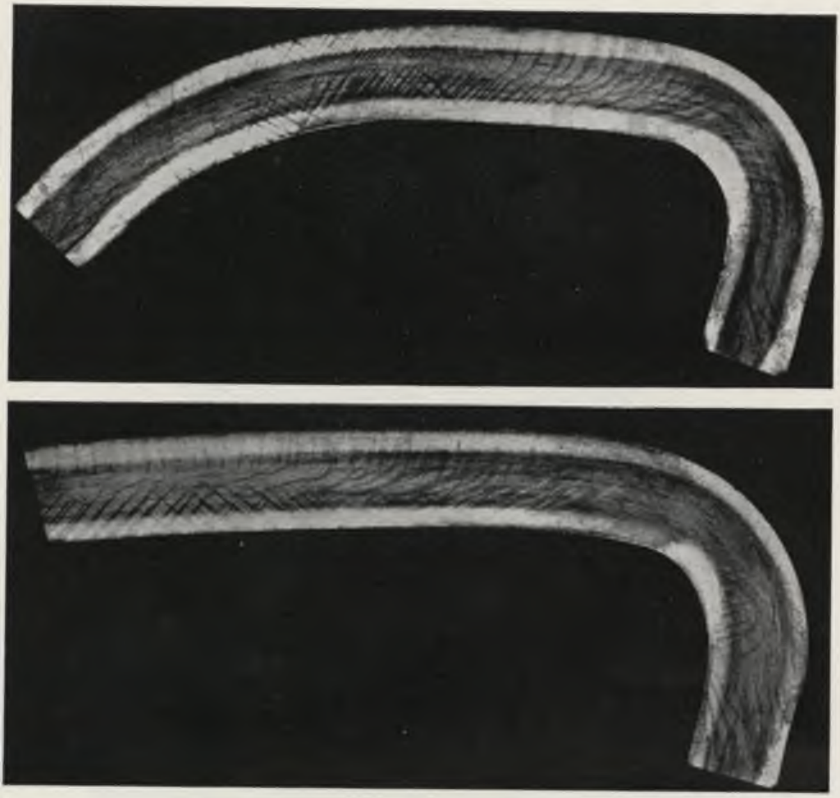

FIG 4.—Flow Phenomena in Heavily Vaulted Boiler End Plates with Side Manhole.
(Slightly reduced in reproduction.)

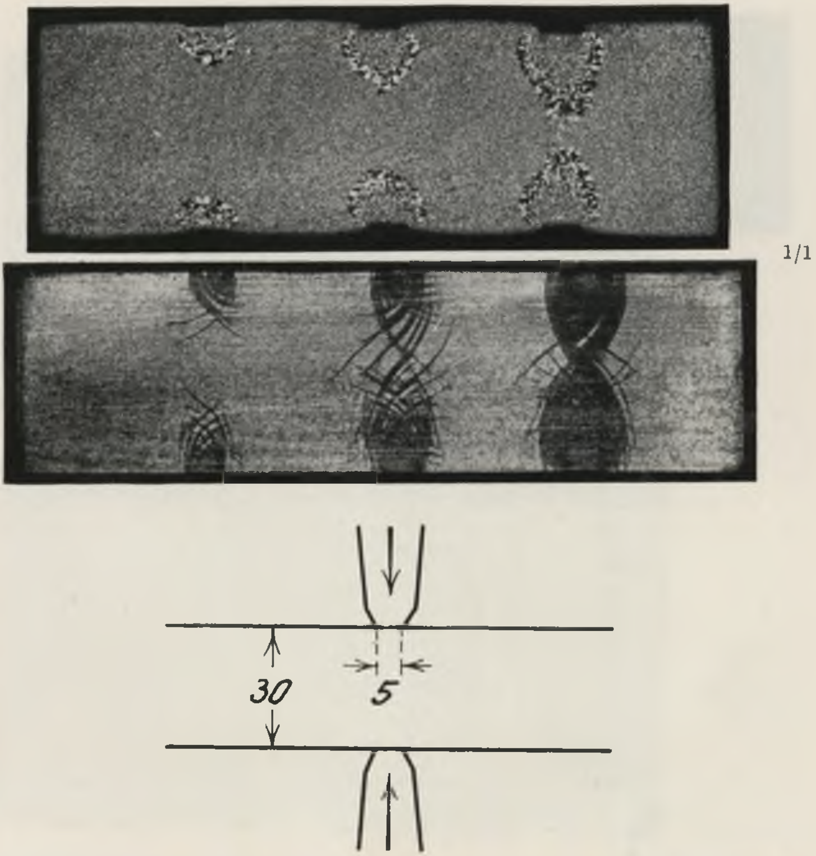

Fig. 6.—Formation of Slip Lines during Working Mild Steel with Narrow-Faced Press Tools.

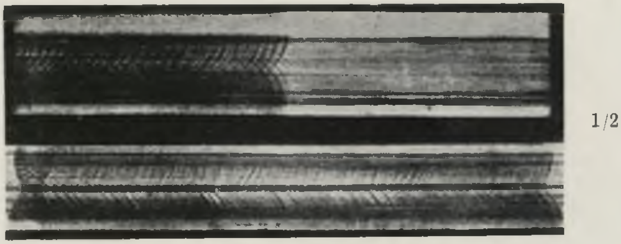

Fig. 8.—Formation of Slip Lines in Cold-Rolling (after Meyer and Nehl).

[*Between pp.* 320 *and* 321.

PLATE XXXI.

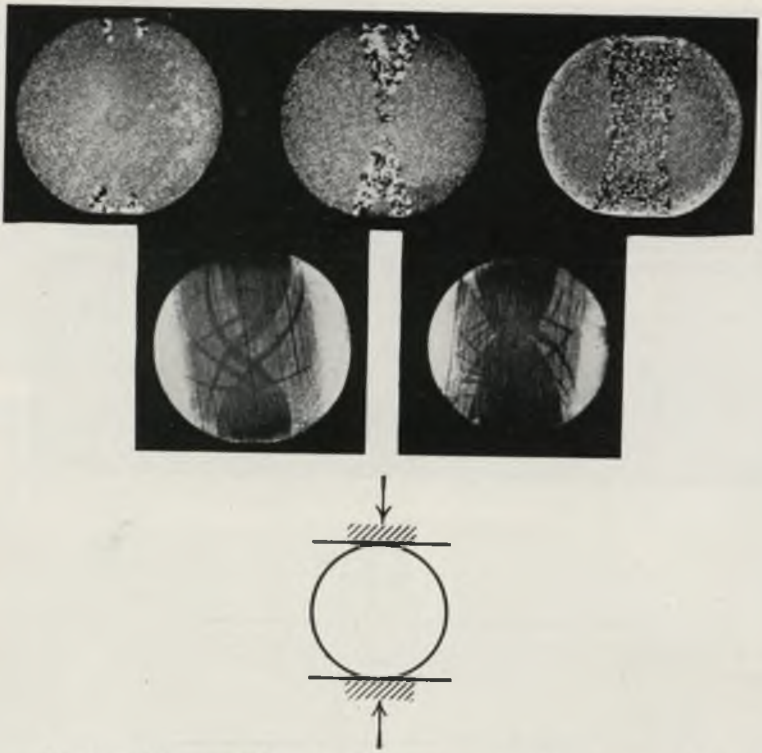

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FIG. 10.—Formation of Flow Lines during Transverse Compression of Steel Cylinders.

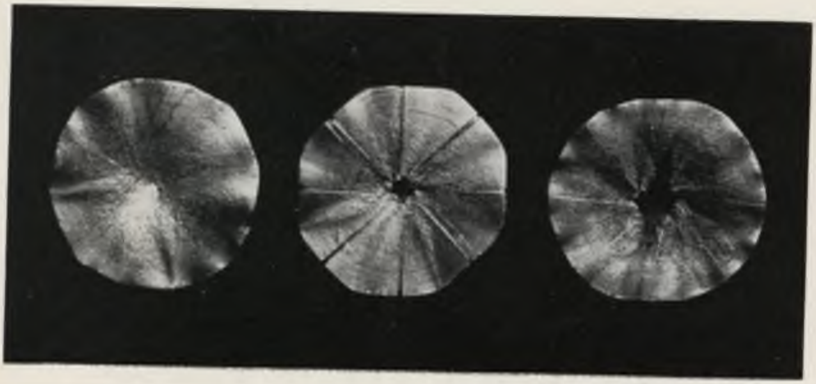

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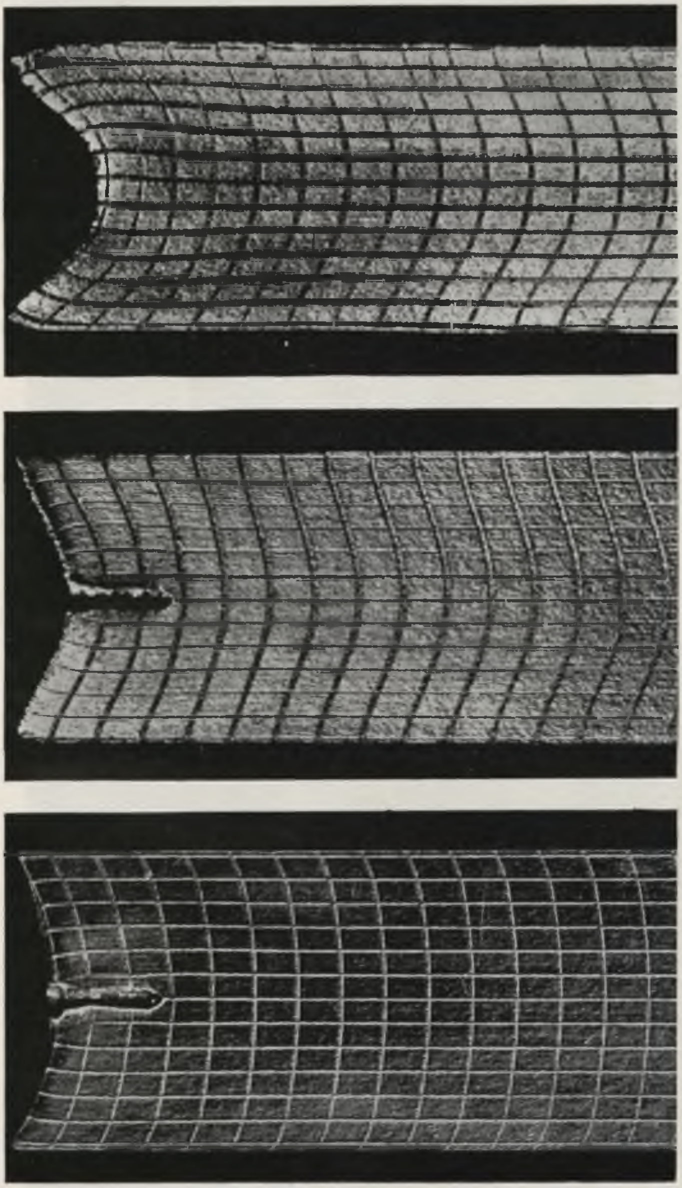
FIG. 11.—Formation of Hole during Transverse Forging of Aluminium Cylinders.

×2



40°.

24°.

12°.

Reduction 36·2%.

FIG. 12.—Drawing Tests.

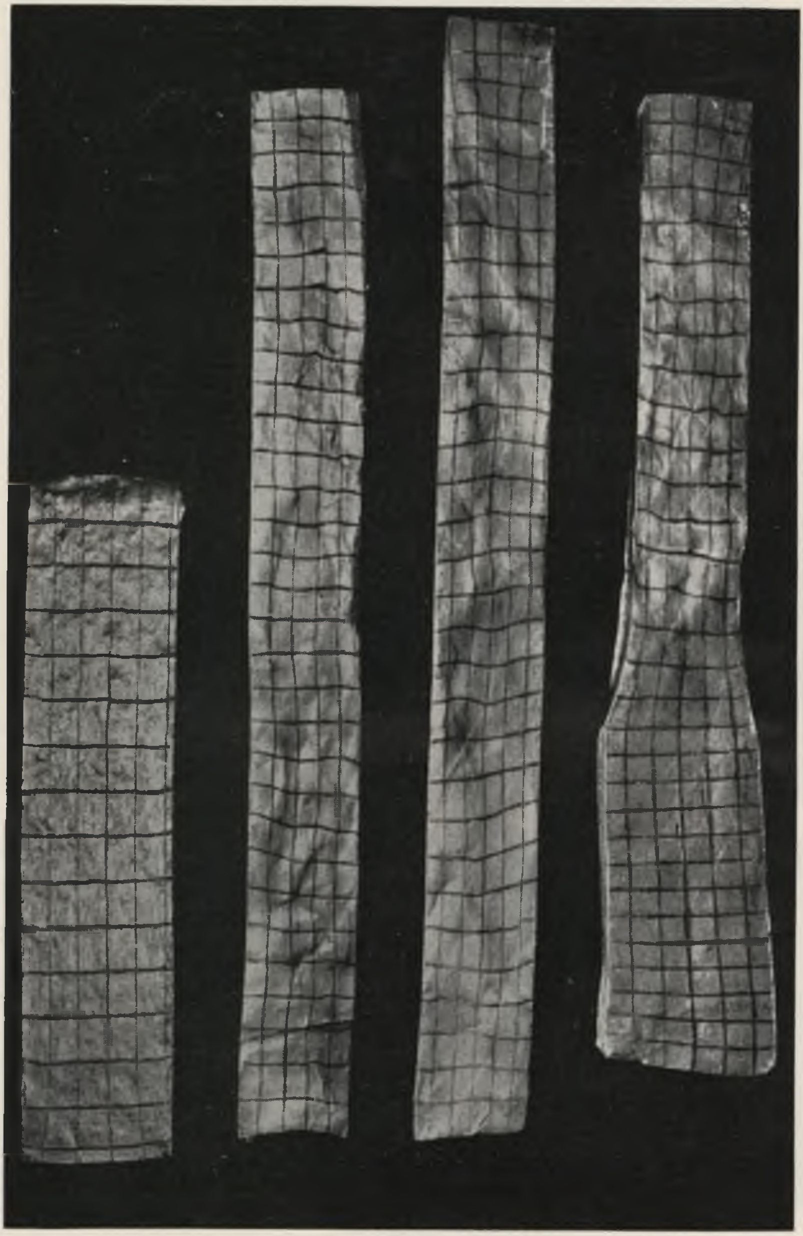


FIG. 18.—Tests on Cold-Rolling.

The laws which such flow surfaces obey have been derived for plane stress conditions by H. Hencky * and L. Prandtl.† The flow-line system sketched in Fig. 5 would correspond with the theoretical requirements in the case of a prismatic test-piece which has been pressed on both sides beyond the yield-point by means of narrow-faced tools. From the corners of the tool the work is penetrated by two groups of flow surfaces which cut one another mutually at right angles, and within the same group are so joined that the angle which they form with one another at the intersections with a flow surface of the other group remains constant. Figs. 5*b*, *c*, and *d* illustrate how the flow lines penetrate deeper and deeper into the metal as the pressure increases; the average compressive stress changes as a flow line is traversed proportionally to the angle through which its tangent rotates. The shading in Fig. 5*d* is intended to show that with heavy pressure within this region the material starts to become completely plastic, and single lines of flow cannot then be recognized.

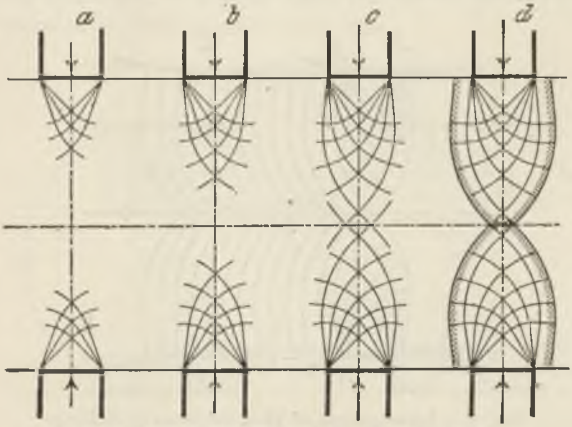


FIG. 5.—Theoretical Course of the Flow Surfaces.

Fig. 6 (Plate XXX), which is a longitudinal section of the test-piece, shows that the flow-line system which has been drawn represents correctly the stress relations which actually exist and the plastic displacements arising therefrom. Etching by Fry's method has made visible the flow lines which are found more deeply in the metal as the pressure increases. With the smallest pressure applied the effect of the narrow tools does not penetrate from both sides to the centre. Thus the

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* H. Hencky, *Z. angew. Math. Mech.*, **1923**, **3**, **241**.

† L. Prandtl, *ibid.*, **1923**, **3**, **401**.

different effects of strong and weak blows in reduction by forging become apparent. In a similar manner, it may also be shown how the stress relations and the process of deformation are influenced by the ratio between the width of the face of the press tool and the thickness of the test-piece.

This dependence of the range of plastic deformation on the pressure may be illustrated in another way. Mild steel has the peculiarity of undergoing coarse recrystallization following critical extension and annealing. If it be subjected to cold-working until it has suffered 5–20 per cent. reduction in area, and is then annealed within the temperature range 700°–900° C., very coarse crystal growth occurs. Under an irregular stress, such as exists on pressing between narrow hammer faces, the portions of the steel which are stressed within the specified critical limits stand out clearly against the more strongly and less strongly deformed regions which have a fine-grained structure. The upper part of Fig. 6 shows the effect of treating half of the rod by this method.

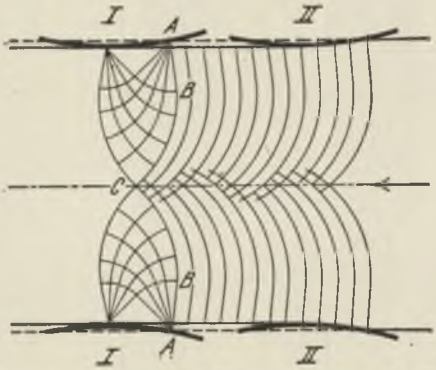

Fig. 7.—Arrangement of Flow Surfaces in Rolling.

That similar considerations may be applied with success to the process of rolling should be apparent from the next two figures. Rolling can be compared with elongation by forging, if one bears in mind that the speed of compression is not the same for all points of the contact surface between the rolling-material and the rolls, which may for this purpose be considered as press faces. The speed of compression falls from a maximum at the point *A* (Fig. 7), where the piece enters, to zero where the latter leaves in the plane of the rolls. This peculiarity in rolling leads one to expect that the flow surfaces originating at the first point of contact of the roll and the material will be especially well marked. Fig. 8 (Plate XXX) shows flow lines which have been observed by H. Meyer and F. Nehl * on cold-rolling mild steel with small reduction. According to expectation, the only flow lines which appear are those formed at the entrance of the material into the rolls.

Corresponding entirely with what has been said on forging, the ratio between the roll diameter and the thickness of the rolling material as well as the relative reduction in thickness of the latter is of decisive importance for the stress in, and therefore the deformation of, the rolled material. Roll diameter and reduction in thickness must be made sufficiently large so that the effect of the rolls completely penetrates the material; otherwise there is the danger of longitudinal tensile stress in the undeformed inner zone.

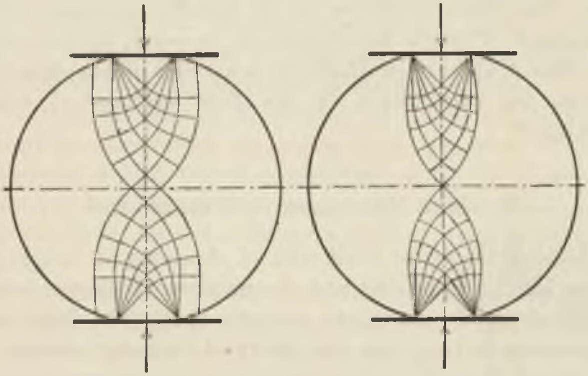

Fig. 9.—Flow Surfaces Formed during Transverse Compression of Cylinders.

A few results on the stress relationships and modes of deformation in the transverse compression of cylindrical bodies which have been obtained by this method of testing will be briefly given. Fig. 9 shows the flow surfaces which are to be expected after forging a cylindrical piece between two flat faces; the figure corresponds with that shown for hammering with narrow-faced tools (Fig. 5). Fig. 10 (Plate XXXI) shows that the result of the test fully confirms the prediction. Only the region of the sample between the press faces is affected by the deformation, and this reaches to the centre only under heavy pressure. If the test-piece be rotated on its axis during this kind of deformation, or rotated between rolls turning in the same direction, as is the case in the oblique rolling process for seamless tubes, then only that portion of the outer

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* H. Meyer and F. Nehl, *Stahl u. Eisen*, 1925, **45**, 1961.

section which is directly under the rolls is deformed, whilst the core is subjected to continuously varying shear stresses. The serious breakdown of the cohesion of the material can thus be understood; it can lead, in the oblique rolling process, to fracture, owing to the effect of the transverse tensile stresses which are set up at the centre, and thus promote the formation of cavities. By striking repeatedly a rolled piece of aluminium in a transverse direction while it is continuously rotated, the production of holes can be easily brought about, as may be seen in Fig. 11 (Plate XXXI).

It has already been stated that the evident formation of flow lines, and thereby the possibility of demonstrating the first steps in plastic deformation, is attributable to the behaviour of mild steel at the yield-point. Steel loses this peculiarity with increase in temperature, so that it shows no difference from other metals during hot-working. The stress condition of all metallic materials before the commencement of plastic deformation is, however, fundamentally the same, so that it appears justifiable to generalize on the distribution of stress from the observation of the flow surfaces of steel after cold-working.

B.—The Mechanism of Deformation.

The possibilities so far dealt with of obtaining an insight into the conditions for the beginning and the progress of plastic deformation admit only of positive assertions when the changes in shape are small. The expressions derived from the theory of elasticity and the theories of Hencky and Prandtl for the plastic state are in particular confined to such small alterations of shape that the original form of the test-piece may be regarded as unchanged. We have now to consider the nature of the technical manufacturing processes with direct reference to the change of external form. The methods of examination so far employed for these processes can yield only qualitative expressions. An exact mathematical analysis of the entire process of shaping is rendered possible by an accurate and detailed knowledge of the deformations that are produced.

A comparison of the initial and final dimensions of the stressed body, on the assumption that the change of shape is the result of a simple deformation on parallelepipedon planes, can serve only as a first rough approximation. That plastic deformation is a complicated process was recognized quite early, on the basis of observations on the commercial shaping methods, as well as on the deformation of stratified test-pieces, whether these were built up of plastic masses * or of metal layers.† In working, flat surfaces by no means remain always flat. In drawing, the outer zone is retarded in relation to the core, probably due to the effect of external friction on the die wall, so that a plane situated at right angles to the axis is distorted in a convex manner after the passage through the drawing die. Similar more or less marked distortions appear in other shaping processes.

In addition to the change in shape attained, which can be measured by the alterations in the external dimensions, other deformations become apparent in the interior of the material. They cannot be derived from the final dimensions of the piece which are the result of the working process. For the conduct of these technical operations they have, however, a certain importance, in that they involve an additional expenditure of power, to which I shall refer later on.

In the deformation of any type of composite test-piece,* † the fact cannot be overlooked that mutual displacements occur in the planes between the individual layers in consequence of active shear stresses, and that they modify the conception of the deformation.

The method devised by T. Adam,‡ of examining after drawing the distortions suffered by the welds in a test-piece made up of different pieces welded together, and that of W. E. Alkins and W. Cartwright,§ of building up the test-piece for drawing from concentric tubes, cannot be considered sufficiently exact or complete for numerical evaluations.

For an accurate investigation of the transformation during drawing, extrusion, rolling, and piercing, E. Siebel and H. Hühne || have recently used a method in the Eisenforschungsinstitut in which the test-pieces were cut longitudinally through the middle and divided on one of the cut surfaces into a series of squares. Since, from considerations of symmetry, no shear stresses can arise on this dividing plane, these test-pieces behave during drawing as though they were uncut.

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* H. E. Tresca, *Compt. rend.*, **1864–1873**; A. v. Obermeyer, *Sitzungsber. K. Akad. Wiss. Wien*, **1868**, 737; F. Kick and F. Polack, *Dingler's Polytech. J.*, 1877, **224**, 465; 1879, **234**, 257; H. Unkel, *Z. Metallkunde*, 1928, **20**, 323. "Über die Fliessbedingung im plastischen Material," Berlin: **1928** (J. Springer).

† A. Hollenberg, *Stahl u. Eisen*, 1883, **3**, 121; P. H. Schweissgut, *Z.V.d.I.*, 1918, **62**, 281; F. Vowinkel and J. Trockels, *Z. Metallkunde*, 1921, **13**, 466; P. Ludwik, *Z. Oesterr. Ing. Ver.*, 1919, **67**, 597; M. Metz, *Stahl u. Eisen*, 1926, **46**, 467; *Arch. Eisenhüttenwesen*, 1927/8, **1**, 193.

‡ T. Adam, "Wire Drawing and Cold-Working of Steel," p. 57. London: 1925.

§ W. E. Alkins and W. Cartwright, *J. Inst. Metals*, 1931, **46**, 293 and 304.

|| E. Siebel and H. Hühne, *Mitt. K.-W.-Inst. Eisenforschung*, 1931, **13**, 43.

It has become known to the author only since the printing of this paper that W. Riedel (*Neues. Jahrb. Mineral.*, 1929, [B], **67**, 151) has used the same method for the study of flow in plastic masses in order to compare the observations so made with geological phenomena.

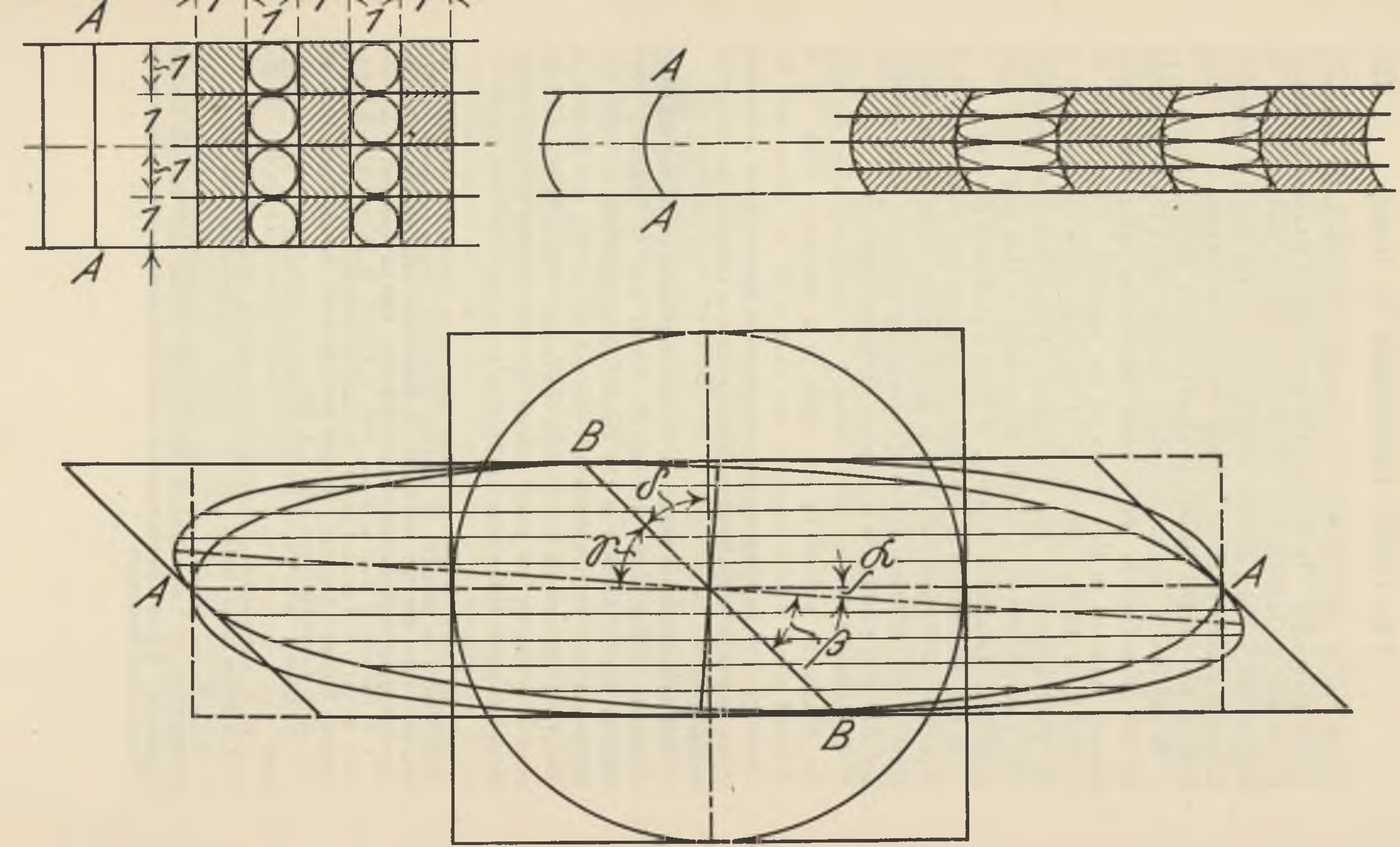

FIG. 13.—Arrangement for the Interpretation of Deformation.

Fig. 12 (Plate XXXII) shows copper pieces of 20 mm. diameter prepared in this manner which have been drawn, with a reduction in area of 36·2 per cent., through conical dies, having angles at the aperture of 12°, 24°, and 40°. It can distinctly be seen that only the squares in the middle zone have been drawn out into rectangles, whilst those near the surface have been distorted into parallelograms. Only in the centre does the deformation correspond to simple elongation; in the outer zones additional slip has occurred to an extent which is greater the larger the angle of the die.

The state of deformation after drawing is evident at every point in the specimen when, as in Fig. 13, one draws in the distorted squares the deformation ellipses into which the circles originally inscribed in those squares have been converted. The complete representation is given by the ellipsoid into which the sphere primarily inscribed in a cubical element is transformed. This ellipsoid remains inscribed within the distorted element after deformation, and its principal axes characterize the impressed changes of form in magnitude and direction. The long axis of the ellipsoid coincides with the axis of the specimen only in the centre zone; and it is only in this region, as mentioned above, that the deformation is purely an elongation. In the outer zones the greater axis of the deformation ellipsoid is inclined to the central axis at a small angle, which increases as the distance from the central axis of the rod increases. The maximum angle is not, however, at the surface of the specimen, but is reached at a point just below this, as is shown in the lower part of Fig. 14. There is possibly a close connection between this view and that of a "conical fibre texture" postulated by E. Schmid and G. Wassermann * from X-ray

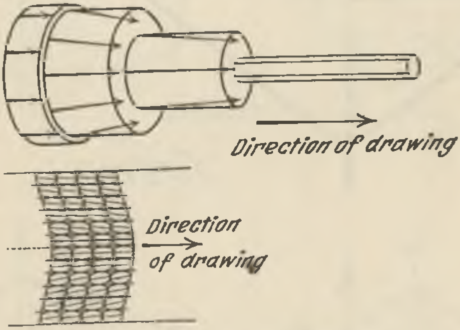

Fig. 14.—Deformation and Structure in Drawing.

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* E. Schmid and G. Wassermann, *Z. Metallkunde*, 1927, **19**, 327.

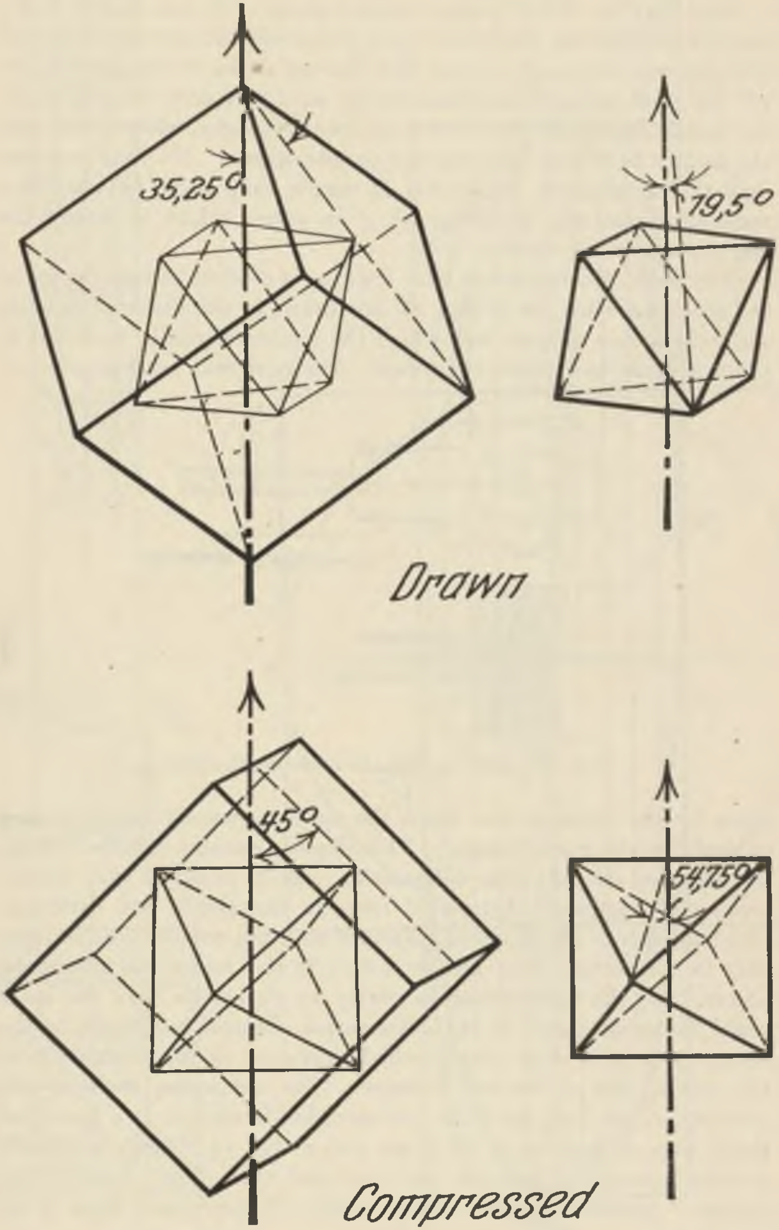

Fig. 15.—Lattice Arrangement for Cold-Worked Copper.

examinations of drawn wires. The upper drawing in Fig. 14, which gives a schematic representation of the deformation structure obtained, demonstrates the similarity in appearance of the two phenomena. The marked similarities are in good agreement with the conclusion reached at the Eisenforschungsinstitut * by means of X-ray investigations carried out on cylindrical bodies stretched or compressed symmetrically

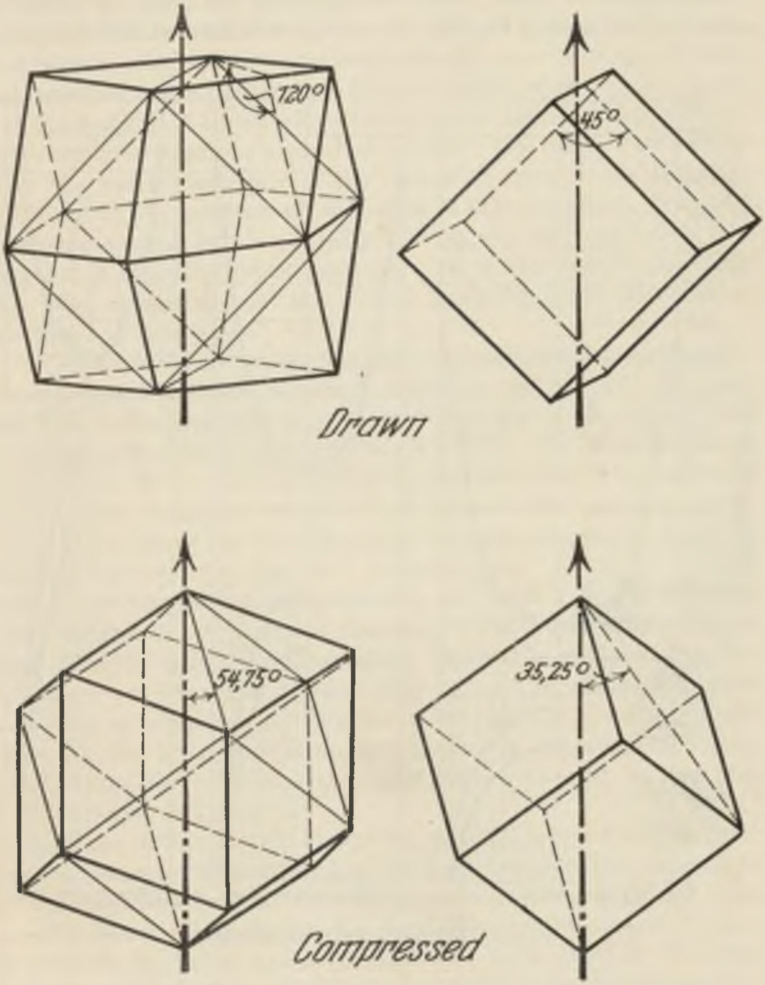

Fig. 16.—Lattice Arrangement for Cold-Worked Iron.

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* F. Wever, *Z. tech. Physik*, 1927, 8, 404.

along their axes—that the resulting deformed structures are distinguished by the tendency of definite crystallographic directions to become oriented along the path of the strongest flow of material.

The result of these X-ray investigations for cubic face-centred metals is illustrated in Fig. 15. For axially symmetrical stretching and compression the final positions are shown to which the individual crystallites tend as the deformation increases. In both cases the densest-packed plane, the octahedral face, is perpendicular to the direction of flow of the material, which in the case of tension is in the direction of the axis, and in that of compression is at right angles to the axis. In Fig. 16, which shows the corresponding results for cubic

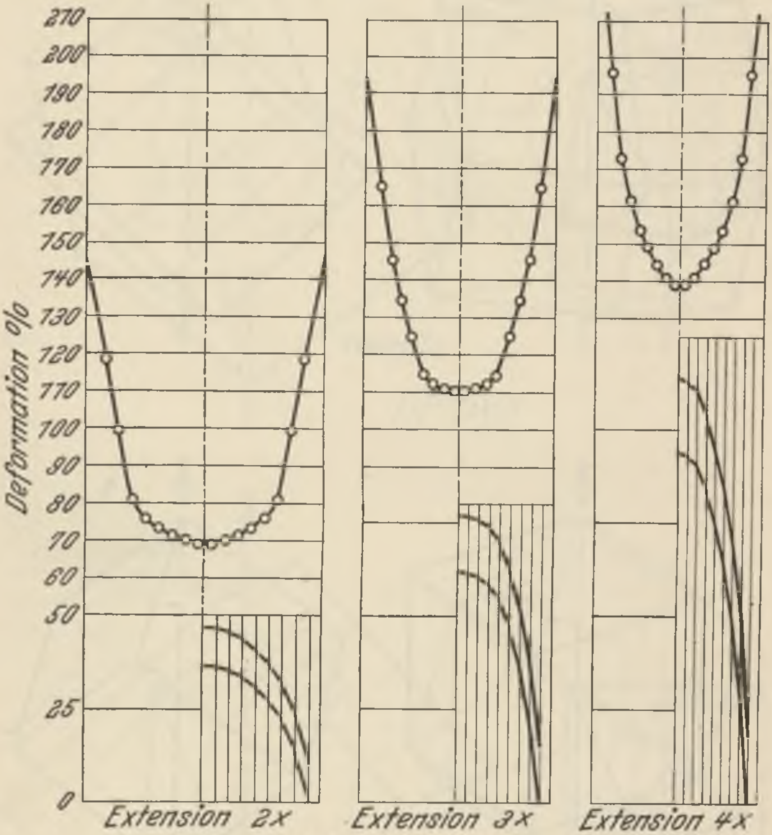

FIG. 17.—Deformation in Extrusion.

body-centred iron, the normal to the rhombododecahedron face lies in the direction of the flow of material.

Following the procedure described with test specimens cut longitudinally, the conditions of deformation which occur in the extensively applied extrusion method of metal working have been determined. A lead cylinder which had been cut longitudinally on a symmetrical plane was extruded from a matrix with different degrees of reduction. In the lower part of Fig. 17 are shown the distortions which have been produced in the originally engraved network of squares. The curves drawn above show the varying amounts of the change in form in the ellipsoids according to the positions of the latter in the test-piece. The total deformation again increases rapidly towards the outer surface in consequence of superimposed movements. Along the central axis nearly pure axial elongation, and thus almost parallelepipedial deformation, was found to take place.

In experiments on cold-rolling between cylindrical rolls, using test-pieces prepared similarly, so arranged that the two halves of the specimen were pressed together by means of lateral guides, the material was deformed, as illustrated in Fig. 18 (Plate XXXIII). Bar I is of aluminium subjected to 21 per cent. reduction in thickness, Bar II of lead with 18·7 per cent. reduction, and Bar III of lead with 26·7 per cent. reduction. In the case of Bar IV, rolling with the same reduction in thickness has been interrupted so that the " transition zone " is visible. In contrast to the observations during drawing and pressing, the co-ordinates perpendicular to the principal direction in which deformation occurs show no noteworthy curvature, either backwards or forwards. The deformation of the rolled material then corresponds closely with pure stretching or compression. This divergent result is possibly brought about by the much smaller amount of friction between the rolling material and the roll surface in comparison with that on the dies during drawing and pressing.

That the deformation in rolling is almost distortion-free is in complete agreement with the result of an X-ray examination undertaken in the Eisenforschungsinstitut,* in which close relationships were revealed between the structure of a metal deformed by cold rolling and by parallelepipedial plane compression with unilateral flow of metal. Fig. 19*a* and *b* show in polar figures, introduced for this purpose by F. Wever,† the ideal deformation structure for the octahedral and cubic faces of a cubic face-centred metal following axial extension and compression ; *c* is the polar figure for the case of parallelepipedial

* F. Wever and E. Schmid, *Mitt. K.-W.-Inst. Eisenforschung*, 1929, **11**, 109.

† F. Wever, *ibid.*, 1924, **5**, 69 ; *Z. Physik*, 1924, **28**, 69.

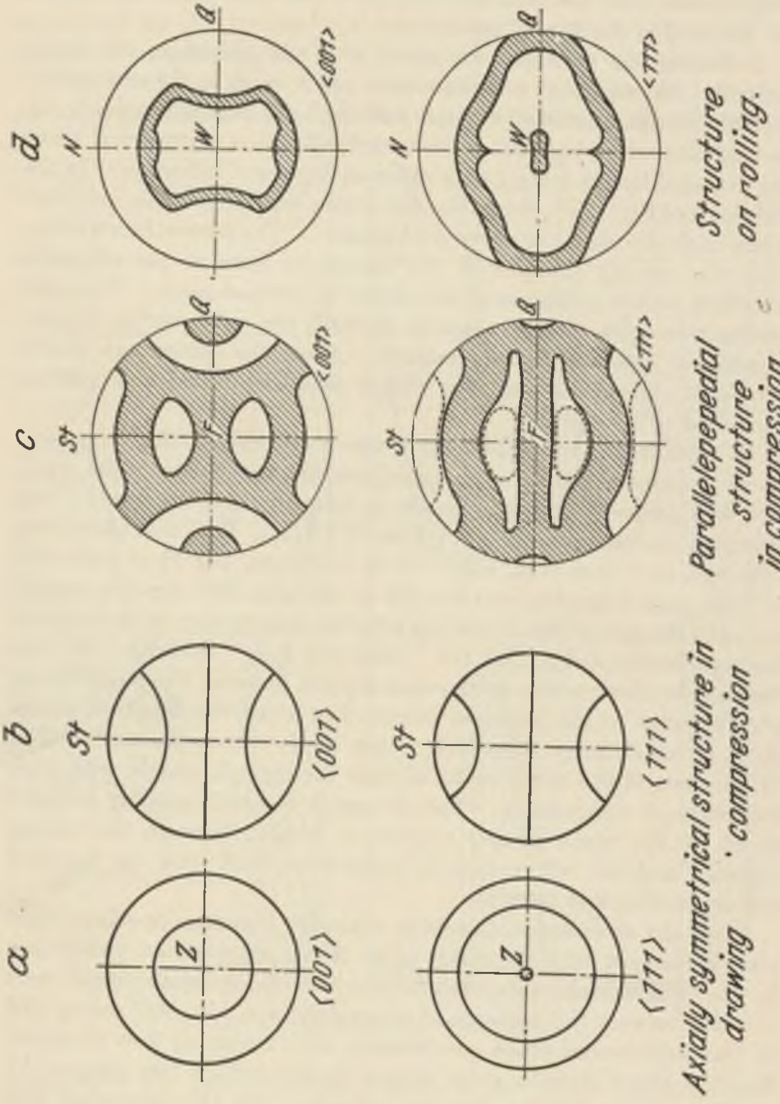

Fig. 19.—Deformation Structures of Aluminium (Represented by Polar Figures).

compression with unilateral flow of the material, and *d* that for heavy cold-rolling. The similarity of these two structures is unmistakable. Between these two processes of deformation, then, there possibly exists a close relationship. In hot-rolling a similar uniform elongation through the entire thickness of the material can be expected only if a uniform temperature distribution is assured.

The final state of deformation after the completion of the treatment has been taken as the basis of the foregoing conclusions. The question now arises whether, in some way, still further internal displacements occur during the actual mechanical operation, the influence of which on the final state of the particles of the material is, however, again nullified by opposing displacements.

The investigation of the deformation during working is possible by the same experimental method if the process is interrupted, as was the case with Bar IV in Fig. 18. In Fig. 20 such a "transition" from unworked to worked material is again given for the case of a copper rod which has suffered 27·8 per cent. reduction in area by drawing through a die having an aperture angle of 40°. Those lines of the inscribed network which are parallel to the direction of movement of the material may in the transition zone be considered as streamlines, so that the rod can be visualized as being split up into concentric stream tubes, numbered I to VI from the outside inwards. The manner in which the individual elements are deformed can be continuously followed along these stream lines, and can be defined, furthermore, by the shape and orientation of the deformation ellipsoids. In the diagrams in Fig. 20 the relations between the distance along the centre axis and the extension in the direction of the stream lines, the transverse deformation and the additional shear, are shown. According to these, deformation takes place in all the stream tubes by a gradually increasing extension, together with a subsequent transverse flow of the material which is approximately uniform on all sides. It is evident that deformation, particularly of the inner stream tubes III to VI, has commenced at some distance from the entrance of the die, and has already finished in the interior before the exit from the die. W. E. Alkins and W. Cartwright * described similar observations at the last Autumn Meeting at Zürich. The additional disturbances are very small in the innermost stream tube VI. They do not attain a maximum value in the outermost tube I, but in II and III, which are situated just within the material. In a similar manner, the deformation occurring during extrusion and in the still more complicated piercing process could be examined, but I must refer you to the original publication † for particulars of the results.

By appropriate differentiation it is possible to calculate from the experimental data obtained in the methods described the deformations for every point in the transition zone, both in magnitude and direction.

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* *loc. cit.*

† E. Siebel and H. Hühne, *loc. cit.*

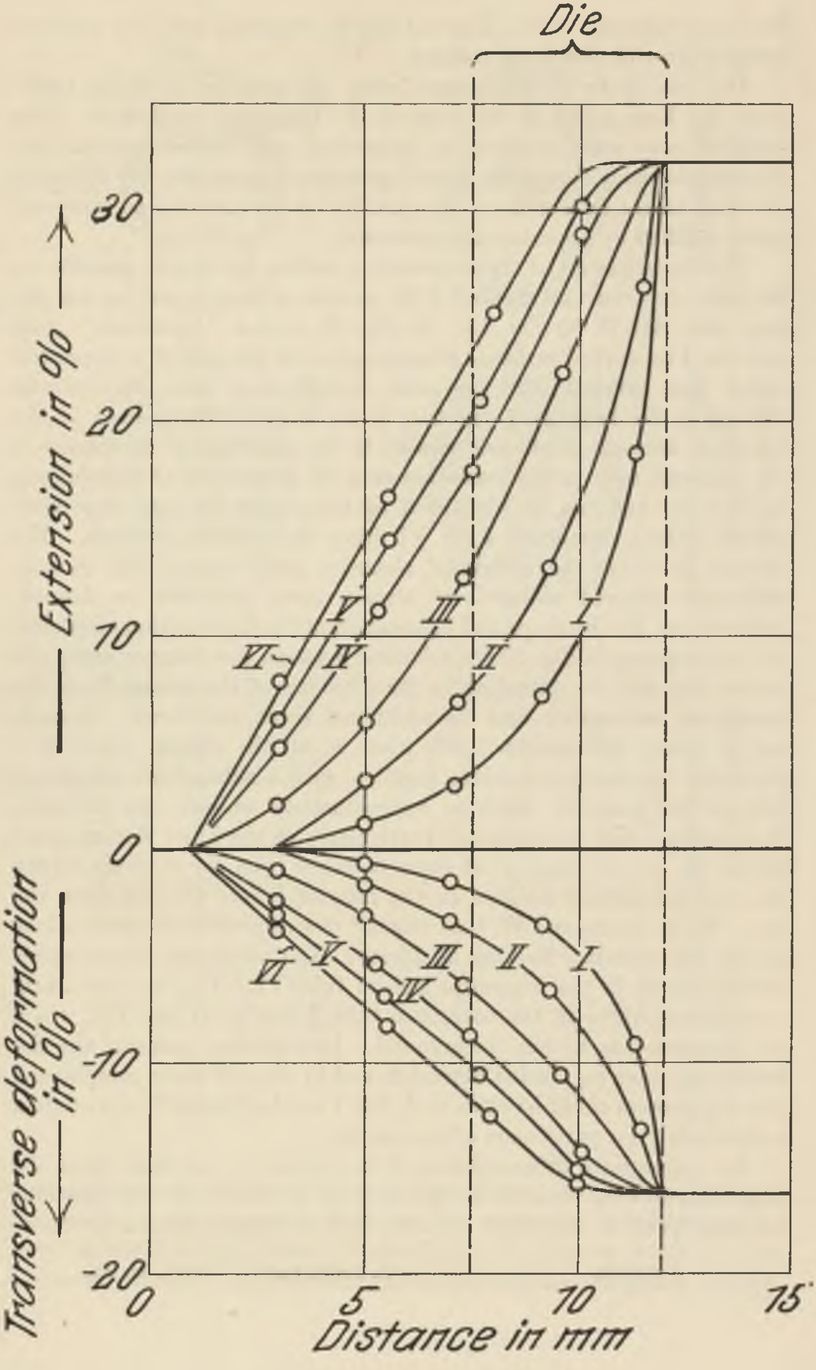

Fig. 20a.—Deformations during Drawing.

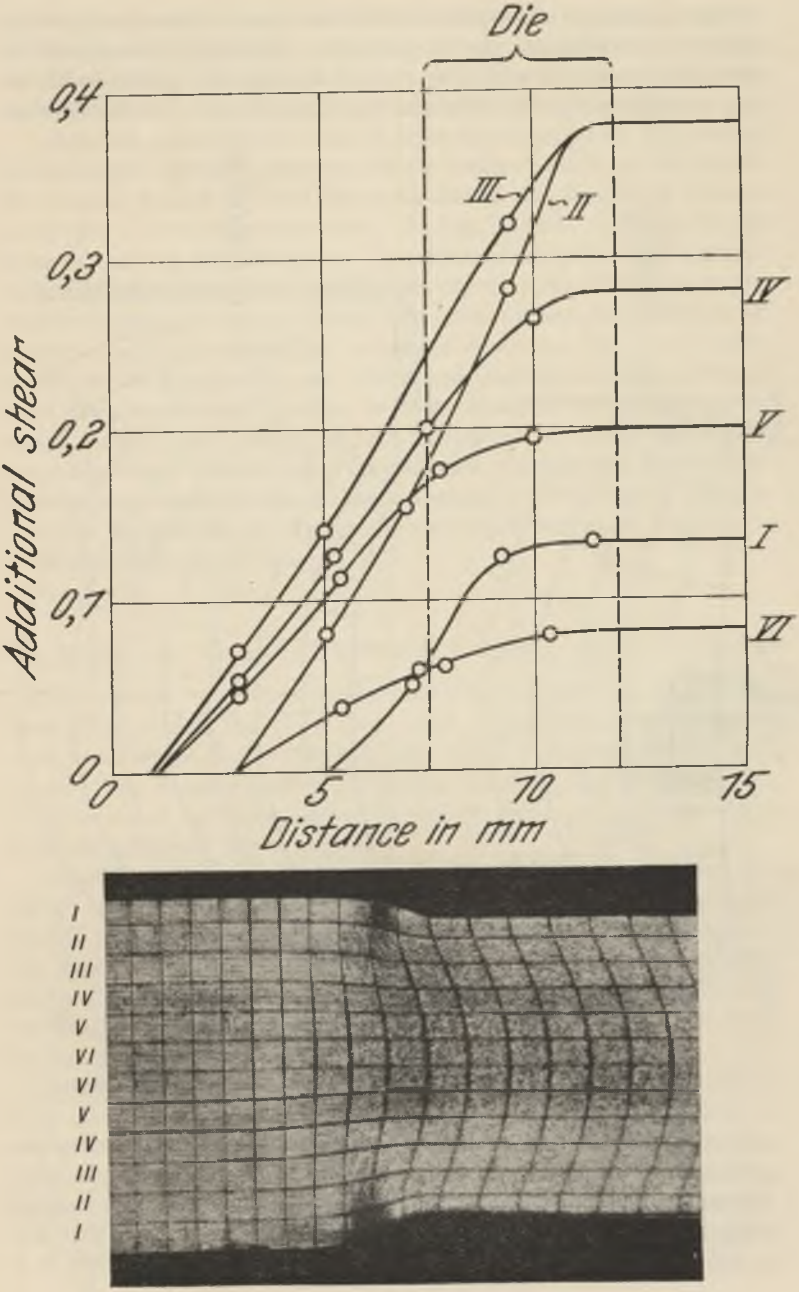

FIG. 20B.—Deformations during Drawing.

This calculation has established the fact that, in consequence of the additional movements, the average true deformation in industrial mechanical treatment noticeably exceeds the amount of stretch derived from a comparison of the initial and final dimensions. For the drawing test with steep angle dies already mentioned, the excess deformation, as compared with pure extension, amounts to more than 15 per cent. This amount becomes less with a smaller die angle and with heavier reductions. In an extrusion test the deformation in excess of that due to simple extension amounts to more than 100 per cent., and in a

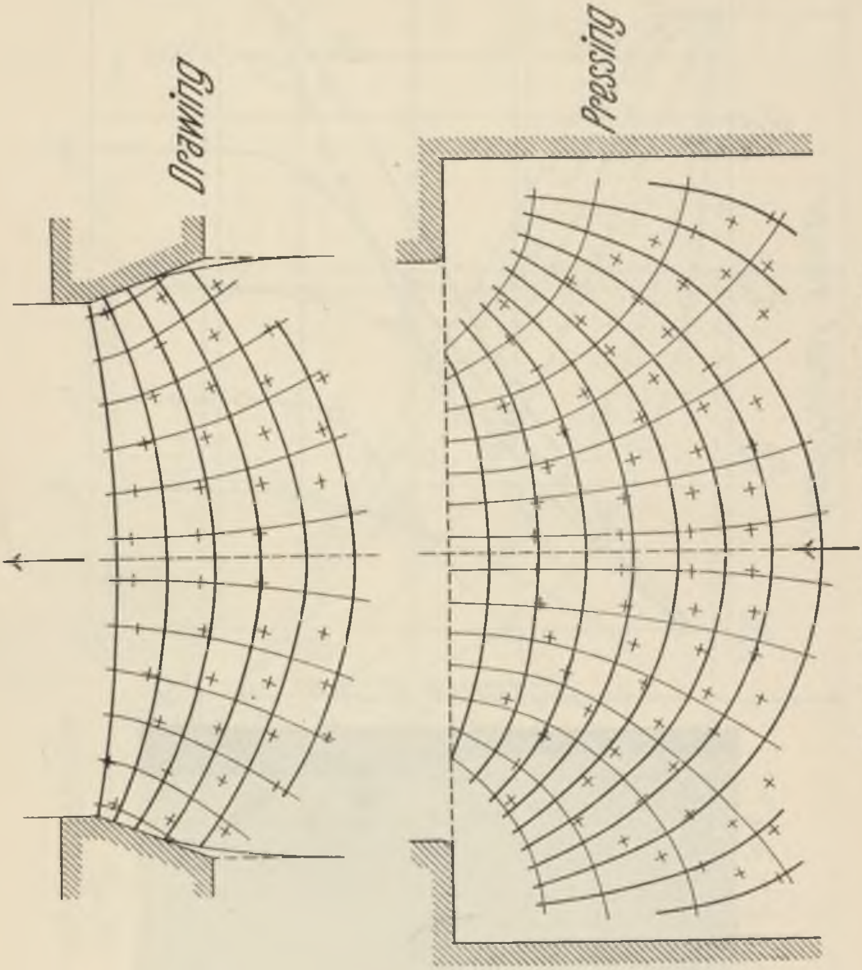

FIG. 21.—Stress Trajectories in the Transition Zone.

piercing test even to more than 200 per cent. of the average elongation of the material. In these processes, owing to additional slip, very considerable internal movements occur which do not effect the desired spread, and therefore have to be accounted as losses in working.

Since the principal direction of deformation coincides with that of the principal stress, the estimation of the course of the stress trajectories is rendered feasible by the determination of the change in form at every point in the transition zone. In Fig. 21 these are given for the tests on drawing and extrusion. The stress distribution in the transition zone has a construction similar to an arch; under the action of the transverse pressure thus produced deformation takes place. It is noteworthy that these transverse compressive stresses are not at right angles to the stream lines, as Alkins and Cartwright have concluded from their researches, but that, as closer analysis of the deformation shows, in the outer layers they are inclined at a small angle to the perpendicular. The method of investigation which has been illustrated thus permits, together with an exact analysis of the course of deformation, the formulation of expressions concerning the stress relations in industrial shaping processes.

C.—POWER AND ENERGY DEMANDS IN TECHNICAL METAL WORKING.

The exhaustive analysis of the processes of deformation which has been given renders feasible a more exact expression for the power or energy consumed in the carrying out of the technical working processes. The fundamental relationships between the resistance to deformation of the material, the roll pressure developed, and the output from the rolls were known long ago.*

According to the relationships derived by C. Fink † for rolling, the energy demand is calculated on the basis of pure parallelepipedial change in form, as the product of the resistance to deformation of the material and the "volume displaced." The latter is given by multiplying the volume of the deformed body by the natural logarithms of the ratio of the dimension of the piece before and after the operation.

According to the shear stress theory, the resistance to deformation of a material corresponds with the constant maximum difference of two principal stresses, which difference determines the occurrence of plasticity. It is a property which suffers no change by hot-working during the transformation, yet is dependent on the working tempera-

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* *Stahl u. Eisen*, 1881, 1, 57. † *Z. Bergwes. Preusz.*, 1874, 22, 200.

ture and the speed of deformation, but which increases rapidly, however, with cold-working, according to the extent to which the form is changed (cold-hardening).

The energy and power required for the transformation, calculated according to these views, are only the lower limiting values to be actually used. In the first place, the augmented deformation due to the additional movements already mentioned demands an additional supply of energy; and in the second place, the friction between the tool and the work tends to increase the power and energy required.

The ratio of the theoretical expenditure of energy in loss-free deformation to the actual amount of energy employed constitutes the "efficiency of deformation" of the process concerned; this factor has proved a suitable standard by which to compare the values of a deformation process under different working conditions as well as those of different processes.* In this manner the actual work of deformation has been calculated from the power transferred from the tool to the material. These power measurements have been made by the help of suitable measuring devices, which, in the case of drawing, were attached to the die-plate, and in that of rolling to the roll bearings. Losses of an electrical and mechanical nature depending on the method of driving the machine employed will not be discussed here. Valuable conclusions which bear on the construction and use of the machines may be reached from a determination of the efficiency. Only the actual losses incident to the working of the material will be further considered in this lecture. They may be divided into internal and external losses. The external losses are due to friction between the material and the surface of the tool; they are strongly dependent on the degree of lubrication, and may be derived only so far as the friction coefficient for conditions in the test concerned is known. The internal losses arise from the inner deformations already mentioned, which are in excess of the amount necessary for the development of the ultimate shape. Fig. 22 shows the result of the valuation of a series of drawing tests conducted by W. Linicus and G. Sachs † with varying reductions in area for different angles of die aperture, recently made by A. Pomp and A. Koch ‡ at the Eisenforschungsinstitut. In every test the total work performed in drawing was split up into that theoretically useful for the operation and that consumed in the external and internal losses. From this diagram (Fig. 22) the most suitable die angle can be read

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* A. Pomp, E. Siebel, and E. Houdremont, *Mitt. K.-W.-Inst. Eisenforschung,* 1929, **11**, 53; E. Siebel and A. Pomp, *ibid.*, 1929, **11**, 73.

† "Spanlose Formung der Metalle. Versuche über die Eigenschaften gezogener Drähte und der Kraftbedarf beim Ziehen," p. 38. Berlin: 1931. (J. Springer.)

‡ A. Pomp and A. Koch, *Mitt. K.-W.-Inst. Eisenforschung,* 1931, **13**, 261.

off for each reduction employed. The increase in the efficiency of shaping with increasing reduction in area, which was found in earlier work,* stands out prominently here too. The external frictional losses, on the contrary, decrease as the die opening becomes steeper, corresponding with resulting shrinkage in the area of contact between the work and the die. As the die angle increases the internal losses become much larger, which is in agreement with the enhanced internal movements of the material observed with large angle dies. The more precisely we become acquainted with the course of deformation in the transition zone, the more trustworthy and complete an opinion we shall be able to give on the internal losses to be expected during the working of a metal.

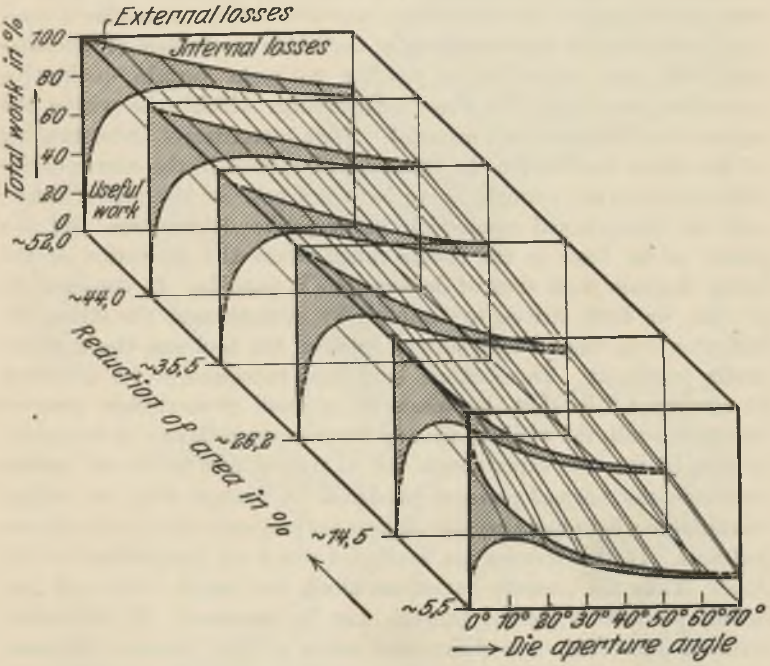

FIG. 22.—Useful and Lost Work in Wire-Drawing.

Systematic researches which have been carried out in the Institut with various kinds of lubricants † disclose how vitally the efficiency of

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* A. Pomp, E. Siebel, and E. Houdremont, *Mitt. K.-W.-Inst. Eisenforschung*, 1929, **11**, 53; E. Siebel and A. Pomp, *ibid.*, 1929, **11**, 73.

† A. Pomp and A. Koch, *Mitt. K.-W.-Inst. Eisenforschung*, 1931, **13**, 261.

deformation and drawing capacity of steel wire may be affected, when all other working conditions remain constant, by the selection of the lubricant. In these tests dry powdered soap has proved most satisfactory, whilst the fats on the whole exhibited a smaller lubricating effect than the oils which were tried.

The methods of investigation which have been reviewed have proved suitable in every case for obtaining a comprehensive insight into the mechanism of industrial shaping processes. They do not suffice, however, to fill a gap in our knowledge, and this makes impossible a complete and detailed understanding of the whole mechanism of deformation. We are, indeed, in a position to make certain qualitative assertions concerning the stress relationships which exist within the region of deformation in a material. For a quantitative understanding of the stress distribution the exact determination of the course of the deformation is not enough, as we have not got, for the plastic range, such an unequivocal connection between the deformation and the stress, as we have in the elastic range where the derivation of the stress diagram from that of deformation is possible. In consequence of this, we have striven to establish by measurement the stress distribution over the contact surface between the tool and the material under treatment. These efforts have been successful so far as rolling is concerned,* in that, by means of a small piezo-electric pressure measuring-cell, the whole of the gap between the rolls can be measured. A plug let into the experimental roll at right angles to the roll surface transfers the normal pressure produced by contact with the rolling material to a flat quartz crystal which is cut perpendicularly to its electrical axis. In this stresses are developed which are proportional to the load. Thus the pressure variations along the length of the roll gap, whilst material is passing through, can be measured. By the simultaneous recording of a differential curve of the pressure diagrams, which is possible by the addition of the necessary apparatus, the alterations in pressure are readily obtained. By laterally displacing the fillets against the plug of the pressure measuring-cell the pressure distribution over the whole width of the roll gap can be recorded.

On the left of Fig. 23 the experimental individual pressure distribution curves have been assembled, in a space model of compressive stresses between the roll and the material. The maximum value of the compressive stress occurs in the region of the roll exit, and decreases on both sides in the longitudinal direction of the specimen. In the transverse direction the distribution of the pressure in the roll gap is

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* Particulars of these measurements undertaken by W. Lueg will shortly be published in the *Mitt. K.-W.-Inst. Eisenforschung.*

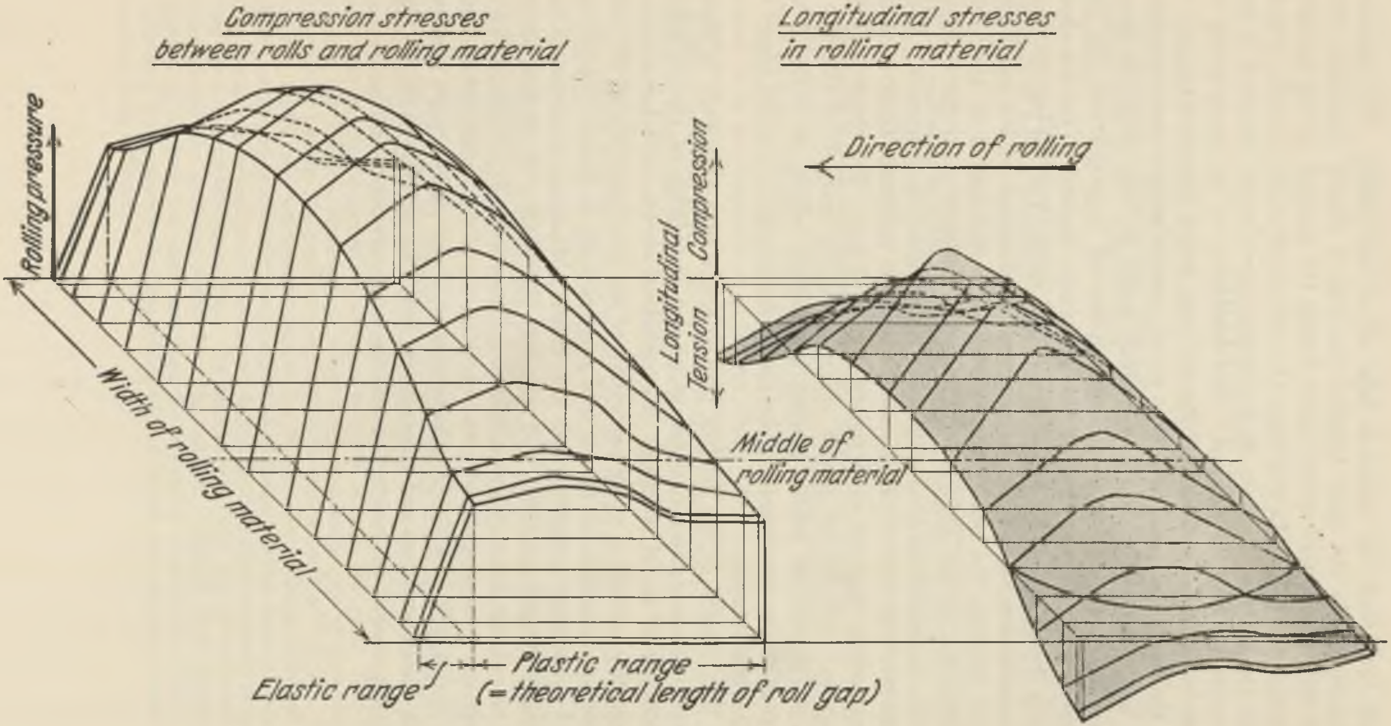

FIG. 23.—Stresses in the Zone between Rolls.

such that from the centre it falls off on each side. The pressure distribution in the space between the rolls is closely connected with the flow phenomena which occur during the passage of the material through the rolls. In this space the movement of the material is such that the individual points on its surface move in the direction of the greatest gradient in pressure. The formation of the parting-line of flow in the neighbourhood of the roll exit, which separates the region of the leading material from that which remains behind, and the spread of metal caused by lateral flow may easily be read from the space model. At each point the pressure measured is proportional to the resistance to deformation of the material. According to the shear stress theory, the latter is the sum of the strength of the material and the resistance to flow in the longitudinal direction at the particular point between the rolls. The stress figures represented in the right half of Fig. 23 are derived by subtracting for each point the strength of the material from the compression stress found for this point. They thus give a picture of the distribution of the resistance to flow in the longitudinal direction at all points of the roll gap. It is clearly evident that with unrestricted spread occurring on the margins of the specimen, longitudinal tensile stresses are caused, which, as is found by experience, assert themselves by producing cracks along the edges of thin rolled sheets.

The results of the studies placed before you constitute without doubt a considerable enrichment of our knowledge of the technical processes of metal working. Nevertheless, we are still far removed from the control, in every particular, of the relationships and the laws which govern them, so that it is of value actively to pursue yet further our systematic researches into this sphere. There is no doubt of the great technical, scientific, and economic significance of the attainment of this object, for only by an exhaustive knowledge of all circumstances that are of consequence in the carrying on of the industrial working of metals, and by a complete appreciation of the various valid relationships between stress and deformation, will it be possible to ensure that these processes are conducted with the maximum of usefulness.

OBITUARY.

Herbert Clifford Dews died on January 22, 1932, in Carshalton Hospital following an attack of influenza.

He was born at Wakefield in 1899 and received his metallurgical training at Sheffield University. After several years as metallurgical chemist to J. Hopkinson & Co., Ltd., he was in 1925 appointed chief metallurgist to Dewrance & Co., which position he held at the time of his death.

He was a Member of Council of, and President of, the London Branch of the Institute of British Foundrymen and recently took over the leadership of the Non-Ferrous Sub-Committee of that Institute. He was also a prominent member of the British Cast-Iron Research Association.

Mr. Dews wrote many papers for technical associations and the Press, and was the author of an exchange paper presented on behalf of the Institute of British Foundrymen to the French Association in 1929. He also wrote a book on " The Metallurgy of Bronze," which has since become a standard work.

Mr. Dews was elected a member of the Institute on March 9, 1921.

Sir William Mills, an Original Member of the Institute, died at Weston-super-Mare on January 7, 1932, at the age of 76.

He was born at Sunderland and there received a private education. At the age of 14 he was apprenticed to George Clark, Ltd., marine engineers, and served with that firm for seven years before taking his first-class certificate as a marine engineer in 1884. He then went to sea, where his work included the salving of ships and laying and repairing submarine telegraph cables. On one occasion he ran a blockade and witnessed the spiking of old-fashioned guns in Chile and Peru.

Sir William Mills first set up in business on his own account in Sunderland as William Mills & Co., Atlas Works, in 1885, and shortly afterwards (in 1891) he designed and patented the Mills Patent Instantaneous Engaging and Disengaging Boat Gear, which won for him the " Fairplay " prize of the Royal Naval Exhibition in competition with fifteen others. This invention also won several other awards. He began experiments with aluminium somewhere about 1890 at his original works, and a few years later was the first to produce castings of the metal on a commercial scale. This important event led in 1905 to the acquisition of works premises in Grove Street, Birmingham, and the opening of the Atlas Aluminium Foundry in order to supply the demands of motor-car manufacturers in the Midlands. It was at this factory that the principal supply of aircraft castings was made during the war. For this purpose Sir William invented an alloy which was subsequently practically taken over by the Government and which is still known as " L.5." His original works were retained to supply the North. Sir William Mills will be chiefly remembered as the inventor of the hand-grenade which bears his name. This device was brought out in February 1915, and 76 millions are said to have been made during the Great War. To demonstrate their use, he prepared an instructional film and also lectured on the subject. Besides other numerous patents which bear his name are those for telescopic aluminium seats, golf-clubs and folding-head shooting-sticks, one of which was regularly used by the late King Edward.

Sir William Mills was Managing Director of William Mills, Ltd., Birmingham, and proprietor of Mills Munitions, Ltd., Birmingham, and of the Sunderland Works. He was formerly Chairman of Triumph Trust, Ltd., and was a Director of the Java Produce Co., Ltd.

Although engaged in so many and varied business activities, Sir William Mills still found time to devote a good deal of his energy to public and semi-public works, and he was thus a Chairman of the James Watt Memorial Trust, a member of the Council of the Birmingham Chamber of Commerce and a member of the Alloys Research Committee, the Imperial Mineral Resources Bureau, and the Institution of Mechanical Engineers.

He was deeply interested in the drama, and was an enthusiastic supporter of the scheme for rebuilding the Shakespeare Memorial Theatre at Stratford-on-Avon. He was also a connoisseur of old pictures, china, and antiques.

Dr.-Ing Werner Morell died, after a short illness, on January 18, 1932, at the age of 32.

He was born on June 8, 1899, at Halle an der Saale, and received his education in Halle and Berlin. He read jurisprudence and economics at the University of Berlin and subsequently in 1920 he studied the metallurgy of non-ferrous metals and metallography at the Technical High School of the same town. He took his degree of Dipl.-Ing. on April 8, 1926.

In June 1925 he became Research Assistant at the Kaiser-Wilhelm-Institut für Metallforschung, Berlin-Dahlem, and in 1928 manager of the corrosion laboratory of that Institute. Together with Professor Dr.-Ing.E.h. O. Bauer, he carried out a comprehensive investigation of the corrosion of aluminium and its light alloys and was occupied with a critical review of all previous work on this subject. Unfortunately, he did not live to see the fruit of his labours. On September 1, 1931, he entered the Abteilung für Metallographie of the Staatliches Materialprüfungsamt, Berlin-Dahlem.

After his death the faculty of Maschinenwesen of the Technical High School of Berlin conferred upon him the degree of Dr.-Ing. in recognition of a dissertation on " The Qualification of the Tensile Test as a Method of Valuation of Corrosion Experiments and the Importance of this Method in Practice," which he had delivered in 1931.

Apart from his scientific work, he will be remembered as a very kind-hearted man, who was always ready to help others.

Dr.-Ing Morell was elected a Member of the Institute of Metals on November 7, 1929. —M. Hansen.

Hugh Philip Tiemann died on January 4, 1932.

He was born in New York and graduated from Columbia University in 1900. A year later he joined the Carnegie Steel Co., and remained with this firm as Assistant Metallurgical Engineer until his death, being first stationed at the Homestead Works and then transferred to the City Office. He was author of a book on " Iron and Steel " and of numerous scientific papers. He was a member of the American Society for Testing Materials, the American Society for Steel Treating, the American Institution of Mining and Metallurgical Engineers, the Association of the American Steel Manufacturers, the Engineers Society of Western Pennsylvania, the Society of Automobile Engineers, and the Iron and Steel Institute.

Mr. Tiemann's varied interests are shown by the fact that he was a member of several athletic societies and also of the Philatelic Society of Pittsburgh and was also prominent in Masonry; at the time of his death he had just completed his service as Worshipful Master of Crescent Lodge, No. 576 and was to have been elected High Priest in December.

Mr. Tiemann was elected a member of the Institute of Metals on December 31, 1912.

Katsumi Ueki died on August 17, 1931, at the age of 28. For six years he was a student at the Technological University at Port Arthur, South Manchuria, taking his degree in July, 1931. The course of research he selected was on non-ferrous alloys, and he was the first student of his college to choose this.

Mr. Ueki was elected a student member on December 19, 1928, and became a full member of the Institute on June 1, 1929.

William Edward Watson, late Managing Director of the Atlas Metal and Alloys Company, Limited, died at his home at Winchmore Hill, London, on May 28, at the age of 66.

Some eighteen months ago Mr. Watson was the victim of an unfortunate accident at his London Club, where he slipped while descending the stairs, seriously injuring both his knees and depriving him of the use of his legs for some period. Although he recovered partly from his accident, he was not able to withstand the strain which was placed on him when he endeavoured to resume his usual active life.

An Original Member of the Institute, his first working years were spent on the sea, but when he was still quite young Mr. Watson became interested in the metal business, and after a few years' experience he took over the management of the Atlas Company upon its formation early in the present century.

He was a great traveller, and built up the world-wide connection of his company by journeys to the Continent of Europe and various other parts of the globe. He made a study of the actual working conditions wherever his firm's alloys were used, and it was this intimate touch with his customers' requirements which enabled him to introduce brands of metals bearing his own name and that of his company, and to withstand the growth of competition during more recent years.

Mr. Watson was of a kindly and genial disposition, and had the happy knack of being able to make himself *persona grata* to men of all classes, creeds, and nations; his loss will be deplored by his many friends throughout the world.

Sir Alfred Yarrow, Bart., an Original Member of the Institute, died at the age of 90, on January 25, 1932.

He early betrayed his inventive genius when at 8 years, he designed an automatic wool winder, then a self-acting candle extinguisher and a clock worked by weights. He was educated at University College School and in 1857 was apprenticed to makers of engines for warships until he reached the age of 21. During this period he attended as many science lectures as possible, and continued to study at University College, where he was a fellow-student of Mr. Joseph Chamberlain.

On the death of his father, he was left without means, and was unable to market inventions which he had patented, until friends and relations supplied the sum of £400. He invented the steam plough, and a steam carriage which, however, was not permitted to be used unless preceded by a man carrying a red flag.

The capital derived from the royalties on the first of these inventions enabled him to open an engineering works on the Thames at the Isle of Dogs in 1866, but it fared badly until he began to build small steam launches. He mounted the first torpedo tube in 1873, thus creating the first torpedo boat, which he followed by the torpedo boat destroyer in 1892. He was created a baronet in 1916.

Sir Alfred Yarrow was one of the most charitable of men, and gave large sums to the Out-Patients Department of the London Hospital, and also for training nurses and for the building of a convalescent home at Broadstairs. His interest in learning is shown by the donation of £100,000 to the Royal Society—devoted to founding research professorships—and £20,000 towards the building of a testing tank for naval construction at the National Physical Laboratory. This was opened in 1911. He was also a generous benefactor to Girton College, Cambridge.

In 1913 he retired to Hampshire, but resumed his work at the outbreak of war, during which period he built twenty-nine destroyers in his yard at Scotstoun, to which he was forced to move in 1906 owing to the high cost of production on the Thames.

Sir Alfred Yarrow took up flying late in life, and went for a tour of Europe by air only last year.

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