Form A. *(Membership Application)*

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

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

The INSTITUTE of METALS

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

Founded 1908. *Incorporated* 1910.

To the Secretary,
The Institute of Metals.

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

Name of applicant in full...

Address...

Business or Profession..

Qualification...

Degrees and/or honorific distinctions...

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

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

Signatures of three Members.

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

To be filled up by the Council.

....

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

Chairman.

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

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

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

54.

EXTRACTS FROM THE RULES

(MEMORANDUM AND ARTICLES OF ASSOCIATION.)

MEMBERS AND MEMBERSHIP

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

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

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

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

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

(*a*) Students of Metallurgy; or

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

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

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

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

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

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

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

SUBSCRIPTIONS

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

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

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

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

DUTIES AND OBLIGATIONS OF MEMBERS

Rule 12.—Every member shall be bound:

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

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

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

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

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

[Elliott & Fry.

Dr. HAROLD MOORE, C.B.E.
President.

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

[Frontispiece.

No. 1 1934

THE JOURNAL
OF THE
INSTITUTE OF METALS

~~2566~~

VOLUME LIV

EDITED BY
G. SHAW SCOTT, M.Sc.
SECRETARY

The Right of Publication and of Translation is Reserved

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

The Institute of Metals is not responsible either for the statements made or for the opinions expressed in the following pages

LONDON
PUBLISHED BY THE INSTITUTE OF METALS
36 VICTORIA STREET, LONDON, S.W.1
1934

Copyright] [*Entered at Stationers' Hall*

P.99/34/1

POLITECHNIKA ŚLĄSKA
BIBLIOTEKA GŁÓWNA
w Gliwicach

Past-Presidents.

Sir William Henry White, K.C.B., LL.D., D.Eng., Sc.D., F.R.S., 1908–1910 (*deceased*).

Sir Gerard Albert Muntz, Bart., 1910–1912 (*deceased*).

Professor William Gowland, A.R.S.M., F.R.S., 1912–1913 (*deceased*).

Professor Alfred Kirby Huntington, A.R.S.M., 1913–1914 (*deceased*).

Engineer Vice-Admiral Sir Henry John Oram, K.C.B., F.Inst.Met., F.R.S., 1914–1916.

Sir George Thomas Beilby, LL.D., D.Sc., F.R.S., 1916–1918 (*deceased*).

Professor Sir (Henry Cort) Harold Carpenter, M.A., Ph.D., A.R.S.M., F.Inst.Met., F.R.S., 1918–1920.

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

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

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

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

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

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

Sir Henry Fowler, K.B.E., LL.D., D.Sc., 1932–1934.

LIST OF OFFICERS
OF
THE INSTITUTE OF METALS
1934-1935

President.

Harold Moore, C.B.E., D.Sc., Ph.D.

Past-Presidents.

Professor Sir Harold Carpenter, M.A., Ph.D., A.R.S.M., F.R.S.
Sir John Dewrance, G.B.E.
Sir Henry Fowler, K.B.E., LL.D., D.Sc.
Richard Seligman, Ph.nat.D.
Leonard Sumner, O.B.E., M.Sc.
Professor Thomas Turner, M.Sc., A.R.S.M.

Vice-Presidents.

W. R. Barclay, O.B.E.	London.
C. H. Desch, D.Sc., Ph.D., F.R.S.	Teddington.
A. G. C. Gwyer, B.Sc., Ph.D.	Warrington.
Professor D. Hanson, D.Sc.	Birmingham.
H. C. Lancaster	London.
E. L. Morcom, M.A.	Birmingham.

Honorary Treasurer.

John Fry	London.

Members of Council.

Professor J. H. Andrew, D.Sc.	Sheffield.
Engineer Vice-Admiral H. A. Brown, C.B.	London.
H. W. Brownsdon, M.Sc., Ph.D.	Birmingham.
Engineer Vice-Admiral Sir Robert Dixon, K.C.B., D.Eng.	London.
Kenneth Gray	Sheffield.
H. H. A. Greer, J.P.	Glasgow.
J. L. Haughton, D.Sc.	Teddington.
Professor R. S. Hutton, D.Sc., M.A.	Cambridge.
Wesley Lambert, C.B.E., A.K.C.	London.
A. H. Mundey	London.
C. J. Smithells, M.C., D.Sc. (representing the Local Sections).	
A. J. G. Smout	Birmingham.
James Steven	Glasgow.
F. Tomlinson	Manchester.
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, 1934.

CORRESPONDING MEMBERS TO THE COUNCIL.

Australia.

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

Canada.

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

Egypt.

H. NORMAN BASSETT, Egyptian State Railways, Bulak, Cairo.

France.

Professor P. A. J. CHEVENARD,
Aciéries d'Imphy, Imphy (Nievre).

Germany.

Dr.-Ing. MAX HAAS, Kreisgrenze I, Lautawerk (Lausitz).

Holland.

J. HAMBURGER, JAZN, Malienbaan 5, Utrecht.

India.

R. MATHER, B.Met., Tata Iron and Steel Co.,
24 Bruce Street, Fort, Bombay.

Italy.

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

Japan.

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

South Africa.

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

Sweden.

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

Switzerland.

Professor Dr.-Ing. E. HONEGGER, 85 Susenbergstr., Zurich 7.

United States of America.

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

CHAIRMEN AND HONORARY SECRETARIES OF THE LOCAL SECTIONS.

Birmingham.

Chairman : Maurice Cook, M.Sc., Ph.D., Messrs. I.C.I. Metals, Ltd., Witton, Birmingham.

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

London.

Chairman : C. J. Smithells, M.C., D.Sc., Research Laboratories, Messrs. General Electric Co., Ltd., Wembley.

Hon. Secretary : J. McNeil, A.R.T.C., Messrs. The Mond Nickel Co., Ltd., Thames House, Millbank, S.W.1.

North-East Coast.

Chairman : W. Richardson, B.Sc., Newcastle-upon-Tyne Electric Supply Co., Carliol House, Newcastle-upon-Tyne.

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

Scottish.

Chairman : J. W. Donaldson, D.Sc., Laboratory, Engineering Department, Messrs. Scott's Shipbuilding and Engineering Co., Ltd., Greenock.

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

Sheffield.

Chairman : Kenneth Gray, Messrs. Mellowes and Co., Ltd., Corporation Street, Sheffield.

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

Swansea.

Chairman : Professor L. Taverner, A.R.S.M., Metallurgical Department, University College, Singleton Park, Swansea.

Hon. Secretary : Roosevelt Griffiths, M.Sc., Metallurgical Department, University College, Singleton Park, Swansea.

CONTENTS

MINUTES OF PROCEEDINGS.

PAGE
ANNUAL GENERAL MEETING, LONDON 13
  Report of Council 13
  Report of Honorary Treasurer 19
  Election of Officers for 1934–1935 22
  Election of Members and Student Members 22
  Re-Election of Auditors 24
  Induction of New President 24
  Vote of Thanks to Retiring President 25
  Votes of Thanks 28

Presidential Address. By H. Moore, C.B.E., D.Sc., Ph.D. 29

Castability of Ternary Alloys. By Professor A. Portevin and P. Bastien, Dr.-es-Sci. With Discussion 45

Minimum Dimensions of Test-Samples for Brinell and Diamond Pyramid Hardness Tests. By G. A. Hankins, D.Sc., A.R.C.S., and C. W. Aldous, B.Sc., A.C.G.I. With Discussion and Correspondence 59

Transverse Tests on Sand-Cast Aluminium Alloy Bars. By C. E. Phillips, A.C.G.I., D.I.C., and J. D. Grogan, B.A. With Discussion and Correspondence 89

Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation. By I. G. Slater, M.Sc., Ph.D. With Discussion and Correspondence 103

The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin. By C. E. Pearson, M.Met. 111

A Note on Some Formulæ Concerning Viscous and Plastic Flow in Soft Metals. By E. W. Fell, Dr.-Ing., M.Sc. 125

Joint Discussion on the papers by Mr. C. E. Pearson and Dr. E. W. Fell . 131

The Malleability of Nickel and of Monel Metal. By Owen W. Ellis, M.Sc. . 145

Alloys of Silver and Beryllium. By H. A. Sloman, M.A. With Discussion . 161

The Diffusion of Zinc and Iron at Temperatures Below the Melting Point of Zinc. By Gilbert Rigg. With Correspondence 183

A Study of the Influence of the Intercrystalline Boundary on Fatigue Characteristics. By H. J. Gough, M.B.E., D.Sc., Ph.D., F.R.S., H. L. Cox, B.A., and D. G. Sopwith, B.Sc.Tech. With Discussion and Correspondence 193

PAGE

The Constitution of Copper–Iron–Silicon Alloys. By Professor D. Hanson, D.Sc., and E. G. West, Ph.D. With Discussion 229

Transformations in the Copper–Palladium Alloys. By R. Taylor, B.A., B.Sc. With Discussion 255

Alloys of Magnesium Research. Part I.—The Constitution of the Magnesium-Rich Alloys of Magnesium and Nickel. By John L. Haughton, D.Sc., and Ronald J. M. Payne, B.Sc. With Correspondence . . 275

ANNUAL MAY LECTURE 285

Election of Members and Student Members 285

Gases and Metal Surfaces. Twenty-Fourth May Lecture. By Professor E. K. Rideal, F.R.S. 287

Obituary 313

Subjects Index 321

Names Index 323

LIST OF PLATES

Dr. Harold Moore, C.B.E., President . . . . . . *Frontispiece*

I. to III. Illustrating Professor Dr. A. von Zeerleder's discussion on Professor A. Portevin and Dr. P. Bastien's paper *between pp.* 56 *and* 57

IV. to V. ,, Mr. C. E. Pearson's paper. *between pp.* 112 *and* 113

VI. to IX. ,, Mr. H. A. Sloman's paper *between pp.* 166 *and* 167

X. to XII. ,, Mr. Gilbert Rigg's paper . *between pp.* 184 *and* 185

XIII. to XVI. ,, Dr. H. J. Gough and Messrs. H. L. Cox and D. G. Sopwith's paper *between pp.* 208 *and* 209

XVII. to XVIII. ,, Professor D. Hanson and Dr. E. G. West's paper . . *between pp.* 240 *and* 241

XIX. to XX. ,, Mr. R. Taylor's paper . *between pp.* 256 *and* 257

XXI. ,, Professor E. K. Rideal, F.R.S., May Lecturer, 1934 . . . . *to face p.* 288

XXII. ,, The late Dr. Walter Rosenhain, F.Inst.Met., F.R.S., President, 1928–1930 . . . . . *to face p.* 312.

THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS.

ANNUAL GENERAL MEETING.

The Twenty-Sixth 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 7 and 8, 1934, Sir Henry Fowler, K.B.E., LL.D., D.Sc., President, occupying the chair at the opening of the meeting.

Wednesday, March 7.

The Minutes of the Annual Autumn Meeting held in Birmingham from September 18 to 21, 1933, were taken as read.

REPORT OF COUNCIL

for the Year ended December 31, 1933.

The Council has pleasure in submitting its report upon the activities of the Institute during the past year, a period that was specially notable both for the celebration of the twenty-fifth anniversary of the Institute's formation and the setting up of improved methods of publication.

The Institute ended another year of the long-continued industrial depression with a slight reduction in its membership and financial resources. In spite of the difficulties encountered, it is felt that the usefulness of the Institute to its members has not only been fully maintained, but even increased. This has been made possible by the encouraging and continued support given by members—financially, in committee, and in other ways—and by the unwearying efforts of the staff of the Institute.

Roll of the Institute.

The number of members on the roll of the Institute, for the second year in succession, shows a fall on December 31, when the totals for the various classes of membership were as indicated in the following table, which gives the membership during the past five years :—

	Dec. 31, 1929.	Dec. 31, 1930.	Dec. 31, 1931.	Dec. 31, 1932.	Dec. 31, 1933.
Honorary Members	5	5	5	5	5
Fellows . .	9	7	7	8	8
Ordinary Members	2035	2083	2146	2073	2038
Student Members .	73	65	74	79	80
	2122	2160	2232	2165	2131

On December 31, 1933, the names of 122 Original Members were included in the total of 2038 Ordinary Members. On December 31, 1908—the end of the Institute's first year—the Original Members numbered 355. 133 members and students were elected during the year, a figure that compares with 120 in 1932 and 205 in 1931.

OBITUARY.

Many losses by death occurred during the year. Among the Original Members who died were P. T. Caird and W. Cleland. In addition to the above the deaths of the following were notified to the Secretary: Dr. N. Fukushima; E. A. Hadley; Dr. K. Hallmann; D. F. John; Colonel A. F. Masury; W. D. Pomeroy; J. Rolland; J. Kent Smith; Professor H. Specketer; Sir Gilbert Vyle; and C. E. Whiteley.

MEETINGS OF THE INSTITUTE.

At the Annual General Meeting, which took place in London on March 8 and 9, thirteen papers were presented, the meeting being followed by a Dinner and Dance at the Trocadero Restaurant. In the afternoon of March 9 members were privileged to pay a visit to the headquarters of the British Non-Ferrous Metals Research Association.

The Annual May Lecture—the second general meeting of the year—was delivered by a distinguished French member, Professor Albert Portevin, whose subject was "Quenching and Tempering Phenomena in Alloys."

The twenty-fifth Annual Autumn Meeting was appropriately held in Birmingham, in which city the first Autumn Meeting was held in 1908. The "Silver Jubilee" meeting was well attended; fourteen papers were presented. The Autumn Lecture was given by Mr. W. R. Barclay, on "Twenty-Five Years' Progress in Metallurgical Plant." Following the reading and discussion of the papers, members visited works and other places of interest in Birmingham and neighbourhood.

The proposal to hold the 1934 Autumn Meeting on board ship was investigated by a Committee of the Council. As a result of a referendum of all members, showing that fewer than 100 persons were prepared to take part in the proposed meeting, the Council decided to abandon the scheme.

By kind invitation of the Organizers of the Shipping, Engineering, and Machinery Exhibition at Olympia, members were enabled to visit the exhibition on Sept. 15 and were entertained to tea.

A joint meeting with the Manchester Metallurgical Society was held on October 25, when two papers that had been read at the Birmingham meeting were re-presented and discussed.

SILVER JUBILEE FUND.

To commemorate the 25th anniversary of the Institute's foundation, the Original Members contributed the sum of £525 to a "Fund in connection with the Silver Jubilee." Subsequently additional contributions, totalling £144 2*s*., were received from other members who desired to be associated with the Fund. As the Fund was established since the end of the last financial year, it is not referred to in the accounts which follow the Treasurer's Report. The Fund is still open.

PUBLICATIONS.

The past year saw considerable activity in connection with the Institute's publications. In response to suggestions made by members, the Council arranged for advance copies of papers to be printed in the *Monthly Journal*. It is hoped that the new method of publication will be generally appreciated by the members, and will result in better discussions, since in many cases members will receive papers some months earlier than would have been possible under the old system.

Members are reminded that the papers now being published in the *Monthly Journal* will not be issued again except when they appear in the half-yearly bound volumes of the *Journal.*

LOCAL SECTIONS.

The work of the Local Sections of the Institute was successfully continued. Before each of the six sections papers were read during the winter months. A list of these papers appears in an appendix to this Report. In the *Monthly Journal* a short account was given, in advance of each meeting, of the papers to be read in the month following its appearance.

INSTITUTE OF METALS LECTURES.

Five "Institute of Metals Lectures" were delivered between January and March, 1933. No lectures were arranged for the session 1933–1934, but as several applications were received for further lectures, it is possible that similar lectures will be arranged for the session 1934–1935. Hitherto the lectures have been delivered by members before metallurgical societies of Universities and University Colleges, and it is possible that the scheme may be extended to include Technical Colleges and Polytechnic Institutes.

BEILBY MEMORIAL AWARD.

The Council are glad to report that a member—Mrs. G. H. Tipper (Constance F. Elam, D.Sc., M.A.)—received a Beilby award of one hundred guineas.

GIFT BY THE TREASURER.

The Honorary Treasurer, Mr. John Fry, presented to the Institute a Victoria Cross, "as representing the highest use to which a piece of bronze could be put." The Cross has been suitably mounted in a case containing the history of the award and can be inspected by members.

LIBRARY.

During the past year nearly 3000 books and periodicals were loaned to members. Eighty-five new text-books were acquired. The number of members visiting the library increased considerably. Many of these callers as well as correspondents have also applied for information which it has, in the main, been possible to furnish.

Members have been particularly interested in the new arrangement, inaugurated this year, whereby manuscript copies of Local Section papers are filed, and are thus made available for loan in the ordinary way. These papers have been much in request.

It is desirable to emphasize once again the connection between the abstracting service and the library. Many members make a practice of studying the abstracts which they receive monthly and then apply to the library for the loan of the articles or books which appear to be of interest to them, but more could undoubtedly obtain much benefit from this service, and it is surprising to find it is not better known. Those who visit the library often say that they are unaware of this valuable privilege of membership. Members who have not access to a good works' library have found the Institute's library and abstracting service particularly useful.

The resources of the Science Library have again been largely drawn upon, and members are reminded that books and periodicals available in this huge library may be obtained on loan (by post) on application to the Librarian of the Institute. Books and periodicals outside the Institute's field of work are thus obtainable through this channel. The assistance that the Science Library is rendering to research by the facilities for loan which are offered cannot be over-estimated, and the Council desires to thank the Director, Brigadier E. E. B. Mackintosh, D.S.O., R.E., and his Staff for their assistance.

Members, particularly those overseas, are reminded of the photostat service, by which they may obtain copies of papers not otherwise easily obtained at a moderate cost. Conditions on which these can be supplied are set out on p. 387, Volume XLII of the *Journal*.

COMMITTEES.

The following Committees of the Council have held frequent meetings during the past year:—

AUTUMN MEETINGS.
COUNCIL NOMINATION.
DINNER.
FINANCE AND GENERAL PURPOSES.
JOURNAL PRINTING COSTS.
LIBRARY.
LOCAL SECTIONS.
MEMBERSHIP.
MEETING AND PAPERS.
PUBLICATION.

REPRESENTATIVES.

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

Sir Charles Parsons Memorial Committee: Sir Henry Fowler (President).

British Standards Institution (Committee on Lead Alloys for Cable Sheathing): H. C. Lancaster.

Chemical Engineering Conference, 1935: Dr. Richard Seligman.

British Science Guild Parliamentary Committee: Sir Henry Fowler (President) and Mr. G. Shaw Scott (Secretary).

Advisory Committee on Metallurgy, City & Guilds of London Institute: Professor T. Turner.

Professional Classes Aid Council: Mr. H. B. Weeks.

CORRESPONDING MEMBERS TO THE COUNCIL.

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

Signed on behalf of the Council,

HENRY FOWLER, *President*.
H. MOORE, *Vice-President*.

G. SHAW SCOTT, *Secretary and Editor*.

January 4, 1934.

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

APPENDIX.

LOCAL SECTIONS' PROGRAMMES, 1933–1934.

BIRMINGHAM LOCAL SECTION.

Chairman: W. E. Ballard.

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

1933.	Programme.
Oct. 5.	V. E. Pullin, C.B.E., B.A., B.Sc. "The X-Ray Analysis of Metals."
Nov. 7.	J. W. Jones, M.Sc. "Interpretation of a Photomicrograph."
Nov. 14.	G. L. Bailey, M.Sc. "Deoxidizers and Fluxes."
Nov. 30.	Symposium on Defects in Cold-Working. Arranged by A. L. Molineaux.
Dec. 2.	Dinner and Dance (Midland Hotel).
Dec. 7.	D. W. Aldridge. "The New Copper Refinery at Prescot."
1934.	
Jan. 4.	W. R. Barclay, O.B.E. "Nickel and Nickel Alloys."
Jan. 16.	C. A. Hadley. "Electric Welding."
Feb. 1.	Open Discussion on the Metallurgical Inspection of Engineering Materials.
Feb. 13.	Maurice Cook, Ph.D., M.Sc. "Age-Hardening Copper Alloys."
Mar. 1.	J. C. Hudson, D.Sc. "Field Tests on Corrosion."
Mar. 20.	J. Parkinson. "The Manufacture of Hot-Rolled Seamless Steel Tubes."

All meetings were held in The James Watt Memorial Institute, Birmingham, at 7 p.m. They formed part of a joint programme arranged by the Midland Metallurgical Societies (consisting of the Birmingham Local Section of the Institute of Metals, the Birmingham Metallurgical Society, and the Staffordshire Iron and Steel Institute).

LONDON LOCAL SECTION.

Chairman: S. L. Archbutt.

Hon. Secretary: J. McNeil, A.R.T.C., Messrs. The Mond Nickel Co., Ltd., Thames House, Millbank, S.W.1.

1933.	Programme.
Oct. 5.	S. L. Archbutt. Chairman's Address.
Nov. 9.	R. Annan. "Gold—Its Sources and Production." (Meeting at the Royal School of Mines, South Kensington, S.W.7.)
Dec. 7.	J. R. Handforth, M.Sc. "A Metallurgist's Outlook on Modern Foundry Productions." (Joint Meeting with the Institute of British Foundrymen.)
1934.	
Jan. 11.	H. A. Sloman, M.A., B.Sc. "Beryllium and Its Alloys."
Feb. 8.	A. G. Lobley, M.Sc. "Electric Annealing and Heat-Treatment Furnaces."
Mar. 15.	G. Barr, B.A., D.Sc., and Miss Hadfield, M.Sc. "Spectroscopic and Microchemical Analysis of Metals and Alloys."
Apl. 12.	Annual General Meeting and open discussion.

The Meetings were, except the second, held in the Rooms of the Society of Motor Manufacturers and Traders, Ltd., 83 Pall Mall, S.W.1, at 7.30 p.m.

NORTH-EAST COAST LOCAL SECTION.

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

1933. Programme.

Oct. 10. Exhibition of Cinematograph Films.
Nov. 14. W. E. Ballard. "Metal Spraying." (Joint Meeting with the Newcastle Branch of the Society of Chemical Industry.)
Dec. 12. J. E. Hurst. "Addition of Non-Ferrous Metals to Cast Iron." (Joint Meeting with the Institute of British Foundrymen.)
1934.
Jan. 9. C. R. Deglon and L. Miller. "The Physical Properties of Deposited Weld Metal in the Arc-Welding and Atomic Hydrogen Processes."
Feb. 13. J. E. Newson, M.Met. Chairman's Address.
Mar. 13. C. E. Pearson, M.Met. "The Flow of Metals in the Extrusion Process."
Annual General Meeting.

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

SCOTTISH LOCAL SECTION.

Chairman: Professor Robert Hay, B.Sc., Ph.D.
Hon. Secretary: Harold Bull, Messrs. Bull's Metal and Melloid Co., Ltd., Yoker, Glasgow.

1933. Programme.

Oct. 9. Display and demonstration at the Royal Technical College, arranged by Professor Robert Hay, B.Sc., Ph.D. (Chairman).
Nov. 13. Discussion of three papers presented at the Autumn Meeting of the parent Institute.
Dec. 11. T. Tyrie. "The Use of Fluxes and Slags in Non-Ferrous Foundry Practice."
1934.
Jan. 15. Sydney W. Smith, C.B.E., D.Sc., A.R.S.M. "Factors in the Solidification of Molten Metals."
Feb. 12. J. A. C. Edmiston. "Combustion Efficiency."
Mar. 12. Annual General Meeting.
J. Arnott. "Some Foundry Experiences and Recollections."

The Meetings (except the first) were 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: Captain F. Orme, M.Met.
Hon. Secretary: H. P. Gadsby, Assoc.Met., 193 Sandford Grove Road, Sheffield 7.

1933. Programme.

Oct. 13. F. W. Rowe, B.Sc. "Centrifugal Casting of Non-Ferrous Alloys."
Nov. 10. W. E. Ballard. "Metal Spraying."
Dec. 8. J. C. Howard, B.Met. "Modern Application of Electric Heat."
1934.
Jan. 12. N. D. Pullen. "Protection from Corrosion of Aluminium and Its Alloys."
Feb. 9. H. G. Dale. "Recovery and Refining of Precious Metals."
Mar. 9. Frank Mason. "'Nickel–Chrome' Plating."

The Meetings were 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. G. Ramsay, B.Sc., Ph.D.

Hon. Secretary : Roosevelt Griffiths, M.Sc., Metallurgical Department, University College, Singleton Park, Swansea.

1933.	Programme.
Oct. 10.	A. G. Ramsay, B.Sc., Ph.D. Chairman's Address.
Nov. 14.	Cecil H. Desch, D.Sc., Ph.D., F.R.S. "Ageing and Age-Hardening."
Dec. 12.	Exhibition of Industrial Films (at University College, Singleton Park).
1934.	
Feb. 20.	Professor F. Bacon, M.A. "Cracking and Fracture of Metals, with Special Reference to Service Breakages."
Mar. 13.	Discussion on Rolling, opened by Professor L. Taverner, A.R.S.M.

The Meetings were held at the Y.M.C.A. at 6.15 p.m. Tea was served before the Meetings.

The President, in moving the adoption of the Report, drew attention to the slight decrease in the membership, but announced that an improvement had taken place since the beginning of 1934.

Mr. John Cartland, M.C., M.Sc. (Member), who seconded, commented on the burden of work which fell on Members of Council, and stressed the value of what he termed the "magnificent abstracting and library service."

Dr. Richard Seligman (Past-President), directed attention to the new experiment of publishing papers in the *Monthly Journal*, and asked members to let the Council know whether the new arrangement appealed to them or not.

The resolution was carried unanimously.

REPORT OF THE HONORARY TREASURER

(Mr. JOHN FRY)

For the Financial Year ended June 30, 1933.

The period covered by this report was one of widespread depression in all directions, and though the non-ferrous industries were not so severely affected as many others, the year was somewhat disappointing from the point of view of the Institute's finances. On the income side there was a decrease in annual subscriptions of £387 2*s.* 4*d.*, and £63 6*s.* 8*d.* in interest on War Loan, although against the latter there was a non-recurrent receipt of £51 2*s.* 2*d.* on conversion. The total expenditure was £230 14*s.* 4*d.* less than in the previous year, as reductions were shown in salaries, *Journal* account, and expenses of meetings. The net result was an excess of expenditure over income of £401 19*s.* 6*d.* as against £226 4*s.* 11*d.* in the previous year. In addition, in the Balance Sheet £585 6*s.* 1*d.* is treated as a liability in respect of a half-yearly volume of the *Journal* which was printed but not actually due to be dispatched to members, and the corresponding cost of which, in previous years, had been included in the accounts of the subsequent year. In reference to the *Journal* Account (£1911 2*s.* 3*d.*), it should be explained that this is the net cost after allowing for receipts from sales and advertisements, and making no allowance for overhead expenses. It is not possible to give an actual figure for the total cost of publication of the *Journal*, owing to the difficulty of correctly apportioning overhead charges, but it is approximately three times the net cost, and thus is far the largest item in the expenditure of the Institute. The financial position of the Institute is a cause of some anxiety to the Council and is receiving

THE INSTITUTE OF METALS

BALANCE SHEET AS AT JUNE 30, 1933.

30.6.1932. £	£	LIABILITIES.	£ s. d.	£ s. d.
		Creditors:		
	136	Sundry Creditors for Accrued Expenses, less proportions in advance	126 6 10	
	284	*Journal* Accounts	1,144 1 9	
1,186	766	Subscriptions paid in advance	737 11 1	2,007 19 8
		Cash:		
	940	Balance due to Bank—Current Account	947 5 11	
873	67	Petty Cash in hand	79 12 8	867 13 3
		Entrance Fees Account:		
	890	Balance as at June 30, 1932	1,112 7 4	
1,112	222	Amount receivable for year to June 30, 1933	201 12 0	1,313 19 4
20		*Woodhouse Fund Account*		13 8 6
1,050		*House Fund Account*		1,049 19 7
		Excess of Assets over Liabilities:		
	5,775	Balance at June 30, 1932	2,794 14 7	
	226	*Less* Excess of Expenditure over Income for the year ended June 30, 1933	401 19 6	
	5,549		2,392 15 1	
2,795	2,754 *	*Deduct* Adjustments on *Journal* Account for year to June 30, 1932, including the half-yearly volume to that date, produced and paid for during the current year ending June 30, 1933	585 6 1	1,807 9 0
£7,036				£7,060 9 4

* Amount written off *Journal*.

30.6.1932. £	£	ASSETS.	£ s. d.	£ s. d.
		Office Furniture:		
200		As at June 30, 1932		200 0 0
		Library Books, &c.:		
100		As at June 30, 1932		100 0 0
		Sundry Debtors:		
	10	For Entrance Fees	12 12 0	
	480	,, Subscriptions	664 13 9	
	182	,, *Journal* Accounts, &c.	151 11 2	
	672		828 16 11	
	90	*Less* Reserve for Doubtful Subscriptions	215 15 6	
582				613 1 5
		Stock of Journals:		
1		At Nominal Valuation		1 0 0
		Investments:		
5,083		£5,111 1*s.* 8*d.* 3½% War Loan at cost		5,082 19 10
		House Fund:		
	1,045	£1,000 3½% War Loan at cost	1,044 19 1	
	5	Cash at Bank	5 0 6	
1,050				1,049 19 7
		Woodhouse Fund:		
20		Balance at Lloyds Bank		13 8 6
£7,036				£7,060 9 4

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 the affairs of the Institute of Metals as on June 30, 1933, according to the best of our information and from the explanations given to us and as shown by the books of the Institute.

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

December 20, 1933.

THE INSTITUTE OF METALS

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED JUNE 30, 1933.

30.6.1932. £		£	s.	d.	30.6.1932. £		£	s.	d.
2,176	To Salaries	2,095	0	0	6,425	By Annual Subscriptions	6,037	18	8
846	,, Wages and National Insurance	960	6	0	280	,, Interest on War Loan	217	4	4
2,063	,, *Journal* Account	1,911	2	3	—	,, Bonus on Conversion of 5% War Loan	51	2	2
830	,, Rent, Telephone, Lighting, and Insurance	831	9	10	9	,, Bank Interest	—	—	—
202	,, Printing and Stationery	198	13	9	19	,, Sundry Donations	17	17	0
418	,, Postages, Travelling, and Sundry Expenses	413	18	10	50	,, House Fund Rent	52	10	0
77	,, Library Expenses	42	5	1	226	,, Excess of Expenditure over Income for Year	401	19	6
180	,, Subscriptions and Grants to Local Sections	178	11	6					
160	,, Expenses of Meetings	97	4	10					
31	,, Repairs and Renewals	9	9	1					
—	,, Bank Charges	14	5	6					
26	,, Audit Fee	26	5	0					
£7,009		£6,778	11	8	£7,009		£6,778	11	8

JOURNAL ACCOUNT FOR THE YEAR ENDED JUNE 30, 1933.

		£	s.	d.			£	s.	d.
1	To Stock of *Journals* at June 30, 1932	1	0	0	1,953	By Sundry Creditors at June 30, 1932	284	7	6
386	,, Sundry Debtors for *Journals* sold and Advertisements at June 30, 1932	181	12	5	2,071	,, Sales of *Journals* and Index and Advertisements	1,741	5	3
5,599	,, Cost of Production of *Journals* including Abstractors' Fees	2,762	12	0	1	,, Stock of *Journals*	1	0	0
284	,, Sundry Creditors at June 30, 1933	1,144	1	9	182	,, Sundry Debtors for *Journals* sold and Advertisements	151	11	2
					2,063	,, Balance transferred to Income and Expenditure Account	1,911	2	3
£6,270		£4,089	6	2	£6,270		£4,089	6	2

"HOUSE FUND" ACCOUNT FOR THE YEAR ENDED JUNE 30, 1933.

		£	s.	d.			£	s.	d.
50	To Rent paid to the Institute of Metals	52	10	0	1,050	By Balance at June 30, 1932	1,049	19	7
1,050	,, Balance at June 30, 1933	1,049	19	7	50	,, Interest on War Loan	42	10	0
						,, Bonus on Conversion of 5% War Loan	10	0	0
£1,100		£1,102	9	7	£1,100		£1,102	9	7

careful consideration. By the publication of the *Monthly Journal*, earlier printing of the papers and abstracts, and in other directions, members are receiving considerably increased advantages, and these can only be continued or extended if funds are available. Members can help by encouraging suitable persons to join the Institute; by purchasing its publications and by supporting the advertisements in the *Monthly Journal*. It is hoped that brighter times ahead will lead to increased income, particularly from countries in which the Institute has a considerable membership, and which have been suffering so severely from the world depression.

Professor T. TURNER, M.Sc., A.R.S.M., Chairman of the Finance and General Purposes Committee, who moved the adoption of the Report in the absence of the Honorary Treasurer, pointed out that in spite of the reduction of working expenses they exceeded income owing to a decrease of subscriptions. He directed attention to the fact that the *Journal* accounted for the largest item in the Institute's expenditure. Members could help to re-establish the finances of the Institute by encouraging suitable persons to become members, by purchasing the publications, and by supporting those firms who, by advertising in the *Journal*, helped to decrease the net cost of the publications of the Institute.

Mr. A. H. MUNDEY (Member of Council), who seconded, also dealt with this subject, and stated that members should realize that the Institute spends as much as it can afford, or a little more, in their service. Members must support the excellent work of the Publication Committee.

The resolution was carried unanimously.

ELECTION OF OFFICERS FOR 1934–1935.

The SECRETARY read the following list of officers elected to fill the vacancies on the Council for the year 1934–1935.

President:

HAROLD MOORE, C.B.E., D.Sc., Ph.D.

Vice-Presidents:

A. G. C. GWYER, B.Sc., Ph.D.
Professor D. HANSON, D.Sc.
H. C. LANCASTER.
E. L. MORCOM, M.A.

Honorary Treasurer:

JOHN FRY.

Members of Council:

Professor J. H. ANDREW, D.Sc.
Engineer Vice-Admiral H. A. BROWN, C.B.
H. W. BROWNSDON, M.Sc., Ph.D.
KENNETH GRAY.
H. H. A. GREER, J.P.
J. L. HAUGHTON, D.Sc.
Professor R. S. HUTTON, D.Sc., M.A.

ELECTION OF MEMBERS AND STUDENT MEMBERS.

The SECRETARY announced that the following members and student members had been elected on October 26 and December 14, 1933, and January 18 and February 15, 1934.

Members Elected on October 26, 1933.

Allen, Clement Paul	Bulawayo, South Africa.
Brandt, Alfred, B.Sc.	London.
Cholewinski, Stanislaw	Warsaw, Poland.
Ellis, Philip Meredith	Birmingham.
Fould, Maurice	Paris, France.
Hedges, Ernest Sydney, D.Sc., Ph.D.	London.
Hilt, Eugene Henry Hugh, Dipl.Ing.	London.
Hoar, Thomas Percy, M.A., B.Sc., Ph.D.	Cambridge.
Humphreys, William Gerald	Newcastle-upon-Tyne.
Kerr, Robert, M.Sc., Ph.D.	London.
Lewis, Philip Stacey, B.Sc., Ph.D.	Bristol.
Louyot, Robert	Bornel, France.
Neave, Digby Percy Cornwall, M.A.	London.
Rouppe van der Voort, Paulus Nicolaas Franciscus Maria	's Hertogenbosch, Holland.
Schirner, Karl	Berlin, Germany.
Schneckenburger, Emil	Schaffhausen, Switzerland.
Summerhill, Gordon Charles	Birmingham.
Tolliday, Joseph Ernest	Sidcup.
Vowles, Charles D.	Birmingham.
Zacco, Henrik Yngve	Finspong, Sweden.

Student Members Elected on October 26, 1933.

Jacques, Arthur	Chorley, Wigan.
Orr, Hazlett Francis	Sydney, N.S.W., Australia.
Thomas, Ronald Charles William	Birmingham.
Williams, Noel Ignace Bond	Birmingham.
Yarrow, Colin Drake	Pinner.

Members Elected on December 14, 1933.

Ayckbourn, Philip John, B.Sc.	New Plymouth, New Zealand.
Ball, Arthur Cyril	Nottingham.
Eatwell, Henry Thomas	London.
Grant, Ivan Stanley	Port Talbot, South Wales.
Hartigan, Thomas Joseph	Sydney, N.S.W., Australia.
Kamienski, Erwin, Dr.-phil.	Glowno k/Lowicza, Poland.
Melvin, Sir Martin J., Bart., J.P.	Olton.
Nagao, Major Takeo	London.
Nicosia, Beniamino	Milano, Italy.
Priestman, Robert Thomas	Birmingham.
Rao, Mannigay Umanath, M.Sc.	Jodhpur, India.
Simpson, Joseph Gordon	London.
Williams, Leslie Ballesat, B.A., B.E.	Matlock.

Student Members Elected on December 14, 1933.

Booth, Leonard Tranter	Birmingham.
Colman, Geoffrey William	Birmingham.
Cowley, Charles Leonard Marshall, B.Sc.	Birmingham.
Mace, Cyril William	Napier, New Zealand.
Robinson, John Herbert	Sydney, N.S.W., Australia.
Thomas, Ivor Henry, B.Sc.	Bankyfelin, Carmarthenshire.

MEMBERS ELECTED JANUARY 18, 1934.

BEDDOWS, John Derek, B.Sc.	Birmingham.
BURKHARDT, Arthur, Dr.-Ing.	Frankfurt a. Main, Germany.
MAZZOLA, Mario	Turin, Italy.
McFARLAND, Professor David Ford, A.M., M.S., Ph.D.	Pennsylvania, Pa., U.S.A.
MEHL, Robert Franklin, B.S., Ph.D.	Pittsburgh, Pa., U.S.A.
MITCHINSON, Robert	Newcastle-upon-Tyne.
MUKUMOTO, Wasaburow, B.Sc.	Osaka, Japan.
SIFF, Alfred, M.A., A.R.S.M.	Johannesburg, South Africa.
SLATER, Horace	Sydney, N.S.W., Australia.
STORKE, Arthur Ditchfield	London.
WARRINGTON, Harold George	Slough.

STUDENT MEMBERS ELECTED JANUARY 18, 1934.

HOMER, Charles Egbert, B.Sc., Ph.D.	London.
JENKINS, John Ephraim	Treharris.

MEMBERS ELECTED FEBRUARY 15, 1934.

BADOCK, Stanley Hugh, LL.D., J.P.	Bristol.
BERMANN, Professor Samuel	Moscow, U.S.S.R.
BURN, Robert Davidson, M.Sc.	London.
MATIGNON, Professor Camille, Dr.-es-Sci.	Paris, France.
MORRIS, Roland William	London.
ORLANDO, Salvatore, Cav. Uff. Dott.	Milano, Italy.
SHAO, Chia Chin, A.R.S.M.	Wuchang, China.
STRAUSS, Kossy, Dr.-Ing.	Birmingham.
STRINGER, Richard Alfred	London.

STUDENT MEMBERS ELECTED FEBRUARY 15, 1934.

ASHTON, Arnold Broadbent, B.Sc.	Oldham.
BROWN, Bernard	Leeds.
GREENWOOD, Hubert, M.Sc.	Todmorden.
HARRISON, Stanley Taylor, B.Sc.	Manchester.
TIMMS, William, B.Sc.	Birmingham.
WADDINGTON, John, B.Sc.	Clitheroe.

RE-ELECTION OF AUDITORS.

Dr. D. H. INGALL proposed, Mr. T. HENRY TURNER, M.Sc., seconded, and it was unanimously agreed that the auditors, Messrs. Poppleton and Appleby, be re-elected.

INDUCTION OF NEW PRESIDENT.

The PRESIDENT: I have been unfortunate in occupying the chair during a time when the world depression has affected us; but times of trouble and difficulty always produce those who rise superior to them, and I feel that your Council has done so during the past two years. It has been a great delight to me to see the way in which the whole of the Council and the officers, the Secretary, Assistant Secretary, and staff, have whole-heartedly done everything that was in their power for the success and future advantage of the Institute. The Institute and its publications hold a very high place in the technical world, and one reason for that is that we have a very good Publication Committee, which has had a most excellent Chairman in the person of the gentleman whom I am going to ask to take this chair. The position which Dr. Moore occupies in the scientific world, makes it almost a very pleasant duty to step down and to ask him to take the Presidential chair. No one has the welfare of the Institute more at heart than Dr. Moore, and if in nothing else, I feel that I have at least been successful in that I have persuaded him to accept the Presidency of the Institute of Metals, which I now ask him to be good enough to do.

Sir Henry Fowler then vacated the chair, which was taken, amid applause, by the incoming President, Dr. Harold Moore, C.B.E.

The **President**: I thank you, Sir Henry, for the extremely kind words you have spoken; I only wish that I deserved them.

VOTE OF THANKS TO THE RETIRING PRESIDENT.

Dr. C. H. **Desch**, F.R.S. (Vice-President): I now have the honour to propose that the very best thanks of the Institute be given to Sir Henry Fowler for his conduct as President during the last two years. Sir Henry has had previous experience as a President, and so he came to us with knowledge and experience in addition to that geniality and energy which we know have always characterized him. He has taken a most active part in all the proceedings of the Institute, and has presided most admirably over the deliberations of the Council; and in all the changes it has been necessary to make in the last two years his guidance and advice have been invaluable. He has throughout the period of the world depression retained a cheery optimism in regard to the progress and future of science and industry which I am sure has been encouraging to everyone who has met him.

Without taking up any more of your time, I will propose that the most hearty thanks of the Institute be given to Sir Henry Fowler for his conduct as President.

Mr. H. C. **Lancaster** (Vice-President): Dr. Desch, with his thorough way of handling any subject, from a simple crystal to a human being, has given us a very careful micro-study of our out-going President, and you have all heard for yourselves that the specimen is a perfect one! I am sure we are all in very close agreement, but it makes it a little difficult for me to follow Dr. Desch, because it is always difficult to add something to that which is already perfect. I do not find any real difficulty, however, because good wine requires no bush. I know that every member of the Council, and I am sure I can add the Secretary, would give their very hearty approval and support to the remarks made by Dr. Desch.

Sir Henry Fowler must have a very large circle of friends, and during his two years of office, has made many more. He has during two difficult years, difficult alike to industry and to societies and institutes, endeared himself to us all by his outstanding patience and never-failing courtesy.

The **President**: I should like to emphasize everything that has been said by Dr. Desch and Mr. Lancaster, and to say how successful Sir Henry has been in filling the office of President of this Institute. His friendliness and geniality are among his most outstanding characteristics, and have done a great deal to assist in the smooth running of the work of the Institute.

The vote of thanks was put to the meeting and carried with acclamation.

Sir **Henry Fowler**: I thank you very much indeed. The period of my presidency has been a very happy one for me, largely owing to the assistance and kindness I have received not only from the Council and the members, but also from the Secretary, the Assistant Secretary, and the whole of the staff. I have had to concern myself with whatever difficulties and questions may have arisen perhaps once a week or once a fortnight, but the Secretary has been confronted with them every day. With such devoted assistance, and having made, as Mr. Lancaster kindly said, so many fresh friends, I shall look back with the greatest pleasure to what will be one of the dearest and deepest memories of my life, the two years during which I have been President of the Institute of Metals. I shall not forget the kindness I have received and I shall never cease to work for the interests of the Institute.

MESSAGE FROM DR. ROSENHAIN.

The **PRESIDENT**: I have received from Dr. Rosenhain the following telegram " Best wishes self and Institute." As you all know, Dr. Rosenhain is prevented from being with us to-day by serious illness. It is extraordinarily kind of him to think of us at such a time and to send this telegram of good wishes. He has so often held us spellbound in this room by his brilliance in discussion and his scientific knowledge that we are bound to miss him very much indeed. I am sure it will be the wish of the meeting to send a telegram to Dr. Rosenhain in reply, expressing our appreciation of his message and our deep sympathy with him in his illness.

PRESIDENTIAL ADDRESS.

DR. HAROLD MOORE then delivered his Address (see pp. 29–44).

Dr. H. W. **BROWNSDON** (Member of Council), in moving a vote of thanks to the President for his address, said that those of them who had had the privilege of close personal contact with Dr. Moore had always recognized that his ability, his love of hard work, and his sincerity, coupled with a genial personality, must sooner or later lead to the highest honour which it was in their power to bestow. They greeted him as their President fully aware that the destinies of the Institute were perfectly safe in his hands, and at the same time not forgetting the yeoman service which he had already rendered to the Institute as Chairman of the Publication Committee, a position of responsibility only second to that of President.

The address which he had given them, and which would be read with the greatest interest, was typical of his broadmindedness and of his progressive ideals. If the members backed him up in the policy which he had outlined, he (Dr. Brownsdon) was sure that metallurgical science and practice would in the future reflect at least some of his ambitions. He was not quite sure what relationship Dr. Moore would have them take up with regard to their ferrous friends. Whilst most of them had wandered into the field of non-ferrous metallurgy, he hoped that all appreciated the advantages to be obtained from close contact with ferrous work.

Dr. J. L. **HAUGHTON** (Member of Council), in seconding, referred to an address which Dr. Moore delivered to the British Non-Ferrous Metals Research Association on the writing of scientific papers and expressed the special pleasure with which he had listened to the President's valuable and illuminating address.

The resolution was put to the meeting and carried with acclamation.

The **PRESIDENT**: I am greatly touched by what Dr. Brownsdon and Dr. Haughton have said. They are both old friends of mine for whom I have the greatest regard. I could not avoid feeling as they were speaking that they really must be talking about somebody else. I do not feel I deserve all that has been said, but I thank all of you most sincerely for the way in which this motion has been received.

COMMUNICATIONS.

The communications of the following authors were presented and discussed: G. A. Hankins and C. W. Aldous; I. G. Slater; H. J. Gough, H. L. Cox and D. G. Sopwith; C. E. Pearson; E. W. Fell; Professor A. Portevin and P. Bastien. A paper by G. Rigg was presented in the absence of the author, but was not discussed. 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.

Thursday, March 8, 1934.

On the resumption of the meeting, communications by the following authors were presented and discussed: H. A. Sloman; C. E. Phillips and J. D. Grogan; Professor D. Hanson and E. G. West, and R. Taylor. Papers by O. W. Ellis; and J. L. Haughton and R. J. M. Payne were presented but not discussed. In each case a hearty vote of thanks to the authors was proposed by the President and carried with acclamation.

CONCLUDING BUSINESS.

The PRESIDENT: This is the first meeting which has been affected by the alteration in the method of publication of the papers. Members have had the papers for a much longer time than usual, and I think the opportunity thus given for more careful consideration of the papers has been reflected in the discussions which have taken place. We have also made some changes which you may have noticed in the procedure of conducting the discussions. Those changes are related to the new method of publication; we have adopted the plan of not taking so many papers as usual but devoting more time to each. For example, nearly the whole of yesterday afternoon was devoted to the discussion of two papers, and in each case we had what appeared to me to be a most excellent discussion. It may have been apparent that that discussion was not entirely spontaneous, and that there had been a certain amount of organization behind it, but I hope that nobody felt that there was any suppression of free discussion. The procedure of inviting speakers in advance is not meant in the slightest degree to prevent anyone who wishes to do so from taking part in the discussion.

The Publication Committee and the Council generally would much like to know the opinion of members on these changes which have been introduced —the new method of publication of papers and the related differences in the methods of discussion—and we should be very glad to receive any comments which members may care to send us, favourable or otherwise. These changes are experimental, and we may return to the old methods. I do not think that we shall, but it would help us when we consider the question if members who are not in direct touch with the Council would let us know their opinion. We are endeavouring to be as democratic an Institute as possible and we want to follow the wishes of the general body of members as closely as we can.

VOTES OF THANKS.

The PRESIDENT proposed and there were carried with acclamation the following resolutions:

> "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."
>
> "That the best thanks of the Institute be and are hereby tendered to Captain B. S. Cohen for permitting the members to visit the Post Office Engineering Research Station, Dollis Hill."

VISIT TO POST OFFICE ENGINEERING RESEARCH STATION.

Members and their ladies, in the afternoon, visited, by invitation, the Post Office Engineering Research Station at Dollis Hill. A brief description of this Station was published on pp. 68–70 of the February, 1934, issue of the *Monthly Journal.*

The meeting then terminated.

PRESIDENTIAL ADDRESS

DELIVERED BY H. MOORE, C.B.E., D.Sc., Ph.D.

March 7, 1934.

Following the example set in previous Presidential Addresses, I shall begin with some observations on current policy and the present position of the Institute, taking, I hope, a not undue advantage of the privilege of being able to express my views on this occasion when they will not be exposed to open discussion.

For three years in succession our expenditure has exceeded our income, although a considerable part of the apparent excess has been due merely to more strict accounting, and paying our bills earlier. Our curve of membership for the last five years shows a type of symmetry which we hope, and believe, will not continue. These are the inevitable effects of the industrial depression from the trough of which we are now rising. There will be, no doubt, a certain lag before we begin to benefit substantially, in our membership and income, from the industrial recovery, just as there was a lag in the effects of the slump. I am confident, however, that our position is healthy and that we need not be disquieted about the future, although the Institute's finances must demand the Council's constant thought and care for the time being. On the question of membership I will only say that there are still large numbers outside our ranks, fully qualified for membership and engaged in industries which greatly benefit from our work.

Not being an original member myself, I can speak more freely than some others of the remarkable response of the Original Members to the suggestion which arose among them of a special fund to commemorate our twenty-fifth anniversary. The Institute already owed much to these members, for their unfailing support and in many cases for much voluntary and often unrecognized work. I feel that we are now still more indebted to them, and that our best way to requite them is to make the sum raised a starting point for something still more substantial. As our Honorary Treasurer has so often pointed out, the Institute has always had to work on too narrow a financial margin. The Council is considering the best way of employing the Fund for the permanent benefit of the Institute, and I cannot, of course, anticipate the decision. Speaking only for myself, I should like to see it become a nucleus for a Foundation Fund which would add substantially to our reserves, and to see the interest augmenting that part of our income used for publication.

The mention of publication leads me to refer to the Council's emphatic view that our first duty, in lean years as well as in fat, is to maintain the high level of our *Journal*. In some quarters we are accused of giving our members more than their subscriptions warrant. If this is so, I hope that members will do all they can to enable us to maintain this generous policy. The most notable change introduced last year was the starting of the scheme for the advance publication of all our papers in the *Monthly Journal*. This step was decided upon only after the fullest discussion, and must still be regarded as experimental. Those who see objections to it may be assured that all possible difficulties were fully considered by the Council and were held to be outweighed by the advantages which have been set out elsewhere. Those which most appeal to me are earlier publication of papers, their receipt by members continuously throughout the year instead of in two large batches, and the convenience of being able to consult all papers in the *Monthly Journal* until such time as they appear in the half-yearly volume. It should be mentioned that the Secretary and staff were the first to advocate this advance in our methods of publication.

We hear criticism from time to time of the type of papers we publish. This is a healthy sign, and indicates a real interest in the matter on the part of our members. As the criticisms we receive from different quarters cancel each other out fairly completely, I think that there is nothing seriously at fault. There are, however, several considerations which critics should bear in mind. In the publication of original papers the procedure of the Institute is one of selection, together with some editing and possibly revision. It is rarely that the Institute asks for, or directly inspires, papers on a particular subject or of a particular type. The Publication Committee considers impartially all papers, within our field, offered from any quarter; thus the papers we publish are a reflection of the output of original work carried out by those who consider our *Journal* an appropriate medium for publication. The quality of the papers is necessarily dependent on the quality of metallurgical research undertaken by the Universities, Government establishments, industrial laboratories, and Research Associations.

There is one familiar complaint on which I might make a suggestion, more serious than may at first appear. The complaint is that the

Institute does not provide a sufficient proportion of "practical" papers. If the practical man who wants more practical papers will turn to and write one—or, still better, several—on the subject about which he probably knows more than anybody else, he will receive nothing but encouragement from the Publication Committee. A cursory examination of our list of members will show that this simple scheme would provide an ample flow of practical papers. The difficulty is really this: The metallurgist who carries out a piece of research always writes a report or paper about it—otherwise his work is almost certainly wasted—and does his best to have it published unless there is some good reason why he should not. The practical man who has improved his particular line of manufacture beyond the average level is often satisfied with the other well-deserved rewards of his ability and work, and has a natural reluctance to tell us all about it. Quite apart from any desire for secrecy, he is often much too busy to write papers, he has not been accustomed to do so, and sees no special reason why he should. I cannot help thinking, however, that some sister Institutes are more fortunate in this respect than we are, and that the leaders in the technical management of their industries recognize some responsibility for describing, in papers to their Institute, the technical developments they have directed. It is also my experience that the first-rate practical man often writes an extraordinarily good paper, not infrequently a model in terse and direct expression which metallurgists might study.

The writing of scientific papers might well form the main subject of a Presidential Address in more competent hands than mine. There are excellent books on the subject, too little known and studied,* and the booklets issued by other Institutions,† as well as our own "Notes to Authors," provide valuable guidance on many points of detail. These publications naturally deal chiefly and at some length with the technique of scientific writing, and in reading them it may be a little difficult to see the wood for the trees. I should like to suggest one way in which an author might consider his paper before, during, and after writing it, and two or three definite rules which are thus brought into prominence. The suggestion is the simple one of regarding the paper from the point of view of the probable readers and their needs. These readers may be of several types, but in general they are busy, hard-working people who want to enlarge their knowledge and to be helped in their own work.

---

* The following are in the library of the Institute of Metals: Clifford Allbutt, "Notes on the Composition of Scientific Papers"; H. A. Watt, "The Composition of Technical Papers"; Trelease and Yule, "Preparation of Scientific and Technical Papers"; T. A. Rickard, "Technical Writing."

† *E.g.* "Information Concerning the Preparation of Papers." Institution of Mechanical Engineers, 1933.

They are not particularly interested in how much labour went to the making of the paper. Sometimes they are even bored by the author's speculations, and they are not examining him as a candidate for a higher degree. The first requirement which is emphasized by this way of looking at a paper is that it should constitute a real addition to knowledge. The experimental work must not only have led to trustworthy results, but must be sufficiently important to justify permanent record. I should have regarded this as too obvious to mention were it not that we sometimes receive papers which are rejected because they do not pass this test.

I consider the merit of conciseness to be next in importance to the reader. In my opinion, there are few papers which are not capable of some improvement in this respect. Many an excellent paper might have been more excellent still if the writer had rigorously revised it, cutting out all superfluous matter, and expressing his meaning in the fewest words consistent with clearness. Some papers containing useful information worthy of publication have to be rejected because they also include unnecessary matter and are far too wordy. There are many ways in which papers may become needlessly lengthy. Abortive experiments may have cost the writer many hours, but the briefest account is usually sufficient to prevent others from doing similar unfruitful work. Experimental evidence must be presented in sufficient detail to support the conclusions reached, but can often be highly condensed with advantage. Polemics can be badly overdone. One of the essential qualities of the good research worker, a clear idea of what he is doing and why he is doing it, is equally important when he comes to write his paper, and will certainly help him to write concisely. Perhaps the worst fault of all, unfortunately not uncommon, is the use in a sentence of twice as many words as are necessary to express the meaning intended. A command of terse, pregnant English is a valuable possession to the writer of a scientific paper, and is worth much trouble and labour in its cultivation. If an author scrutinizes one sentence after another, he will often be surprised to find how many might be put in fewer and shorter words, with no loss whatever, and often with a gain, in force and clarity. Brevity in papers is important to the Institute in its effect on cost of publication. Printing and publishing costs alone (which are by no means all the expenditure involved) are of the order of 25*s*. per page of the *Journal*. With a given limit of expenditure, an average reduction of length of papers by 20 per cent. (not an unreasonable estimate of what might often be possible, without any injury to the paper) would enable us to publish about seven more papers every year. In urging authors to be as brief as possible, I do not forget that occasionally a paper is written describing some advance which is so outstanding as to justify great detail and elaboration. Possibly some authors are more inclined to put their own papers in this class than are Publication Committees. Such papers form only a small proportion of the useful research reports which will always constitute the bulk of scientific publication.

In connection with publication costs, members may not be aware that the gross cost of our abstracts is not less than £1 per member per annum. I do not think our abstracts are surpassed anywhere in completeness, promptitude, and quality, but we are now considering whether further improvement might not be possible, perhaps in the direction of excluding a certain proportion of papers of relatively small importance or leaving to other abstracting bodies some fields of work on the border line of our own. The space thus saved might be used for fuller abstracts of papers which are more important to us.

I should like to devote the remainder of my time and space to some broader consideration of the field of work of the Institute and the related branches of industry and of science. In particular, I wish to refer to certain developments in co-operation, actual or possible, within and without our special field, which are of moment to us.

In a recent book * T. A. Rickard has expounded, with a wealth of historical fact, the theme that " civilization was developed on a metallic basis." On this question it is not easy to distinguish between cause and effect. Whether man's early steps towards civilization led to, or alternatively were conditioned by, his gradually increasing use of metals may be a matter for argument. Certain it is that metals are the chief material basis of our present industrial civilization. Some other materials stand higher than the metals as primary necessaries, in the quantities used, or in money value, but every kind of production, industry, transport, and communication is now dependent on metallic tools, machinery, and other equipment. The extent to which this dependence has increased in our lifetime is illustrated by Rickard's statement that during the first twenty-five years of the present century the world consumed a larger quantity of the metals than in all preceding time. Figures given by Sir Harold Hartley, in the 1933 James Forrest Lecture, for the world's production of twenty-one metals in 1900 and in 1930 show that production had at least doubled for all the common metals in these thirty years, whilst in some cases the increase was far greater; for example about thirty-six times as much aluminium was produced in 1930 as in 1900. In quantity produced, iron exceeds all other metals combined. The world is equipped to-day to produce not

---

* T. A. Rickard, " Man and Metals." New York and London: 1932.

less than 130 million tons of steel per annum, as compared with probably not more than 8 million tons of other metals in all forms. In variety and value, however, the ratio is very different. Further, one of the main metallurgical trends of the present time is the increasing dependence of iron on non-ferrous metals, both as alloying additions and as protective coatings, for overcoming its corrodibility and improving its other properties.

An indication of the importance of the non-ferrous metals industries in Great Britain is given by the Census of Production figures for 1930, which show that the value of non-ferrous metals and alloys, excluding the precious metals, produced as ingots, castings, plate, rod, tube, and similar forms is not less than £40,000,000 in a normal year, copper and copper alloys accounting for about half this amount.

These few figures are sufficient to show that the field of this Institute in the study of the non-ferrous metals and their utilization is large, important, and increasing. In this sphere the Institute has played a great part in the encouragement of science. It exists " to promote the science and practice of non-ferrous metallurgy," but as practice becomes more and more dependent on science, I do not think that I am biassed in suggesting that we are, and must always be, primarily a scientific body. Although some of our most active and helpful members modestly disclaim any considerable scientific knowledge, they often do themselves injustice in this matter, and I think that their membership is proof of their interest in and support of science. It is an obvious truth that the increasingly rapid progress of science and its application to every side of life is one of the outstanding characteristics of the present day. Indeed, our progress in this direction has been blamed for the unpleasant symptoms of industrial and economic dislocation which continue to shake our civilization. That this view is fundamentally erroneous has been well shown very recently by Mr. H. T. Tizard.* Other causes, immensely potent, amply account for the economic troubles of the world, and I find it impossible to believe that our difficulties of the last few years would in any way have been lessened if science and its application had halted in their progress. There is indeed much to be said for the view that the effects of the industrial depression have been mitigated in some directions by scientific progress, and certainly some of the newer industries which have arisen purely as a result of the advance of science have suffered far less than the primary producing industries and the long-established so-called basic industries.

---

* " Science and the Industrial Depression." Presidential Address to the Science Masters Association, January 1934.

The dangers of a civilization which rests so largely on a basis of applied science while a truly scientific outlook is confined to a very small proportion of the population have often been pointed out. I hesitate to say whether they are any greater than the dangers to which all civilizations have been exposed—dangers so abundantly illustrated throughout history. They are, however, very real, and I think that there can be little doubt that the stability of our civilization would be steadily strengthened by a growth of the scientific outlook throughout all sections of the population. This is primarily a matter of education, but education is by no means confined to schools and universities, vastly important though these agents are. I suggest that in promoting the spread of scientific ideas throughout the metallurgical and other industries we serve, we are doing far more than merely making these industries more profitable to those who are dependent on them : we are encouraging forces making for stability and ordered progress in civilized life.

I have spoken of stability and of civilization resting on applied science. These expressions may be misleading. Whatever modern civilization may do, it cannot rest, nor can its stability be of the static kind we seek in our structures. It can only be a balance, continually adjusted, of powerful forces and perpetual movements. We must abandon the ideas of permanence, of keeping things as they are, of a goal where we can rest when we have reached it. Continual change is our lot. Indeed, it has always been so, although to us it may seem that the rate of change is faster than ever before.

All this may be thought to be remote from the matters which primarily concern this Institute. What I want to suggest is that in the industries and institutions in which we are interested, we must accustom ourselves to the idea of constant change, of continual progress, of the rapid absorption and application of new knowledge and fresh ideas. The alternative is growing disharmony in our technical and economic organization as we fail to change in a changing world. In industry it is not merely a matter of losing markets to our competitors; this is a symptom, though a distressing one, of a failure to take our part in the march of progress. It must be admitted that in some sections of industry there is still great inertia. Reluctance to take part in the search for useful new knowledge, and even to make use of knowledge which is freely offered, is still too prevalent.

Our Institute provides one powerful co-operative agency for overcoming this inertia. By affording facilities for publication and the exchange of information and opinion among its members and all who are interested throughout the world, it gives a great impetus to the application of science. It assists and supplements the work of the industrial research laboratories and Research Associations which are the main channels for the utilization of science in manufacture.

Anyone considering the present position of science in industry must first be impressed by the extent to which the industrial scientific organizations, and the use of really scientific methods in manufacture, are the creation of the last twenty years. Some important and active research laboratories have been maintained much longer than this by the dyestuffs and other branches of chemical manufacture, and by the electrical industry, but it is broadly true that the large industrial research laboratories of to-day either did not exist, or were merely a fraction of their present size, twenty years ago. The staff of the National Physical Laboratory, which has a large output of industrial research as well as other work, was about 150 in 1913 and 590 in 1933.* A Bulletin of the National Research Council (U.S.A.) issued in 1933 gives particulars of 1575 industrial research laboratories in the U.S.A., few of which were in existence twenty years ago. It has been estimated that about £4,000,000 is spent annually on metallurgical research and development in the United States.† The Mellon Institute of Industrial Research was founded in 1913, and the Battelle Memorial Institute is more recent in origin. These are two outstanding examples of many large institutions undertaking metallurgical research for industrial purposes. None of the British Research Associations is yet twenty years old.

It is perhaps more interesting to study, beyond the mere growth of industrial research, the ways in which co-operation has fostered this growth. Towards the end of the War the Government began its great experiment resulting in the establishment of more than twenty Research Associations, in which different sections of an industry, and many different industrial concerns, co-operate among themselves and with the Department of Scientific and Industrial Research to carry out research and development for the benefit of the industry. The lately issued Annual Report of the Department gives in some sixteen pages a broad review of the experiment from its beginning, when " the scheme visualized the formation of national research organizations to stand behind and supply with new ideas, new methods, new standards of quality, the principal industries of a nation dependent for its very existence on its power to feed itself by means of the sale of its manufactured articles." Not less than £3,000,000 has been applied by the Associations in research and related activities within fifteen years, but

---

* See the annual *Reports* of the National Physical Laboratory.

† C. E. MacQuigg, " Research and Development in Metallurgy," *J. Franklin Inst.*, 1932, 213, 583–604.

while recognizing the substantial success of the experiment, the Department is emphatic in its view that research associations are in their infancy, and that a substantial development of the movement is needed.

In our own industries there are three main groups, engaged respectively in the mining and production of metals, in the manufacture of semi-finished products, and in the production of finished articles. Each group overlaps the others to some extent, but the classification holds broadly. Until comparatively recently the producers of the raw non-ferrous metals rarely took much interest in their products after they had sold them, and incidentally they regarded the field of the Institute of Metals as being outside their province. A profound change in their attitude, gradual at first, is now proceeding rapidly. The nickel producers have found it worth while to study in great detail the ultimate uses of nickel, and to spend large sums in research and in the development work necessary to secure the application of the results of research. In similar or other ways the producers of aluminium, copper, and tin are following the same policy. It is especially interesting to note that this is leading to co-operation, not merely between the producers of a particular metal—as, for example, in the International Tin Research & Development Council—but between the primary producer and the manufacturer of semi-finished products, and, further, between the groups in these two classes in several different metals. Thus the British Non-Ferrous Metals Research Association includes in its membership producers of copper, aluminium, nickel, tin, zinc, lead, and other metals as well as the manufacturers of plate, bar, tube, wire, &c., and many classes of users. In this way all these interests jointly support and control research for the non-ferrous metals industries generally.

There is, however, one considerable section of industry which as yet is scarcely touched by the movement towards co-operation in the advancement and application of science. Sir Frank Smith, whose position as Secretary of the Department of Scientific and Industrial Research enables him to keep his finger on the pulse of science in industry more constantly than probably anyone else, has pointed out, in his 1932 Norman Lockyer Lecture, that in 128,000 factories employing about 5 million workers less than 500 employ more than 1000 workers each, and more than 100,000 factories employ fewer than 100 workers each. These figures show that the great majority of these 5 million workers are employed in small industrial units. In the industries using non-ferrous metals there are thousands of concerns which, although as a rule individually small, in the aggregate constitute a most important section of manufacturers, as measured by the total capital used, the number of workpeople employed, and the value of their total production. They are engaged in the manufacture, from the intermediate products which they buy, of finished articles of enormous variety, by processes of drawing, spinning, welding, brazing, soldering, and so on. They apply surface finishing processes such as polishing and electro-plating. By long experience, trial and error, and empirical skill often raised to great perfection, they may be thoroughly expert in their particular line of work, but it is rarely that they regard themselves as in need of any scientific knowledge. Here is an undeveloped field for the extension of science in industry, and there is no doubt that these concerns might profit greatly from association with technical organizations. More scientific training and knowledge among the controlling personnel of these small units appear to be needed if they are to take advantage of what science can do for them. Thus we are brought back to the question of the scientific outlook.

I should now like to turn from the definitely industrial aspect of our work to the more purely metallurgical in the scientific sense, and to suggest that here again co-operation can be further extended with advantage. Within the Institute co-operation is fostered among those interested in each of the many sides of non-ferrous metallurgy. Some of us have difficulty in understanding others, and when, for example, our eminent corrosion experts are expounding their theories, the X-ray worker is apt to talk to his friends in the entrance hall. In spite of the wide differences in outlook among our members, we ought, I am sure, to continue to encourage the corporate spirit, the exchange of experience and opinion among those working in different fields or on different economic levels, those whose interests are mainly industrial and those occupied more with the scientific side. It is often remarked that this is an age of specialization. I regard specialization in any one direction, so far as it results in the neglect of other aspects of science, or indeed other aspects of culture and of life, as a necessary evil. Necessary undoubtedly, since we need increasingly the man who learns more and more about less and less, but also an evil, and most certainly an evil if begun too early in life. I do not know whether the bad effects of a needlessly early specialization are more in evidence in metallurgy and the metallurgical industries than in comparable circles, but they certainly exist there. I see no reason whatever to think that our scientific and technical personnel of the future will be any the worse in their own special work if, while they are still young enough, they become acquainted with other branches of science and develop a real interest in wider fields of knowledge and activity. Economic developments and difficulties of the last few years surely indicate one direction in which the tremendously increased productivity of industry might be applied with great benefit, and that is in extending the years of real education in which wider interests can grow, and in postponing the cramping specialization which cuts off so many from a fuller life. I suggest that the development, in earlier years, of a wider scientific knowledge and a wider common culture will make it easier for members of an Institute such as this to understand each other, and to meet on common ground when, in later years, they have become concentrated on diverse special interests. This must apply mainly to coming generations, but possibly we can do something to encourage progress in this direction.

A suggestion has been made that the Institute might from time to time organize discussions appealing to selected groups of members. For example, those interested in equilibrium diagrams of alloy systems might have a meeting for their special benefit at which several constitutional papers would be presented and discussed. I hope that we shall follow up this suggestion. I am sure, however, that such sectional meetings ought not to replace our general meetings, at which members may learn at first hand something of the original scientific and technical work being done in fields other than those in which they are themselves working. It is not uncommon that the results of research can be applied in quite unexpected directions.

So far I have had in mind the many different sections of non-ferrous metallurgy, but it may be profitable to consider also the interdependence of ferrous and non-ferrous metallurgy. No one will dispute that there is no sharp division between these two branches of our science, and not a few of those who have attained distinction, including more than one of my predecessors in this chair and several members of our Council, have been equally eminent in both fields. Again, many engineers and users of the metals are equally interested in iron and steel and in the non-ferrous materials. Such research laboratories as the National Physical Laboratory, those of the defence services, as at Woolwich and at Farnborough, and the Research Departments of the railways consider impartially ferrous and non-ferrous materials in both the metallurgical and engineering aspects. The schools of metallurgy at the Universities, of course, teach and work on both sides, although perhaps at Sheffield steel has had the preference, and the non-ferrous materials at Birmingham. Thus there is no lack of points of contact. Nevertheless, many metallurgists, naturally and properly, work entirely in the one field or in the other, and sometimes their concentration on their own field leads to a certain neglect of progress in the other and of the lessons which may be learned from it. The separation is more definite on the manufacturing side, and it is not uncommon to find those in technical control in steel works or in non-ferrous metal works rather conspicuously ignorant of corresponding processes in the other fields, and perhaps a little scornful of them.

The two Institutes which have these two fields for their respective provinces have always been on the most friendly terms. It is not long since they held a most successful joint Autumn Meeting. They have many members in common, and even some Members of Council. They are alike in constitution, and generally in their methods of working, although some differences in details of operation—for example, in publication—have developed. The scientific and technical sections of their respective subjects are very similar, with one important exception. The Iron and Steel Institute includes in its field process metallurgy (the extraction of the metal from its ores) and to some extent mining, which we do not, mainly because these subjects, for non-ferrous metals, are the province of another active Institute. This inclusion of process metallurgy by the Iron and Steel Institute corresponds with the much closer association of the primary, intermediate, and finishing processes of manufacture, the operations of mining, smelting, conversion into steel, and rolling into the finished product not infrequently being carried out by the same company as a co-ordinated sequence, and sometimes within the same ring fence. We have seen a certain tendency towards a closer association of the successive stages in the non-ferrous industries, actually very advanced in the aluminium and nickel industries, but in others mainly evidenced by a greater interest on the part of the producers as to what becomes of—perhaps I should say what can be done with—the raw metal they endeavour to sell.

The division of the field of metallurgy into halves by the two Institutes has all the advantages of specialization, and certainly the field is sufficiently vast thoroughly to justify this division, but perhaps it accentuates what is after all a somewhat arbitrary separation. Occasionally our own Publication Committee has to consider whether a paper submitted to it is genuinely non-ferrous—at any rate to the extent of 50 per cent.—and no doubt our neighbours are now and then faced with a similar question. Then there is the puzzling case of the paper which, quite properly, and indeed with great gain to the treatment of the subject, deals with closely similar phenomena both in steel and in non-ferrous alloys.

It will at once be admitted that on the purely scientific side the distinction between ferrous and non-ferrous metallurgy is wholly artificial. The problems of crystallization from the liquid state, effects of hot- and cold-working, constitution of alloys, and control of structure and properties by heat-treatment are essentially similar; so also are the various complex phenomena exhibited by metals and alloys when subjected to stress—elasticity, plastic distortion, creep, fatigue, and so on. Several alloy systems show their own characteristic phenomena not found in other alloys; this is true of the iron–carbon system and the extraordinarily complex and varied series of alloys based on that simple binary system. The progress now being made by Dr. Hume-Rothery, at Oxford, in his search for wide generalizations, based on crystalline and atomic structure, seems likely to bring more order into the apparently unrelated differences between different alloy systems, and possibly in time the peculiarities of some alloys may appear to be less peculiar from the scientific point of view.

Even on the practical side, where the distinction is a very real one, there is much common ground in ferrous and non-ferrous metallurgy, and it may be worth while to consider briefly some of the sections of metallurgy in which the common interest of the ferrous and non-ferrous sides has some special features. The subject of corrosion will at once occur to us all, because of its practical and economic importance, together with the difficulty and scientific interest of the problems it puts to us. If the subject is held to include corrosion-fatigue and oxidation at high temperatures, the durability of metallic structures and components depends almost solely on corrosion and abrasive wear. Research on corrosion is now probably more active than ever before. In our own country several large industrial laboratories are taking a large share, perhaps mainly on somewhat empirical lines, a good deal of attention properly being paid to methods of testing corrosion-resistance which will give a trustworthy guide to behaviour in service. The more fundamental work proceeding in the laboratories of Dr. U. R. Evans at Cambridge and of Dr. G. D. Bengough at Teddington is well known to all of us. This Institute was responsible for much pioneer work in its condenser tube corrosion research, transferred a few years ago to the British Non-Ferrous Metals Research Association, and still in active and fruitful progress. In its atmospheric corrosion research, extending over a number of years, that Association did much to establish and extend the explanation of corrosion-resistance by the formation of oxidized protective films. The building up of these films, before or during exposure to corrosive conditions, their continuity, adhesion, and impermeability, their damage by mechanical or other action, their effective repair when damaged, are now recognized as the essential features of corrosion-resistance in metals and alloys when not protected by coatings of other materials. It is obvious that corrosion research cannot be sharply divided into ferrous and non-ferrous, the mechanism of oxidation, general or local, and of film formation or breakdown, being much the same in steel as in many non-ferrous alloys. The phenomena of intercrystalline attack under corrosive conditions, exhibited in so marked a degree by the earlier austenitic chromium–nickel steels of the 18 : 8 type after certain kinds of heat-treatment, are found in a number of non-ferrous alloys, and the explanation found in the one case may have application in others, as may also the remedy.

Corrosion leads to protection, and the position here strikingly illustrates the non-ferrous invasion of ferrous metallurgy. The stainless steels contain large percentages of non-ferrous metals, but still more important is the use of non-ferrous metal coatings to protect steel from corrosion. Tin, zinc, nickel, chromium, cadmium, aluminium, applied by hot-dipping, electrodeposition, or other method appropriate to the metal used for protection are all effective for particular conditions of use. The suppression of porosity in tin coatings, of cracking in chromium plating—to mention two directions in which there is need for progress—would benefit a number of industries. This is clearly a field in which there is no rivalry between ferrous and non-ferrous metallurgy, but a call for co-operation in a common aim.

In a widely different section, the casting of metals and the production of ingots and castings free from defects which reduce their serviceability, the connection is less obvious. The methods of steel melting and the scale on which it is commonly carried out, as well as the special characteristics of liquid steel, might be thought to render the production of sound steel ingots an entirely individual problem. The five substantial reports of the Heterogeneity of Steel Ingots Committee of our sister Institute make little reference to non-ferrous ingots. Nevertheless, these reports may profitably be considered together with a book just published on the Casting of Brass Ingots.* The phenomena of crystallization, shrinkage and piping, segregation, gas cavities, effects of turbulence of the stream of metal in the mould, and oxidation of the surface of the liquid metal are common to most alloys, including steel, although their relative importance varies widely in different materials. The intricate problems connected with gases in metals are particularly difficult to attack in the case of steel, because of the high temperatures concerned and the complexity of the chemical and physical equilibria applying, of which so little is known. It is not unlikely that the somewhat more amenable, although still difficult and important problems of gases in copper and aluminium and their alloys may yield more readily to investigation. Extensive researches on these materials are in fact leading to generalizations which may have application to many other alloys, including steel.

---

* Genders and Bailey, "The Casting of Brass Ingots." British Non-Ferrous Metals Research Association. London: 1934.

Engineering and chemical progress continue to make more insistent demands for materials to withstand high temperatures. This has led to intensive investigation of the creep of materials under stress at high temperatures. Much of this work is necessarily empirical, amounting to the determination of the creep characteristics of steels of different types and the study of the effects of different alloy elements on creep. Attention is being given, however, to the fundamental causes and mechanism of creep, which are probably much the same in the creep at atmospheric temperatures of metals and alloys of low melting point as in steels at high temperatures. The effects of crystal size, recrystallization, &c., are more easily investigated at ordinary temperatures, and it seems probable that the study of creep in alloys of lead, tin, and other metals of low melting point, a study practically important in itself in other connections, may also throw light on the mechanism of high-temperature creep in alloys of high melting point, including steels.

After this rapid and extremely incomplete reference to some close contacts of ferrous and non-ferrous metallurgy, I make no apology for returning to the subject of publication. Those who remember the facilities for periodical metallurgical publication in English of twenty years ago know how inadequate they were. Apart from the *Journals* of the Iron and Steel Institute and the Institute of Metals, publishing original papers in half-yearly batches, there were scarcely any English periodicals of standing devoted solely to metallurgy, and metallurgical papers and articles were scattered over a large number of periodicals dealing mainly with other subjects. We depended a good deal on the engineering press, which deserves commendation for the attention devoted by it to our subject. Even now the position is not wholly satisfactory. A list I have prepared shows sixteen English periodicals of standing published in London which frequently contain original scientific papers in metallurgy, apart from process metallurgy. Only three or four of these periodicals are primarily concerned with scientific metallurgy, the others being chiefly occupied with other subjects or trade matters.

It was a dream of mine in those earlier years that if the Iron and Steel Institute and the Institute of Metals could have collaborated in the publication of a monthly periodical, it might have been the best metallurgical journal issued in the English language, and probably in the world. According to my vision it would have contained all the papers presented to the two Institutes, complete abstracts, ferrous and non-ferrous, authoritative reviews of progress in particular branches of our work, with other articles and matter of permanent value. The financial and other difficulties of such a scheme were great even twenty years ago, and have probably increased considerably with passage of time, but even now is it too late to consider co-operation in some form in the publication of abstracts? Both Institutes provide their members with an admirable abstract service, although there are differences in method. The necessary interest taken by each in sections of metallurgy important to both fields is instanced by a considerable overlap in abstracts, a number of papers being quite properly abstracted in both *Journals*. To the metallurgist with wide interests this division of metallurgical abstracts into two series, with an important overlap, is not an unmixed blessing. The far more difficult general question of the great amount of repetition and overlapping which now occurs in the various excellent series of abstracts issued, in English alone, in different metallurgical and chemical publications, grows bigger and more serious every year. It is not uncommon for independent, and usually good, abstracts of an important metallurgical paper to appear in at least six widely used periodical publications in the English language. The burden of cost, to which I have already referred, is by no means the only serious drawback to this needless multiplication of effort. There is no ready solution, but many of us think the problem must be tackled in some way. If the limited co-operation which I have suggested could be part of some larger scheme co-ordinating the publication of abstracts in metallurgy, the gain all round would be greater still. The standard which our own abstracts have now reached must, however, make us consider with the greatest care any proposal affecting the value of this essential service to our members.

In this address I have touched upon a number of diverse topics, strung together on the thread, perhaps a slender one, of the benefit to be gained in so many directions by co-operation and a wider outlook. I think, indeed, that it is more a question of necessity than of benefit, and that we may echo the well-known words of Benjamin Franklin, spoken on a momentous occasion, " We must all hang together, else we shall all hang separately."

I cannot conclude without saying how deeply sensible I am of the great honour you have done me in electing me as your President. I am only too well aware of my own limitations. To fill the high office of President of the Institute of Metals at the same time as that of Director of the British Non-Ferrous Metals Research Association is a heavy responsibility, which I should not undertake were I not assured of the help and support of my many friends on the Council and throughout the membership of the Institute.

CASTABILITY OF TERNARY ALLOYS.*

By Professor A. PORTEVIN,† Member, and P. BASTIEN,‡ Dr.-es-Sci.

Synopsis.

The ability of a molten metal or alloy to fill a mould completely is termed "castability"; it can be determined by ascertaining the length of a spiral cast-iron mould filled by the metal under predetermined casting conditions. The castability of a pure metal is a linear function of the difference between the pouring temperature Θ and the melting point F; the slopes of the castability $(\Theta - F)$ curves vary with the viscosity of the metal. The castability of binary alloys varies with the solidification range and with the mode of crystallization, being greater when polyhedral crystals separate than when the primary crystals are dendritic. Maximum castability occurs with the eutectic composition and minimum at the limit of solid solubility. The castability of ternary alloys varies inversely with the primary solidification range, and, in cases where this is nil (*i.e.* along the binary eutectic lines in the ternary system), it varies with the secondary solidification range reaching a minimum at compositions corresponding with the transition from two-phase to three-phase fields. These laws are illustrated with reference to several binary antimony alloys and to ternary alloys of lead, tin, and bismuth, and of iron, carbon, and phosphorus. Finally the value of this method of testing alloys for practical foundry work is discussed, and it is shown to be useful in determining the composition of eutectics and of saturated solid solutions in metal systems.

I.—Definition of the Term "Castability" and the Laws which Control the Castability of Pure Metals and Binary Alloys.

The ultimate aim of every foundry operation is to obtain a complete and perfect filling of the mould with the liquid metal, so that, after cooling, the casting exactly resembles the pattern and is of the required dimensions within the limits of error imposed by the nature of the metal. The realization of such a result implies the knowledge of the two fundamental properties of metal founding, *castability* and *shrinkage*.

Castability has been defined by one of us[1] as being the ability of a molten metal to fill a mould completely, and it can be determined by using a standard test-mould of as simple a form as possible.

During the casting operation the mould itself is heated as the metal cools and solidifies; the castability, which we shall designate by the

---

* Manuscript received September 27, 1933. Presented at the Annual General Meeting, London, March 7, 1934.

† Professeur Suppléant à l'École Centrale des Arts et Manufactures, Paris.

‡ Chef de travaux à l'École Nationale Supérieure de l'Aéronautique; Répétiteur suppléant à l'École Centrale des Arts et Manufactures, Paris.

symbol Λ in what follows, depends, therefore, on all the factors which control foundry practice. These can be classified as follows:

(*a*) Factors relating to the mould and the contact between the mould and the casting (*e.g.* nature of mould dressing).
(*b*) Factors depending on the casting (shape and dimensions).
(*c*) Factors defining the casting conditions (casting temperatures and rate of pouring).
(*d*) Factors depending on the metal.

Selected Experimental Conditions.

To determine the castability of metals we have adopted a standard cast-iron mould [2] in the shape of a plane horizontal spiral fed by a vertical riser provided with a flap-valve [3] for regulating the initial rate of feed. In order to avoid deterioration of the mould and to maintain the iron in a constant physical state we have confined our experiments to the less easily oxidized metals with a relatively low melting point (F), namely antimony, bismuth, tin, lead, zinc, cadmium, and aluminium.

The casting temperature (Θ) and the initial mould temperature (θ), kept constant at 18° C. throughout the experiments, were measured by means of thermocouples.

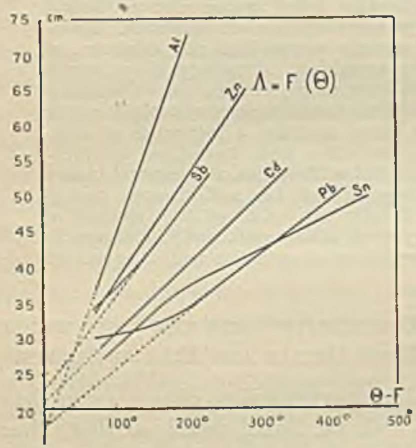


Fig. 1.—Castability of Pure Metals.

For all the metals, except antimony and aluminium, the castability was determined for values of $\Theta - F = 100°, 200°$, and 300° C.; for antimony and aluminium, the melting points of which are relatively high, the castability was measured for values of $\Theta - F = 100°, 150°$, and 200° C.

Results Obtained for the Castability of Pure Metals.

The experimental results [4] are summarized in Fig. 1 and show that for a sufficient degree of overheating the castability is practically a linear function of $\Theta - F$ and that the slope and ordinate at the origin of these lines vary from one metal to another.

The probable shape of the curves $\Lambda = f(\Theta)$ can be deduced from the following argument. The length Λ of the casting in the spiral obviously varies inversely with $F - \theta$; the castability increases when the temperature of the mould rises and the value of $F - \theta$ diminishes, and becomes infinite when the temperature of the mould is equal to that of the metal, *i.e.* for $\theta = F$.

The mean temperature of the mould increases with $\Theta - F$, and then the more rapidly the higher are the specific heat (c) and the density (d) of the metal; it also increases, independently of $\Theta - F$, with the latent heat of solidification (L) of the metal. Hence the simplest expression for the castability may be written as :—

$$\Lambda = K \,.\, d \,.\, \frac{c(\Theta - F) + L}{F \,.\, \theta} \quad . \quad . \quad . \quad . \quad (a)$$

A mathematical study of the problem [5] leads to the more complex relation :—

$$\Lambda = A \frac{c \,.\, d}{k} \,.\, \mathrm{Log} \frac{\Theta - \theta}{F - \theta} + B \frac{L \,.\, d}{k(F - \theta)},$$

where k is the heat conductivity of the mould.

This expression, as regards the practically linear portion of the curve $\Lambda = f(\Theta)$, reduces to

$$\Lambda = \alpha \,.\, \frac{c \,.\, d(\Theta - F)}{F - \theta} + \beta \,.\, \frac{L \,.\, d}{F - \theta} \quad . \quad . \quad . \quad . \quad (b)$$

which is of the same form as (a). The factors α and β depend on the nature and dimensions of the mould, on the casting conditions (height of pour and method of feeding), and also (but to an extent difficult to determine owing to the lack of precise numerical data) on the viscosity (η) of the metal.

If in expression (b) α and β are considered, as a first approximation, to be constants, it will be seen that :

(1) The curves of $\Lambda = f(\theta)$ are equilateral hyperbolæ.

(2) The curves of $\Lambda = f(\Theta)$ are straight lines the slopes of which are a function of the specific heat of the liquid metal and the ordinates of which at the origin should depend on the latent heat of solidification.

If now we compare the curves of $\Lambda = f(\Theta)$ obtained experimentally with the lines given by the expression (a) for the different metals which have been studied we see that :

(1) The classification of the ordinates at the origin agree in both cases showing that the factor β varies little from one metal to the other, and that the viscosity does not appear to have any effect.

(2) On the other hand, the slopes of the lines obtained experimentally cannot be arranged in the same order as that of the products

$\frac{c\,.\,d}{F-\theta}$; this indicates that the factor β varies from metal to metal and is a function of the viscosity.

Castability of Binary Alloys.

Among the factors which can influence the castability of alloys two are of particular importance, namely :—

(1) The process of solidification (solidification range).

(2) The crystallization (faces and speed of crystallization).

As we have already said, the metal crystallizes during its travel along the spiral mould, and we can therefore forecast that the solidification range will have an effect on the castability; further, we can distinguish three stages in this range from the point of view of the continuity or the dispersion of the phases,[6] namely :—

(1) The crystals of the solid phase are not yet sufficiently developed to make contact with one another and, therefore, swim in the liquid; the liquid phase is continuous and the solid phase discontinuous, hence the two phases are susceptible to displacement;

(2) The crystals of the solid phase are sufficiently developed to make contact with one another, and are thus immobilized to a felted mass through which the liquid can circulate; both liquid and solid phases are continuous, but only the former is susceptible to relative displacement;

(3) The development of the crystals of the solid phase is such that they form partitions immobilizing the liquid; the solid phase is continuous and the liquid phase discontinuous, hence no relative displacement and no important segregation are possible.

The relative importance of these three stages depends not only on the solidification diagram and the composition of the alloy, but also on the rate of crystallization and on the crystal form. Thus it is obvious that the mode of crystallization will have an effect on the castability, and that alloys in the neighbourhood of the eutectic will show a characteristic behaviour, since, in their case, the first stage is relatively much the most important.

From the results of tests we have made on binary alloys of antimony with lead, cadmium, and tin we have deduced the following laws :—

With a constant degree of overheating, $\Theta - F$,

(α) The castability varies inversely with the solidification range, reaching a relative maximum when the melting is congruent (pure metals, eutectics, and alloys of a composition corresponding with a maximum on the liquidus line) and a minimum for saturated solid solutions. The castability of antimony–lead alloys (Fig. 2), which form a simple eutectiferous system with a limited solid solubility at

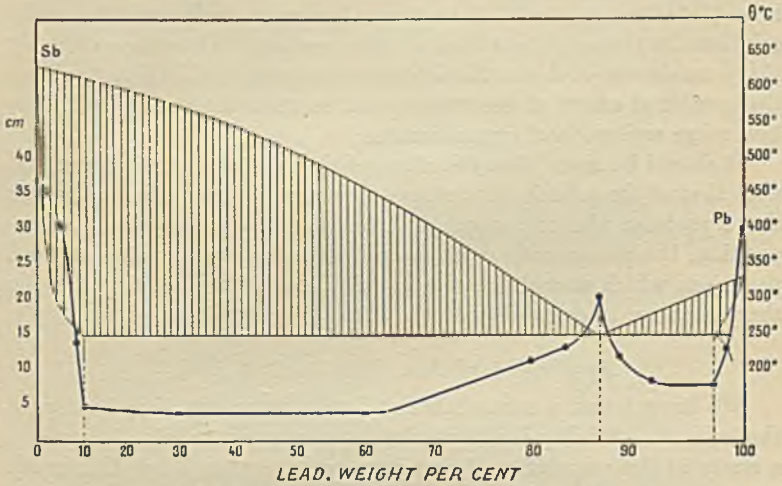


Fig. 2.—Castability of Antimony–Lead Alloys.

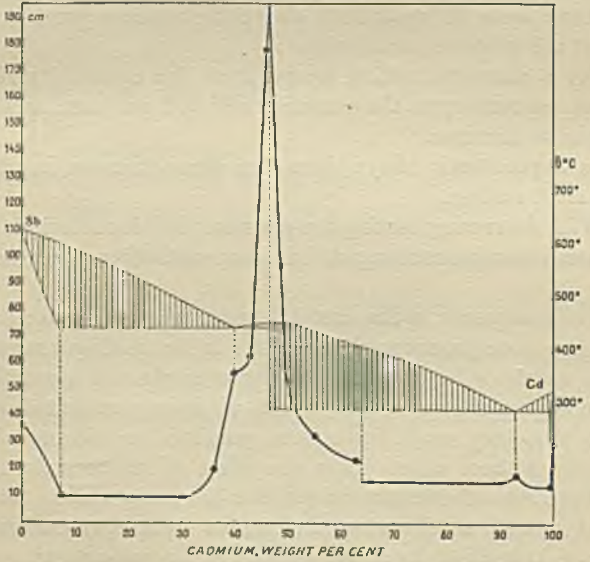


Fig. 3.—Castability of Antimony–Cadmium Alloys.

both ends, shows clearly the variation of A inversely with the solidification range.

(β) The castability depends on the shape of the crystals formed and is relatively much greater when the primary crystals have convex faces (definite compounds) than when they separate in dendrites (solid solutions in the neighbourhood of pure metals). Thus the extremely sharp maximum of A for the definite compound SbCd (Fig. 3) shows the combined effect of the two factors mentioned above: solidification range and mode of crystallization.

It should be noted that the effect of the crystal shape is connected with that of the solidification stages mentioned above; thus, a convex shape prolongs the first stage, and, for alloys near the eutectic composition, the pro-eutectic crystals are less numerous and do not form partitions which immobilize the liquid. The latter fact explains the sharp increase in castability at the eutectic composition.

Application of these Rules to Cast Iron.

We have found a remarkable and very interesting application of the laws of castability in the results recently published by Berger [7] on a study of the castability of cast iron carried out at Liège University under the direction of Professors Thyssen and Périn. From casting experiments on iron–carbon alloys with 2–4·5 per cent. of carbon at temperatures from 50° to 300° C. above the melting point Berger has arrived at the following conclusions :—

(1) For a constant casting temperature the castability rises with the carbon content up to the eutectic point (4·3 per cent. carbon) then commences to decrease.

(2) In hypoeutectic alloys there is a sharp increase in castability at 4 per cent. carbon.

(3) With decreasing casting temperature the characteristic shape of the curves remains unchanged, but the castability decreases in all cases.

(4) The maximum in the castability curve at the eutectic composition is the more pronounced the higher is the casting temperature.

These conclusions provide a striking example and a complete confirmation of the rules and laws which we have enunciated above, so much so that they could have been predicted in advance from the application of these rules. Here the effect of solidification range, of overheating, and of eutectic composition is clearly visible; as regards the rapid increase of the castability above 4 per cent. carbon, this is due to the transition to alloys in which the pro-eutectic period of solidification is entirely in the first stage, *i.e.* the primary crystals are not contiguous, and it is quite unnecessary to explain this fact on the basis of the intervention of viscosity as Berger does.

II.—Castability of Ternary Alloys.

The interesting results obtained with binary alloys have incited us to study the variation of the castability of ternary alloys, and especially to determine the effect of successive crystallization intervals and their relative importance.

For these tests we have again made use of the cast-iron mould with a horizontal plane spiral which we used in the study of the castability of pure metals and binary alloys.

As a simple ternary system composed of metals with a low melting point and with little tendency to oxidize, we have taken the lead–tin–bismuth system, the crystallization surfaces of which have been studied by Charpy [8] and by Shepherd [9]; they consist of three liquidus surfaces falling from the pure metals to the eutectic point at 32 per cent. lead, 15·5 per cent. tin, and 52·5 per cent. bismuth and 96° C. (Fig. 4). Further, in the neighbourhood of the pure metals there are regions of ternary solid solutions the extent of which are still poorly defined.

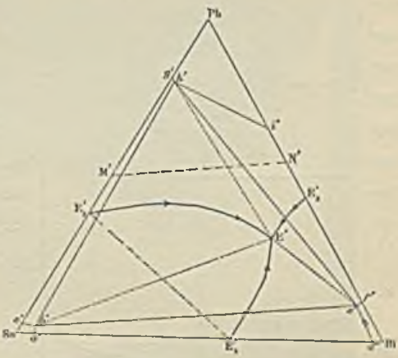


Fig. 4.—Equilibrium Diagram of the Tin–Lead–Bismuth System.

All the experiments were made, as in the case of the binary systems previously studied, with constant overheating of the metal, $\Theta - F = 100°$ C.

Binary Systems of Tin–Bismuth, Bismuth–Lead, and Lead–Tin.

These binary systems consist of solid solutions of the metals taken in pairs and of mixtures of these; experiments on these alloys have shown that their castability follows the laws which we have previously defined, namely the castability is at a minimum for the saturated solid solutions and at a maximum for the alloy which melts congruently (*i.e.* the eutectic).

Ternary System Tin–Lead–Bismuth.

We have explored the triangular region representing the composition of the tin–lead–bismuth alloys with the aid of sections normal to the plane of concentration of the following three types:—

(1) A transverse rectilinear section, such as $E'_1E'_2$ passing through the two binary eutectics E_1 and E_2 (see Figs. 4 and 5).

(2) A rectilinear section such as $M'N'$ parallel to the vertical plane passing through the binary eutectics E_2 and E_3.

(3) Three curvilinear sections, E'_1E', E'_2E', and E'_3E', passing through the binary eutectic lines of the system (Figs. 4 and 6).

From our experiments we have reached the following conclusions :—

(A) The castability of the ternary eutectic alloy is an absolute maximum, and is much greater than that of any of the binary eutectics in the system. The values obtained for the four eutectics were as follows :—

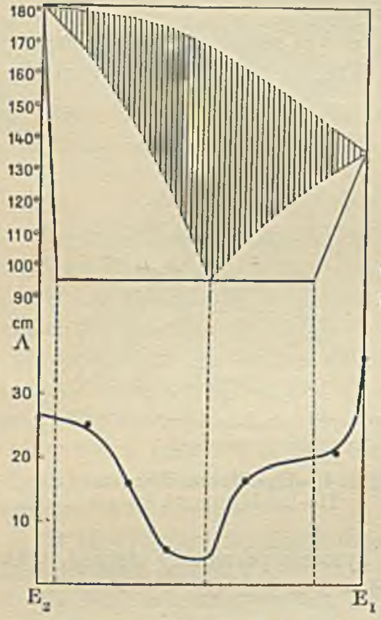


Fig. 5.—Castability of Alloys along the Section E_2E_1 of Fig. 4 (Similar Variation along the Section MN).

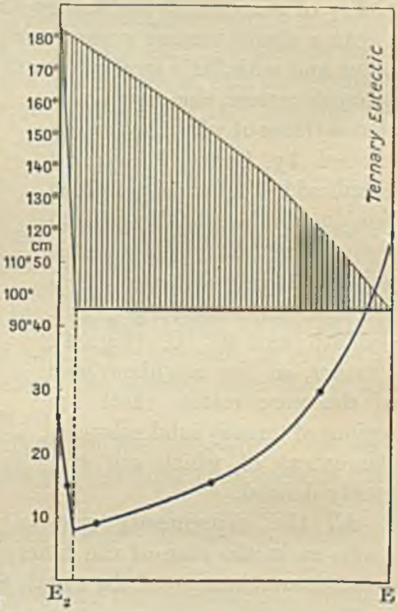


Fig. 6.—Castability of Alloys Along the Binary Eutectic Line E_2E.

$\Lambda_{Sn\text{-}Bi} = 36$ cm.; $\Lambda_{Bi\text{-}Pb} = 30$ cm.; $\Lambda_{Pb\text{-}Sn} = 26$ cm.; $\Lambda_{Pb\text{-}Bi\text{-}Sn} = 55$ cm.

The influence of the crystallization stages already mentioned in connection with binary alloys is thus applicable to explain the sharp peak on the castability surface corresponding with the ternary eutectic.

(B) The castability of ternary alloys varies inversely with the primary solidification range, the effect of which is of paramount importance; the secondary solidification range simply acts in the nature of a corrective. From this it follows that :—

(1) The binary eutectic lines E_1E, E_2E, E_3E, characterized by the

equilibrium of two kinds of crystals in the presence of liquid (primary solidification range nil) correspond with the lines of the crests in the castability surface. The castability along these crests varies inversely with the secondary solidification range (Fig. 6). Especially noticeable is the minimum of castability for the alloy situated at the junction of the two- and three-phase fields; this minimum corresponds well with a maximum in the secondary crystallization range.

(2) The lines *bE*, *cE*, *hE*, of intersection of the surfaces governed by the secondary crystallization correspond with the valleys in the ternary castability surface. This is easily explained if it is assumed that the primary crystallization range is a maximum for alloys which separate along the lines $b'E'$, $c'E'$, $h'E'$. The intersection of one of these valleys of the ternary castability surface is shown clearly on the section $E_1'E_2'$ (Fig. 5), where it corresponds with a minimum of Λ and with the maximum of the primary crystallization range shaded. The section $M'N'$ gives a similar result.

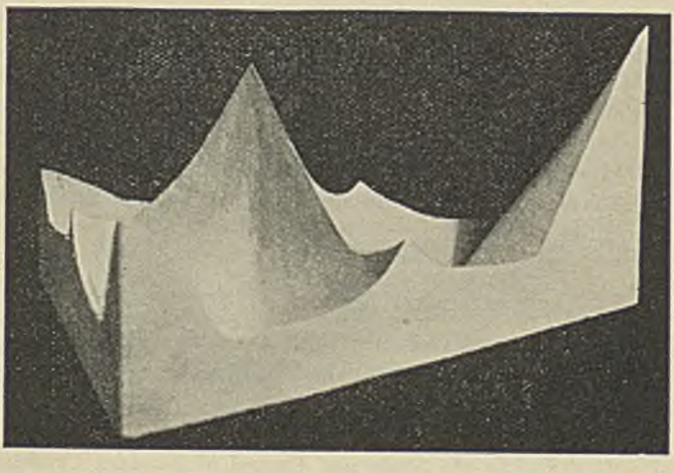


Fig. 7.—Castability Surface of Alloys in the Ternary System Tin–Lead–Bismuth.

(3) Finally, for equal solidification ranges alloys in which the primary crystals are bismuth with polyhedral faces have a greater castability than those in which the primary crystals are lead or tin dendrites. This fact confirms absolutely the effect we have already noted in the case of binary alloys of the shape of the primary crystals.

The laws enunciated above are in perfect harmony with those established for binary alloys; they are simply complicated by the presence of two solidification ranges.

Fig. 7 is a photograph of a wax model representing the castability surface of tin–lead–bismuth alloys showing the results described above, particularly the sharp peak corresponding with the ternary eutectic and the crests corresponding with the binary eutectic curves.

An application of these casting laws is found in the work of Berger on the castability of phosphoric cast iron, the results of which have just been communicated to us by Professor Thyssen. The author reaches the following conclusions :—

"For a constant casting temperature and constant carbon content the castability increases with the phosphorus content up to the eutectic composition based on the carbon content. With a further increase in the phosphorus content the castability decreases rapidly at first and then remains fairly constant. In the hypoeutectic region the increase in castability is the more marked the nearer the composition approaches that of the eutectic."

These conclusions are in perfect agreement with the laws we have enunciated. Further, on the curve of castability of phosphoric cast iron there is a similar minimum along the binary eutectic line, as we have indicated above.

III.—THE CASTABILITY METHOD OF STUDYING ALLOYS.

The castability test can be applied in a practical sense in the study and control of foundry practice, as well as in a theoretical sense in the confirmation of solidification diagrams.

I.—*Practical Use in the Study and Control of Foundry Conditions.*

We summarize below the value of the castability test in the foundry, referring the reader to our previous publications [10] for fuller details.

(*a*) It provides a method for choosing alloys with good casting properties and with a large margin of safety in casting; the latter is defined as that temperature range the lower limit of which is controlled by the castability and the upper limit of which depends on the mechanical properties of the metal, the other phenomena and faults of founding (piping, shrinkage, cracking, &c.), the reactions of the molten metal on the mould, and the chemical changes in the metal.

(*b*) It provides a method for controlling the casting temperature for a given casting, having the advantage of adjusting the temperature by the same property which comes into play in founding, thus eliminating the unknown function $\Lambda = f(\Theta)$.

(*c*) It provides a method for preventing impairment of the quality of the metal, especially in the case of light and ultra-light alloys.[11]

(*d*) It provides a means of choosing mixtures for moulds and a method of selecting mould temperatures, especially for the study of the effect of factors which affect the cooling by modifying the thermal properties (conductivity, heat of vaporization or of decomposition of substances incorporated in the moulds).

We have already given examples of these in the casting of magnesium.[11]

Speaking generally, it is thus possible by the castability method to study and control one factor in foundry practice while keeping the other factors constant.

II.—*Application of Castability in Determining Solidification Diagrams.*

By reference to the castability diagrams given in this paper it will be obvious that this method provides a convenient way of determining the position of eutectics or of saturated solid solutions.

Here is a striking example : When we determined the castability of antimony–lead alloys we used the equilibrium diagram of Dean, Hudson, and Fogler,[12] which shows only a lead-rich solid solution. The tests having shown a sharp fall in castability at the antimony end with alloys containing about 10 per cent. lead and a large change in the slope of the castability curve starting at the 10 per cent. lead alloy, we concluded that in all probability there existed a solid solution of lead in antimony containing a maximum of about 10 per cent. lead. On looking through more recent work on the equilibrium diagram, we found that Broniewski and Sliwowski [13] have shown that the lead–antimony system comprises two solid solutions and two mixtures, the limit of solid solubility of lead in antimony being 11 per cent. at the eutectic temperature.

From the results of castability tests on the ternary lead–tin–bismuth system we have been able to make several corrections in the solid solution ranges, the extents of which have so far been indicated only in outline.[9] Thus in the curvilinear sections E'_1E', E'_2E', E'_3E' the transition from a two-phase to a three-phase field is marked by a well-defined minimum of castability. Similarly, in the vertical sections, such as $E'_1E'_2$ and $M'N'$, the points where these planes cut the lines bE, eE, hE, of intersection of surfaces controlled by the secondary crystallization correspond with minima in the castability curve.

As a result of all our work on the castability of binary and ternary alloys, it seems to us that the determination of this complex property provides a new method of finding the eutectic composition in an alloy system and of delimiting the solid solution ranges.

References.

[1] A. Portevin, " Leçons à l'École Supérieure de Fonderie," 1931, pp. 152, 156.
[2] L. Guillet and A. Portevin, *Compt. rend.*, 1932, **194**, 599.
[3] Courty, *Rev. Mét.*, 1931, **28**, 169.
[4] A. Portevin and P. Bastien, *Compt. rend.*, 1932, **194**, 599.
[5] P. Bastien, *Bull. Tech. Service Recherches Aéronautique*, No. **20**, 1933.
[6] A. Portevin, " Introduction à la Chimie des Alliages-métalliques," *Traité de Chimie Minérale*, 1933, XII, p. 84; Paris: Masson.
[7] René Berger, " Mise au Point d'une Éprouvette de coulabilité et son Application à l'Étude du Système Fer-Carbone," *Fonderie Belge*, 1932, (17).
[8] G. Charpy, *Compt. rend.*, 1892, **126**, 1569.
[9] Shepherd, *J. Physical Chem.*, 1902, **6**, 519.
[10] A. Portevin: *Congrès de Fonderie de Paris*, 1932, Sept.; A. Portevin and P. Bastien, *Congrès de Fonderie de Prague*, 1933, Sept.
[11] A. Portevin and P. Bastien, *Congrès de Fonderie de Prague*, 1933, Sept.
[12] Dean, Hudson, and Fogler, *Indust. and Eng. Chem.*, 1925, **17**, 1246.
[13] Broniewski and Sliwowski, *Rev. Mét.*, 1928, **25**, 397.

DISCUSSION.

Professor Dr. A. von Zeerleder * (Member): This paper describes a very interesting scientific application of Professor Portevin's method of determining the castability and fluidity of aluminium and its alloys based on more scientific investigations. The experiments show a very interesting parallelism between the equilibrium diagram and the length of the cast spirals; the castability test also gives results of interest to the practical foundry man. Since the method was first published in 1931, the foundry laboratory of the Aluminium-Industrie A.-G. has adopted it for studying the castability of aluminium alloys. When the test conditions are identical, *i.e.* having exactly the same metal and mould temperatures, the results obtained with the same alloy differ only by 5–10 per cent. from each other, so that an average of three tests gives very precise results. Modification in carrying out the test showed that the instructions must be followed exactly as they are given in a paper by André Courty.†

Figs. A (Plate I) and B show the different parts of the cast-iron mould to be used. *A* is the crucible, in which the metal is cast. As this crucible must be kept filled up level with the top during the casting of the spiral, a certain amount of metal flows through the overflow pipe *D* in a second crucible *E* or in an ingot mould. The bottom of the crucible *A* is provided with a small iron pipe *B* of ⅝ in. diameter, which is closed on both sides by a thin lead peg *L*. Before pouring the metal into the crucible *A*, the pipe *B* is covered by a small graphite crucible *H* which is turned upside down to protect the lead stopper against direct contact with the metal being poured into the crucible. As the crucible is filled with metal, the graphite floats on the surface, the lead stopper melts and the metal runs into the mould *G*, first filling the big, central part *J* of the mould and finally running into the spiral *K*. In this way, all the lead is collected on the bottom of the central part *J* and does not influence the spiral.

Fig. C (Plate II) shows the influence of different metals of different fluidity on the length of the spiral, *1* being pure aluminium, *2* Anticorodal with 2 per cent. silicon, 0·4 per cent. iron, 0·7 per cent. manganese, and 0·6 per cent. magnesium, *3* being the same alloy with 5 per cent. silicon instead of 2 per cent.,

---

* Chief Engineer, Aluminium-Industrie A.G., Neuhausen, Switzerland.

† "Contribution à l'Étude de la Coulabilité" (*Rev. Mét.*, 1931, **28**, 169–182, 194–208).

PLATE I.

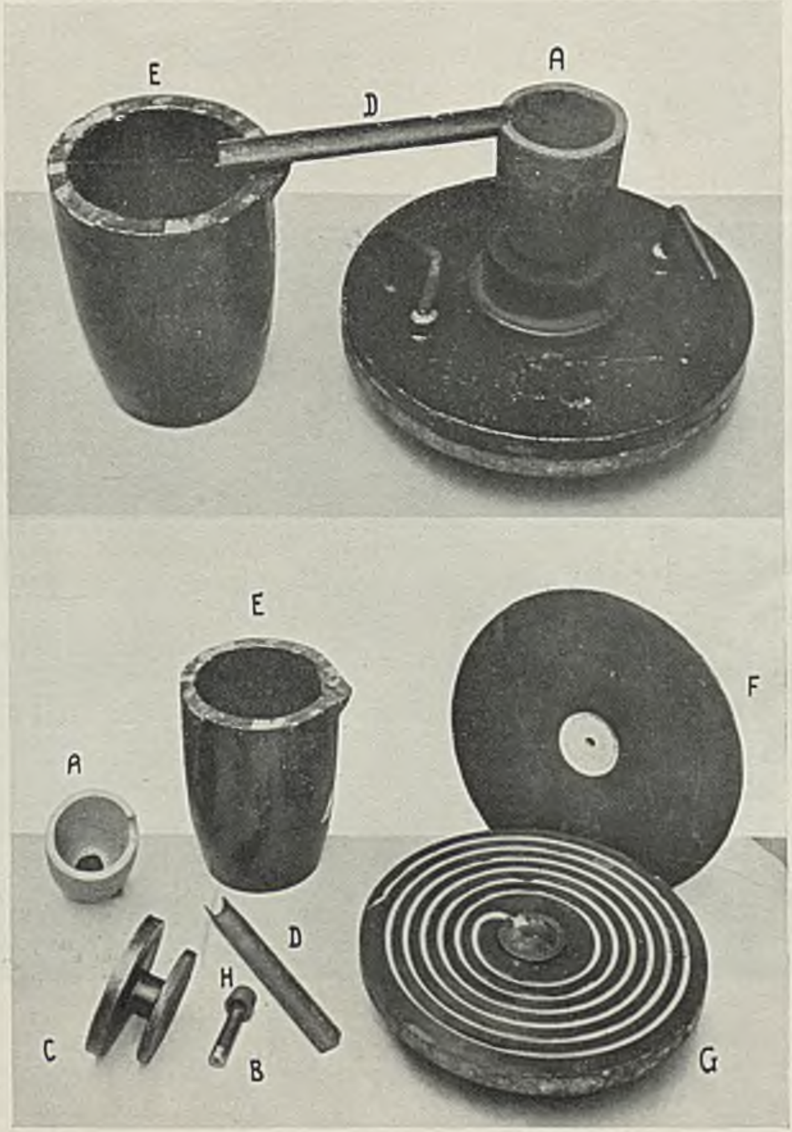


FIG. A.

[*To face p.* 56.

BIBLIOTEKA
POLITECHNIKI

PLATE II.

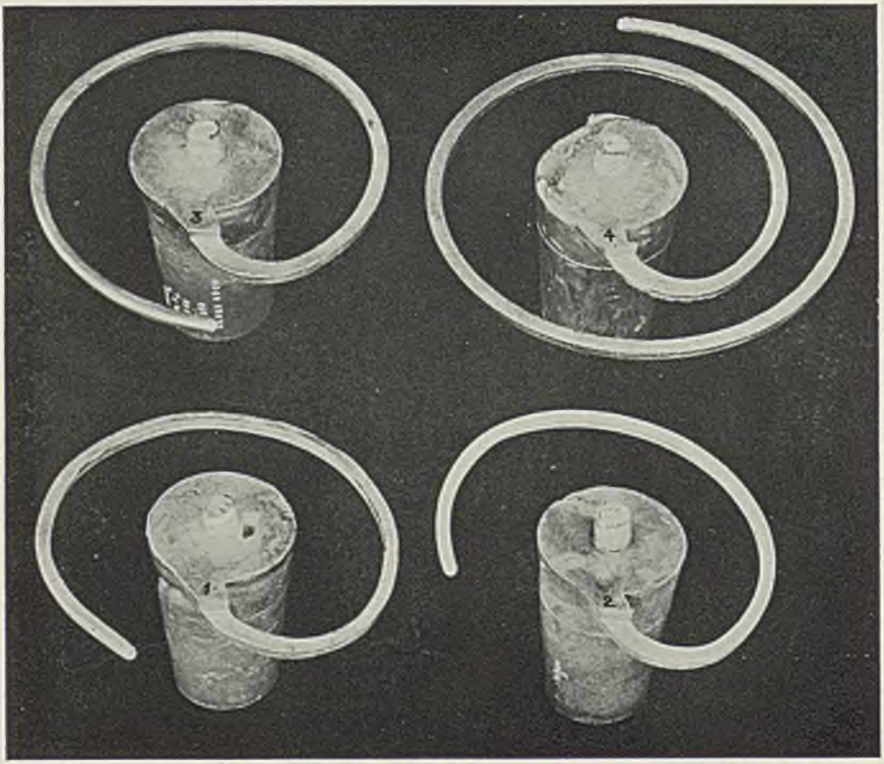


FIG. C.

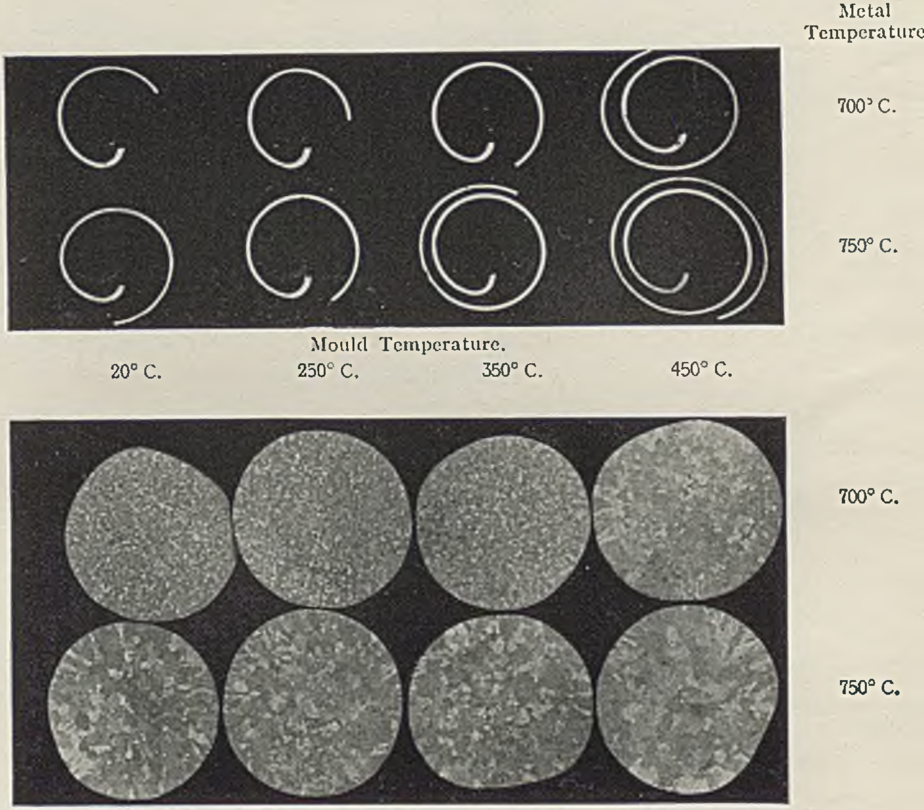


FIG. D.

BIBLIOT… POLITECHNI…

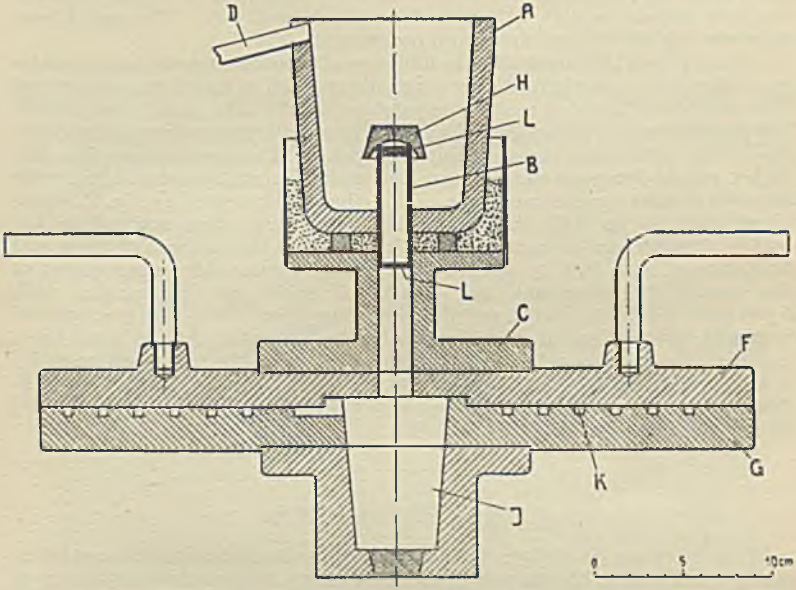


Fig. B.

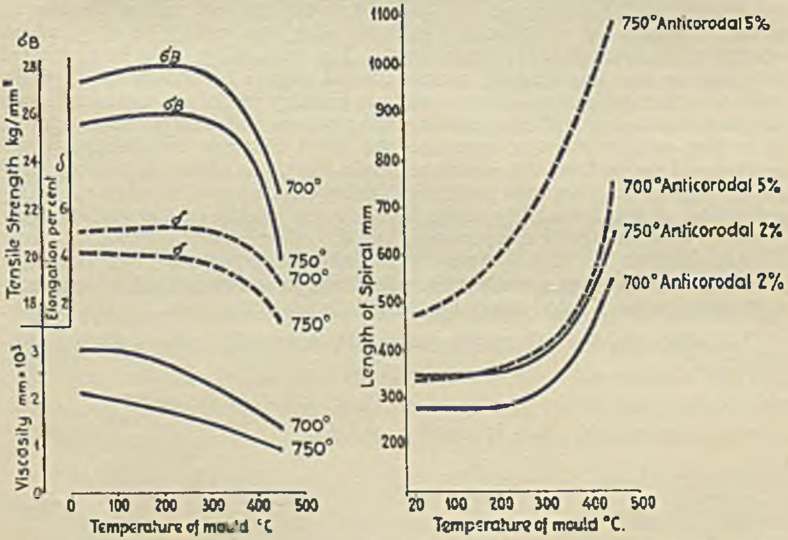


Fig. E.—Influence of the Metal and Mould Temperatures on Mechanical Properties and Viscosity. (Anticorodal A.)

and *4* showing the well-known Alpax with 13 per cent. silicon. The lengths of the four spirals are 400, 310, 410, 730 mm. respectively. The metal temperature was 680° C. and the mould temperature 300° C.

Fig. D (Plate III) illustrates the influence of mould and metal temperatures on Anticorodal containing 5 per cent. silicon with a metal temperature of 700° and 750° C. and a mould temperature of 20°, 250°, 350°, and 450° C. The same figure also shows the influence of the mould temperature on the grain-size of test-bars cast under the same conditions. It is a well-known fact that higher mould temperatures increase the grain-size and decrease the tensile strength of most aluminium alloys. This effect is illustrated by Fig. E, which shows that up to 300° C. the mould temperature does not reduce the tensile strength and elongation of Anticorodal, but the increase of the mould temperature from 200° to 300° C. gives a very appreciable improvement of the castability, increasing the length of spiral for Anticorodal with 5 per cent. silicon at 700° C. metal temperature from 360 to 410 mm. and for a casting temperature of 750° C. from 600 to 750 mm. At the same time, however, the increase of metal temperature reduces the tensile strength by 2 kg. from 28 to 26. This investigation shows that the best casting conditions for Anticorodal are at a mould temperature of 300° C. with a metal temperature between 700° and 750° C.

CORRESPONDENCE.

The Authors (*in reply*): We thank Dr. von Zeerleder for his very interesting contribution to the use of the castability test in the fabrication of aluminium and aluminium alloy castings. The automatic valve represented by the small inverted crucible appears to us to play a more important part than the lead plug in giving regular results, since in our experiments, although we started with a lead plug, we later abandoned its use. From the results given in Fig. C the effect of the eutectic alloy can readily be seen, which confirms the laws we have enunciated. The castability, as a fundamental property in the founding of metals, should always be considered together with the other properties of importance in foundry work * in order to deduce the best thermal conditions (casting temperature and mould temperature); it is just as important to examine the effect of these conditions on the mechanical properties, the structure (grain-size), the chemical homogeneity (micro-segregation) and the soundness (micro-cavities and blowholes). Consideration of the castability alone leads to the raising of the casting temperature and the mould temperature, but the other factors mentioned above militate against too high an increase in either temperature. This is clearly shown by the example given by Dr. von Zeerleder which indicates that these temperatures are limited solely by the mechanical properties.

---

* A. Portevin, "Metallography and the Foundry," *Bull. Assoc. Tech. Fond.*, 1932, 6, 19.

MINIMUM DIMENSIONS OF TEST-SAMPLES FOR BRINELL AND DIAMOND PYRAMID HARDNESS TESTS.*

By G. A. HANKINS,† D.Sc.(Eng.), A.R.C.S., and C. W. ALDOUS,‡ B.Sc.(Eng.), A.C.G.I.

SYNOPSIS.

The investigation was carried out to determine the effect of variations in the dimensions of test samples on the results of Brinell and diamond pyramid hardness tests, and to enable minimum dimensions of test samples to be suggested. The work, which is of particular importance in regard to Brinell tests on bars and thin plates, and in regard to both Brinell and diamond pyramid hardness tests on metal sheet and strip materials, comprises an experimental examination of (*a*) effect of width of specimen on Brinell hardness test results; (*b*) effect of thickness of specimen on Brinell hardness test results; (*c*) effect of thickness of specimen on diamond pyramid hardness test results. The metals investigated include copper, brass, aluminium, and steel.

It is concluded that a width of test-specimen of 4½ times the diameter of the impression is satisfactory for accurate Brinell tests on all the materials examined. In regard to the thickness of samples for Brinell tests, the limiting value of the ratio of thickness of test sample to depth of impression for accurate results appears to be a characteristic of the test material; a value of the ratio of 6 is required for mild steel, about 15 for copper, and more than 20 for spring steel. In carrying out diamond pyramid hardness tests on thin samples, a limiting value of the ratio of test-sample thickness to impression diagonal of 1½ gives results which are practically independent of test-sample thickness for the majority of sheet metals, with the exception of soft copper and soft brass.

INTRODUCTION.

BRINELL and diamond pyramid hardness tests are widely used in the testing and inspection of nearly all ferrous and non-ferrous engineering materials, and these are now the standard hardness tests in use in Great Britain. Their value is fully recognized and need not be discussed here, but experience has shown that the results obtained in such tests may be dependent, in limiting cases, on the sizes of the test impressions relative to the dimensions of the particular samples of metal on which the tests are made. Thus, if ordinary Brinell hardness

---

* Manuscript received October 7, 1933. Presented at the Annual General Meeting, London, March 7, 1934.

† Senior Scientific Officer, Engineering Department, National Physical Laboratory.

‡ Junior Scientific Officer, Engineering Department, National Physical Laboratory.

tests be made on the side of a mild steel bar of say ⅜ in. × ⅜ in. square section, using a load of 3000 kg. and a 10-mm. diameter ball, the impressions will be larger than those obtained in similar tests on a bar of the same material of say 1 in. × 1 in. square section; similarly, if diamond pyramid hardness tests with a load of 30 kg. be made on a copper sheet 0·01 in. thick, the impressions will not be the same size as those obtained with the same test on a sheet of similar material 0·2 in. thick. This behaviour is well known in normal testing practice, and certain minimum requirements for dimensions of test-pieces are indicated in the British Standard Specifications for Brinell and diamond pyramid hardness tests. These requirements, however, appear to be based on very limited test data, and experience of hardness testing at the National Physical Laboratory has shown that the standard requirements, whilst satisfactory in some cases, do not necessarily apply to all cases. The present investigation has accordingly been carried out to determine, for a number of materials, the effect of variations of test-piece dimensions on the results of Brinell and diamond pyramid hardness tests. The work has been carried out in the Engineering Department of the Laboratory as part of the general research programme authorized by the Executive Committee.

The experimental investigation comprises three sections:

(1) Effect of width of specimen on Brinell hardness test results;
(2) Effect of thickness of specimen on Brinell hardness test results;
(3) Effect of thickness of specimen on diamond pyramid hardness test results.

The study of these effects does not, of course, cover the whole range of possible variations in test-piece dimensions, but these variations are the most important which may arise in normal commercial and laboratory test work.

I.—EFFECT OF WIDTH OF SPECIMEN ON BRINELL HARDNESS TEST RESULTS.

In order to study the effect of width of test-specimen on Brinell hardness test results, test-bars were prepared which were uniform in thickness, but tapered uniformly in width along the length of the bar. Standard Brinell hardness tests were made along the centre lines of the bars, the impressions being sufficiently far apart not to affect each other. In this way it was possible to carry out similar tests on a uniform bar under conditions in which the width of the bar was the only variable. Tests of this type, carefully made in accordance with the recommendations given in British Standard Specification No. 240, 1926, were carried out on bars of soft copper, hard copper, mild steel, and spring steel. Each impression was measured in two directions at right angles (along and across the length of the bar), the readings being correct to about ± 0·001 mm. The results obtained on the softest and hardest materials are shown in Fig. 1, from which it can be seen that the apparent Brinell hardness numbers are independent of the width of the test-piece at the higher values of the width, but decrease rapidly with decreasing width at the lower width values. Eight series of tests similar to those recorded in Fig. 1 were carried out, but as the type of result obtained was more or less the same in all cases, detailed results are not given; the materials investigated, however, are indicated in Table I. It should be noted that at least two test-bars were required for each series of tests in order to obtain a fair variation in width, and that all the test-bars were specially selected for their high degree of uniformity.

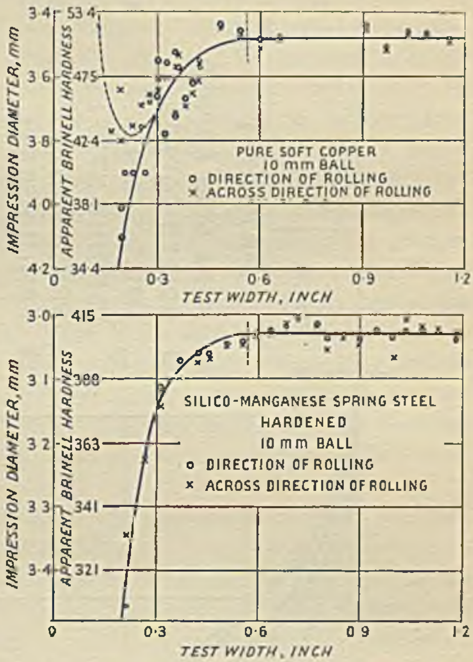


Fig. 1.—Minimum Dimensions of Brinell Test-Pieces. Variation of Impression Diameter with Width of Test-Piece.

Table I.—*Effect of Width of Specimen. Materials Investigated.*

Material.	Correct Brinell Hardness Number.	Load Used in Test Series, kg.	Ball Diameter Used in Test Series, mm.
Soft copper (commercially pure) . .	51	500	10
Rolled copper	95	500	10
,, ,, ...	95	125	5
Mild steel	110	3000	10
Silico manganese spring steel (as rolled) .	275	3000	10
,, ,, ,, ,, ,, .	275	750	5
Silico manganese spring steel (hardened and tempered)	327	3000	10
,, ,, ,, ,, ,,	408	3000	10

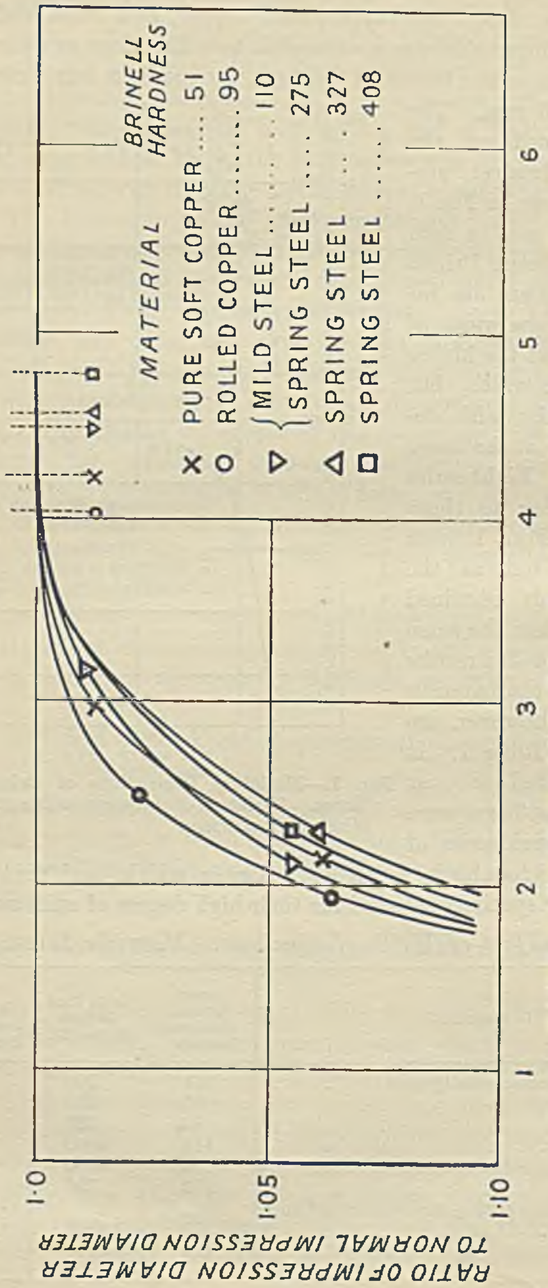


Fig. 2.—Minimum Dimensions of Brinell Test-Pieces. Variation of Impression Diameter with Width of Test-Piece.

In order to afford a general comparison of the results, the mean curves obtained in diagrams similar to Fig. 1 can be plotted on a non-dimensional basis as shown in Fig. 2, in which "ratio of impression diameter to normal impression diameter" is plotted against "ratio of test width to normal impression diameter," the "normal impression diameter" in these ratios being the diameter of impression corresponding with the flat parts of the curves of the detailed results. Plotting the curves in this way allows all the test series to be compared on the one diagram; it should be realized that each curve of Fig. 2 represents the results obtained from 20 to 30 individual tests. The results of the tests on rolled copper and spring steel, using the 5-mm. diameter ball, were practically coincident with those using the 10-mm. diameter ball and are not shown separately. It can be seen from Fig. 2 that the form and position of each curve are largely independent of the nature of the actual material; thus, if the test width is greater than about 4½ times the diameter of the test impression, the result obtained is not affected by the width of the specimen; when, however, the test width is about 2¼ times the diameter of the test impression, the diameter obtained in a test is of the order of 5 per cent. greater than the correct diameter.

The relevant clause from British Standard Specification No. 240, 1926, dealing with test width is as follows: "The centre of the impression shall be not less than two and a half times the diameter of the impression from any edge of the test specimen." The present tests show that this requirement is satisfactory for all the materials investigated.

II.—EFFECT OF THICKNESS OF SPECIMEN ON BRINELL HARDNESS TEST RESULTS.

In order to examine experimentally the effect of thickness of test specimen on Brinell hardness test results, test-bars were prepared which were uniform in width, but tapered uniformly in thickness. Standard Brinell hardness tests were made along the centre line of each bar, and in this way it was possible to carry out similar tests on a uniform bar under conditions in which the thickness of the test-bar was the only variable involved. Series of tests of this nature were carried out on each of the materials listed in Table II.

Before discussing the results in detail, it is useful to consider the quantitative part of the relevant clause in British Standards Specification No. 240, 1926, in regard to thickness of test-specimen; it states that: "The thickness of the test specimen shall be at least seven times

TABLE II.—*Effect of Thickness* (*Brinell Tests*). *Materials Investigated.*

Material.	Brinell Hardness Number.	Load Used in Test Series, kg.	Ball Diameter Used in Test Series, mm.	Detailed Results Shown in Fig. No. :
Annealed copper . . .	43	500	10	3
,, ,, . . .	45	125	5	3
Soft copper (commercially pure)	about 49	500	10	3
Rolled copper . . .	95	500	10	4
Mild steel	116	3000	10	5
Silico-manganese spring steel (as rolled) . . .	275	3000	10	5
,, ,, ,, ,,	275	750	5	6
Silico-manganese spring steel (hardened and tempered) .	327	750	5	6
,, ,, ,, ,,	411	750	5	6

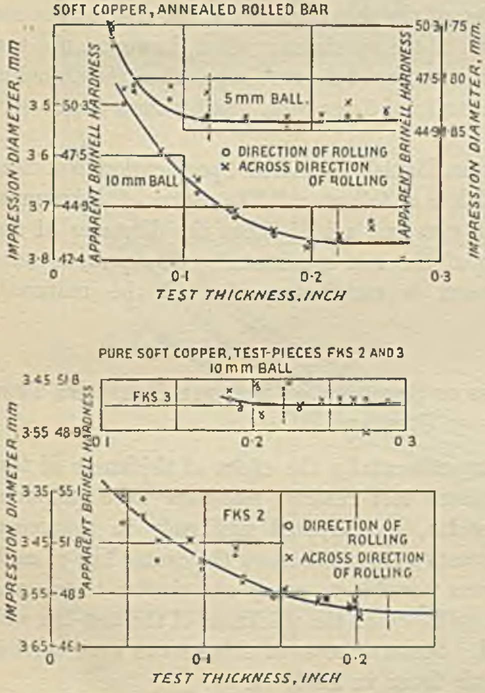


FIG. 3.—Minimum Dimensions of Brinell Test-Pieces. Variation of Impression Diameter with Thickness of Test-Piece. Hardness of Backing, 950.

the depth (t) of the test impression as given by the formula $t = \frac{P}{\pi DH}$ where

t = Depth of impression,
P = Load used in test (kg.),
D = Diameter of ball used in test (mm.),
H = Brinell hardness number.”

It will be noted that a constant value of the ratio of size of impression to thickness of material is specified for all materials; so far as the authors are aware, the only previous detailed investigation of the matter was that carried out by Moore *

---

* H. Moore, *Proc. Internat. Assoc. Test. Mat.*, 1909, No. 9.

and the value of the ratio, *viz.* 7, appears to be taken from his tests.

Detailed Consideration of Thickness Results (*Brinell Tests*).

(a) *Annealed and Soft Copper.*—The detailed results of the tests on annealed copper are shown in Fig. 3. It will be noted that beyond a particular limit, the apparent Brinell hardness number *increases* as the material diminishes in thickness; this is clearly shown in the tests with both the 5-mm. and 10-mm. diameter ball. As would be expected, the results of the tests with balls of the two different diameters are in fair agreement as to the relative thickness at which the apparent hardness begins to increase; thus, the mean curve begins to rise at a test thickness of about 0·12 in. for the tests with the 5-mm. ball and at a thickness of about 0·22 in. for those with the 10-mm. ball; on the basis of geometrical similarity the value for the 10-mm. ball should be twice that for the 5-mm. ball, and accordingly the results of the two sets of tests are in fair agreement. The results of the tests on the pure soft copper, shown in Fig. 3, are similar to those on the annealed copper bars. Two separate bars were used which differed slightly in average hardness, but taking the two sets of results together, it can be seen that below a thickness of about 0·22 in. the apparent hardness number increases with diminishing test thickness in the same way as for the annealed copper. When the results are expressed in terms of the ratio of test thickness to depth of impression as in the Standard Specification, it appears that the ratio should be about 15 for results independent of thickness to be obtained. With a test thickness of 7 times the depth

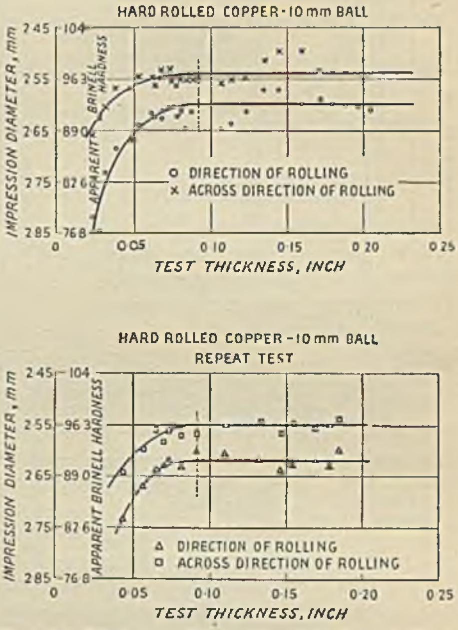


Fig. 4.—Minimum Dimensions of Brinell Test-Pieces. Variation of Impression Diameter with Thickness of Test-Piece. Hardness of Backing, 950.

of impression the error in the apparent Brinell hardness number of soft copper would appear to be about 7 per cent.

(b) *Rolled Copper.*—The detailed results of the tests on rolled copper are shown in Fig. 4. It has already been stated that each test impression was measured in two directions at right angles, and in the tests on rolled copper the differences in the two directions were quite definite. The curves show that below a certain limiting value the apparent Brinell hardness number *decreases* with decrease in thickness of test specimen, and the behaviour is accordingly quite different from that of soft copper. The thickness effect begins at a ratio of test thickness to depth of impression of about 14.

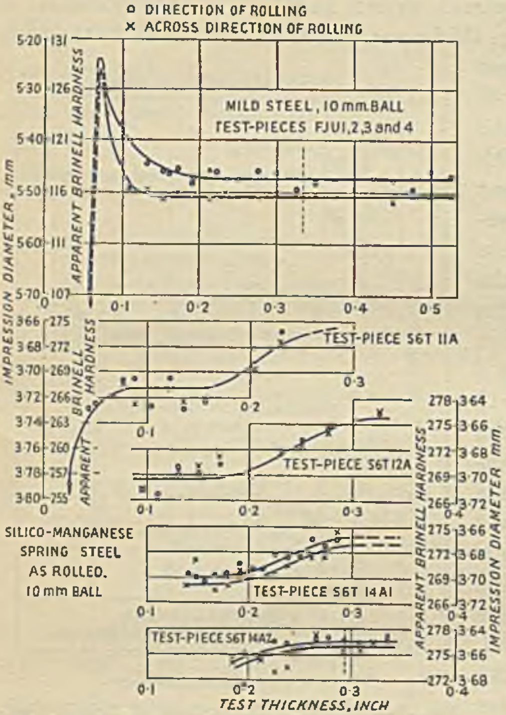


Fig. 5.—Minimum Dimensions of Brinell Test-Pieces. Variation of Impression Diameter with Thickness of Test-Piece. Hardness of Backing, 950.

(c) *Mild Steel.*—Detailed consideration of the results on mild steel, shown in Fig. 5, is of interest. In the first place, it will be noted that the material possessed definite directional properties, in that the impressions were all slightly longer across the direction of rolling than along the direction of rolling. With diminishing thickness of the test specimen the apparent Brinell hardness number began to increase, but when the tests were continued at very low thicknesses the apparent hardness number decreased below the original average value. No great reliance can be placed on the tests on very small thicknesses, however, since the test material was so thin that marked bending occurred around the impressions. The next point of interest is the ratio of test thickness to depth of impression at which the apparent Brinell hardness curves first begin to rise. At a specimen thickness of about 0·17 in. the ratio is just over 5, and accordingly a value of 7, as recommended in the Standard Specification, would give accurate results. The present results are in approximate agreement with those of Moore,* although the methods used in the two cases are quite different. In confirmation of the present results, a further series of tests was carried out on mild-steel boiler plate, and the results also showed that

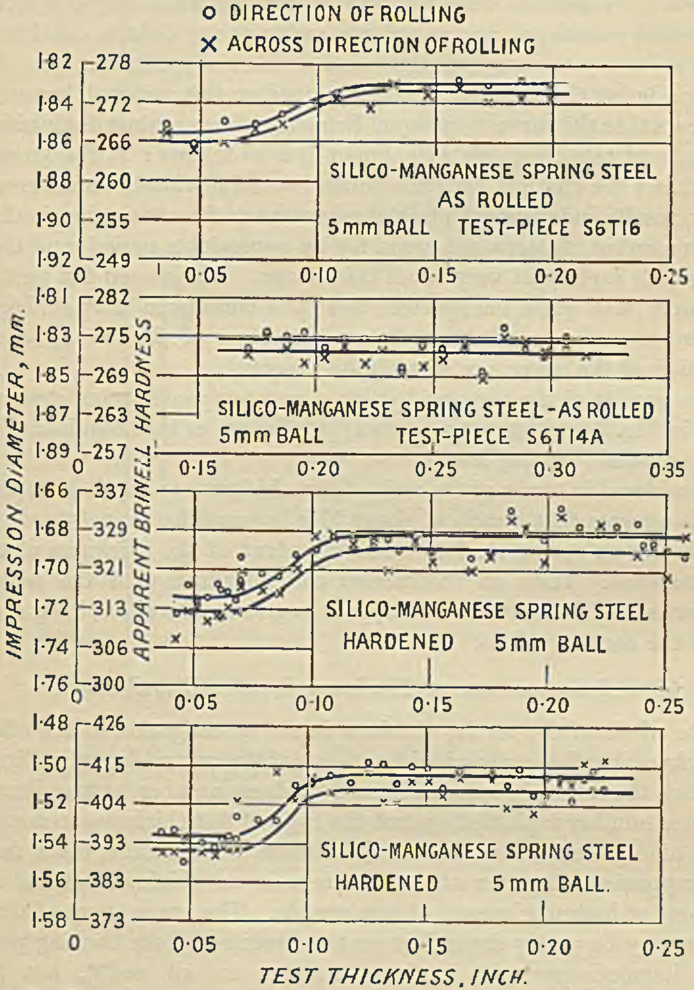


Fig. 6.—Minimum Dimensions of Brinell Test-Pieces. Variation of Impression Diameter with Thickness of Test-Piece. Hardness of Backing, 950.

---

* *Loc. cit.*

a test thickness of six to seven times the depth of impression gave accurate results.

(d) *Spring Steel.*—The results of the tests on spring steel in the "as rolled" condition were not very convincing when only one series of tests was considered, and in order to arrive at any definite conclusion it was necessary to carry out tests on a number of specimens.

Considering the complete results obtained on this material, however, it appears that the curve of apparent Brinell hardness against diminishing thickness of test-piece (see Figs. 5 and 6) is as follows: at the greater thicknesses the curve is flat (this portion would obviously be necessary if any results independent of thickness were to be obtained); it then falls somewhat, flattens out again for an appreciable period, and then finally falls rapidly at very small thicknesses. The second flat part of the curve was quite unexpected, but it is considered that sufficient tests were made to establish the general form of the curve; exact definition of the curve can scarcely be expected.

The results of the tests on hardened and tempered spring steel are given in Fig. 6, and show the same type of curve as that obtained with the "as rolled" spring steel.

Considered in terms of the ratio of test thickness to depth of impression, it appears that a ratio of about 20 is required for Brinell hardness test results on spring steel to be independent of the thickness of the test material. Tests on thicknesses corresponding with the second flat portions of the curves would appear to give results about 5 per cent. below the correct values.

General Comparison of Thickness Results (Brinell Tests).

The whole of the results obtained in the investigation of the effect of thickness can be summarized by means of the curves shown in Fig. 7, in which the ratio of apparent Brinell hardness number to true Brinell hardness number is plotted against the ratio of test thickness to normal depth of impression, the true Brinell hardness number being taken from the impression diameter at which there is no thickness effect, *i.e.* hardness at high thicknesses of test sample. The exact forms of these curves may be partly dependent on the hardness of the backing plate (950 diamond pyramid hardness number in all cases), but the approximate forms and the points at which the first deviations from the horizontal occur should be largely independent of the backing plate and dependent on the characteristics of the test materials.

It is clear from these curves that no general limiting value of the ratio of thickness of test-specimen to depth of impression can be stated for all materials; for Brinell hardness numbers to be independent of thickness of test-specimen, the value of the ratio may vary from about 6 for mild steel to more than 20 for hardened spring steel. Values of the limiting ratios for the materials investigated are given in Table III.

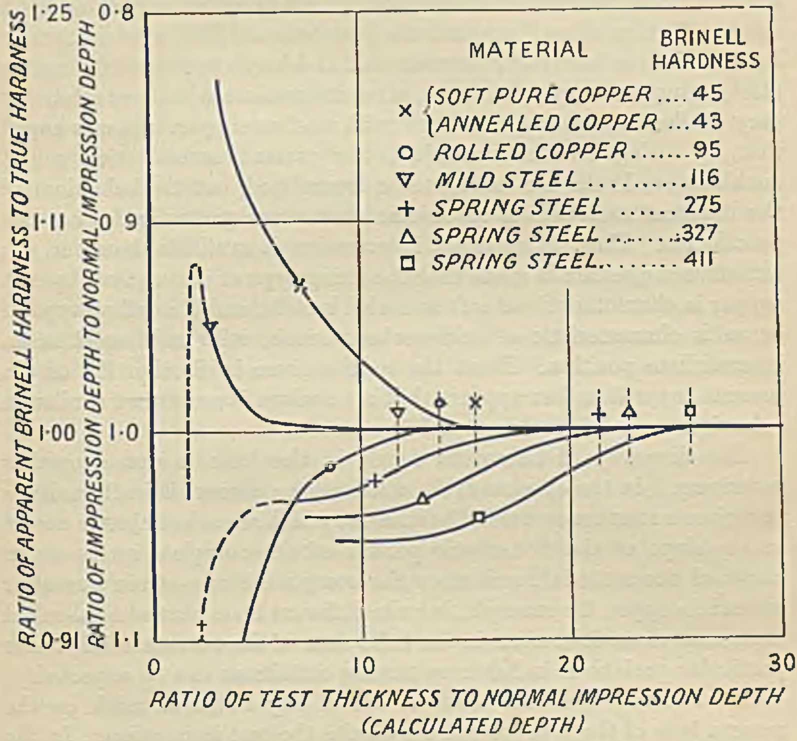


FIG. 7.—Minimum Dimensions of Brinell Test-Pieces. Variation of Impression Diameter with Thickness of Test-Piece. Hardness of Backing, 950. Summary of Results.

TABLE III.—*Limiting Thicknesses for Brinell Hardness Tests.*

Material.	Brinell Hardness Number.	Ratio of Test Thickness to Depth of Impression for Correct Results.	Approximate Error when Using Standard Thickness (ratio = 7), %.
Annealed copper	43	15	7
Soft copper (commercially pure) .	49	16	7
Rolled copper	95	14	4
Mild steel	116	6	nil
Spring steel (as rolled) . . .	275	21	4
Spring steel (hardened and tempered).	327	22	4
" " " " " .	411	25	5

The materials used in the work were purposely selected to be typical, to a certain extent, of various types of behaviour in hardness tests; thus, annealed soft copper usually gives impressions which lie below the surface of the surrounding material, whilst rolled copper shows a marked "ridge effect" around the impression. Mild steel is usually intermediate in behaviour between soft and hard copper, whilst spring steel, owing to its great hardness, gives impressions which are relatively very shallow when compared with mild steel or copper. It was hoped that, by using selected materials, the present investigation might enable general rules for testing to be formulated, but the behaviour of the different materials is so diverse that exact general rules are not practicable. Until more exact information is available, however, the tentative suggestion is made that the rising type of curve given by soft copper is characteristic of soft annealed metals, and the falling type of curve is characteristic of cold-worked metals, with mild steel in an intermediate position. From the results given in Section III of the present paper it rather appears that aluminium is somewhat similar in behaviour to mild steel (see p. 73).

The diversity of behaviour found in the tests is not altogether surprising. In the opinion of the authors, the normal Brinell hardness test gives a rough measure of the stress at which a marked change occurs in the slope of the non-elastic portion of the complete stress–strain curve of the material, and since the complete stress–strain curve for annealed copper, for example, is quite different from that of hard-rolled copper, obvious differences in the behaviour of the two materials under particular variations in hardness testing conditions can be expected.

No mention has been made so far of any bulge or mark on the reverse face of the test-specimen opposite the test impression. In the Standard Specification it is stated that the thickness of the test-specimen shall be such that no bulge or other marking showing the effect of the load shall appear on the side of the piece opposite the impression. A specification clause of this nature can scarcely have any very exact quantitative value, but observations throughout the present tests suggest that when the reverse side of the specimen is polished, the appearance of a mark showing the effect of the load on the reverse face usually indicates that the specimen is too thin for accurate test results to be obtained.

III.—EFFECT OF THICKNESS OF SPECIMEN ON DIAMOND PYRAMID HARDNESS TEST RESULTS.

In the investigation of limiting dimensions of test-specimens for diamond pyramid hardness tests it was unnecessary to consider any variation of dimensions other than thickness, since the test impressions are quite small and in practically all applications of the test adequate width and length of test-specimen is available. In using the diamond pyramid test on metal sheet and strip material, however, consideration of the effect of thickness of test sample is important, and it is this application of the test which has been borne in mind in the present work. Attention has already been given to this matter experimentally by Cook and Larke,* but the results obtained in the present tests do not support the conclusions of these workers.

One advantage of the diamond pyramid test over the Brinell hardness test is that in the former a standard load related to the dimensions of the indenting tool is not required. Accordingly, the effect of thickness on test results can be investigated by carrying out a series of tests at different loads on material of constant thickness; if the material is uniform and there is no thickness effect, all the results should be the same, but when the load is too great for the thickness of material under test, low results are obtained. This method was used by Cook and Larke, and has also been used in the present investigation; the present work includes in addition, however, several test series at constant test loads on specimens either tapering in thickness, or in which successive layers were machined from the backs of the test-specimens between series of tests. The constant load method needs special preparation of test-specimens, but it appears to give more accurate results than the

TABLE IV.—*Diamond Pyramid Tests at Constant Thickness, Details of Materials and Test Conditions.*

Material.	Thickness, inch.	Probable Correct Diamond Pyramid Hardness Number.	Number of Tests Averaged for Each Individual Result.	Limiting Loads Used in Tests, kg.	Detailed Results Shown in Fig. No. :
Soft aluminium . .	0·078	24	4	1–40	8
,, ,, . .	0·035	24	4	2–10	8
Soft copper . . .	0·073	57	8	3–110	8
,, ,, . . .	0·035	60	6	1–20	8
Soft brass . . .	0·039	74	6	1–20	8
Hard copper . .	0·027	81	6	2–120	9
,, ,, . .	0·038	92	6	4–120	9
Mild steel . . .	0·030	132	6	2–60	9
Hard aluminium alloy .	0·042	171	4	4–100	9
,, ,, ,, .	0·034	176	4	2–100	9
Aircraft steel . .	0·010	365	6	2–50	10
,, ,, . .	0·013	380	6	2–60	10
Razor blade . . .	0·006	840	6	1–30	10

---

* Cook and Larke, *J. Inst. Metals*, 1933, 51, 215.

constant thickness method, since tests at small loads are avoided. In considering the tests in detail, it is convenient to deal first with the tests at constant thickness and then with the tests at constant load. All the tests were carried out by the same observer in a Vickers diamond pyramid hardness testing machine, the machine and microscope being carefully calibrated prior to the tests.

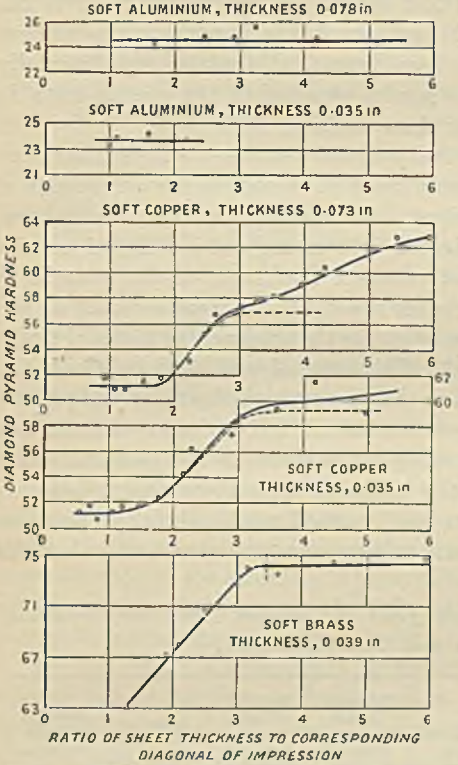


Fig. 8.—Minimum Thickness of Test-Sheets for Diamond Pyramid Hardness Tests. Tests at Constant Sheet Thickness.

(A) *Tests at Constant Thickness.*

The materials used in this work were specially selected for their uniformity as judged by preliminary tests, and were lightly polished on the test faces.

For each specimen several tests were made at each of a number of different loads, the range of loads being selected, as far as possible, so that the results of the tests at low loads were uninfluenced by the thickness of the test material, whilst results at the high loads were obviously influenced by the thickness. The same hard steel anvil (950 diamond pyramid hardness number) was used throughout. Particulars of the materials and tests are given in Table IV.

The results of the tests are shown in detail in Figs. 8–10. In each case the horizontal scale used is the ratio of sheet thickness to diagonal of test impression so that the points towards the left-hand side of the curve were obtained with high loads and those towards the right-hand side with low loads; each point in a diagram is a mean figure obtained in several tests as indicated in Table IV. It will be noted that the majority of the curves consist of a horizontal portion over which the hardness number is approximately constant, and a sloping portion in which the hardness number diminishes with decreasing ratio of sheet thickness to diagonal of test impression; in other words, below a particular test load the diamond pyramid hardness number is independent of the load for a given sheet thickness, but above this particular load the hardness number is low; the low hardness numbers being due to the test-sheet being too thin for correct results to be obtained at the higher loads. In the case of the soft aluminium there is no falling portion to the curve, and apparently for this material satisfactory results are obtained at quite low values of the ratio of sheet thickness to diagonal of impression, although distinct marks showing the effect of the load occur on the reverse side of the test-piece.

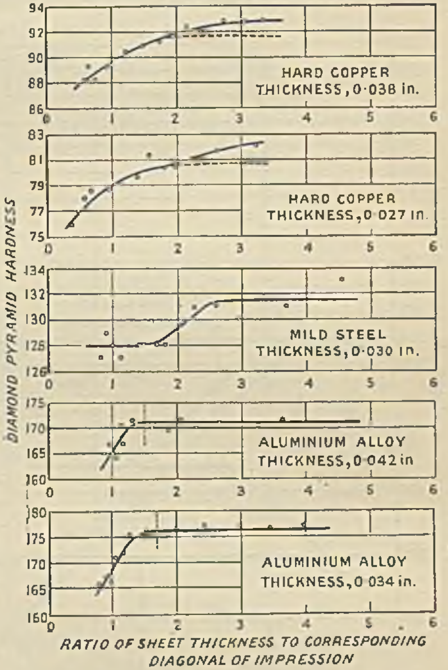


Fig. 9.—Minimum Thickness of Test-Sheets for Diamond Pyramid Hardness Tests. Tests at Constant Sheet Thickness.

The results of the tests on copper cannot be regarded as satisfactory, since there is no definite indication of the real hardness of the material uninfluenced by thickness, *i.e.* there is no definite horizontal portion of the curve at the lower loads (high values of ratio of sheet thickness to diagonal of impression). It is considered that this behaviour was due to the test surface of the metal being slightly harder than the main body of the metal, arising either from the polishing of the surface or in the manufacture of the sheet. The probable diamond pyramid hardness numbers uninfluenced by thickness are shown by the dotted lines in the diagrams, but it is not possible to be positive in regard to these values. It was largely because of the element of doubt in these tests on copper that the more laborious tests at constant load were subsequently undertaken. It is considered, however, that the left-hand flat portion in each of the soft copper curves is a real result and not open to doubt; it will be noted that a similar curve was obtained in the tests on mild steel.

The whole of the results of the tests at constant thickness are summarized in Fig. 11, in which the mean curves of the detailed figures have been re-plotted on a non-dimensional basis. The horizontal scale of Fig. 11 is the same as that previously used, being the ratio of sheet thickness to corresponding diagonal of impression, but the vertical scale is the ratio of apparent to true diamond pyramid hardness number.

Fig. 11 shows that for the materials examined, and excepting mild steel, soft brass, and soft copper, a limiting ratio of test thickness to diagonal of impression of 1½ gives results which are largely independent of the thickness of the test material. This ratio gives an error of about 3 per cent. for mild steel and 10 per cent. for soft brass and soft copper. It should be mentioned that the results of a further series of tests on mild-steel sheet suggested that markedly low values could be obtained at ratios greater than 1½ when the test-sheet was not flat and in good contact with the hard backing plate.

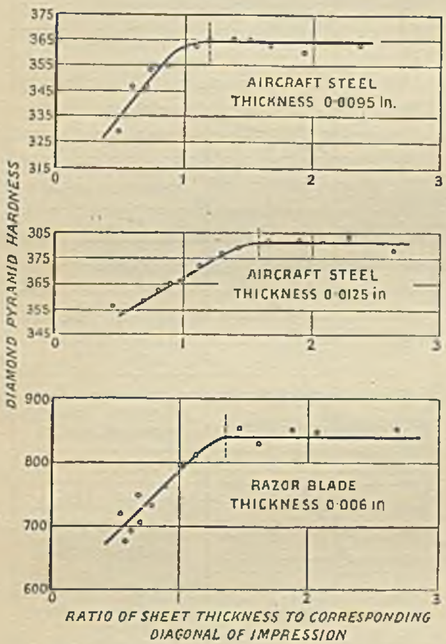


Fig. 10.—Minimum Thickness of Test-Sheets for Diamond Pyramid Hardness Tests. Tests at Constant Sheet Thickness.

The relevant clause in British Standard Specification No. 427, 1931, " British Standard Tables of Diamond Pyramid Hardness Numbers," in regard to thickness of test specimens is : " The thickness of the test specimens should be at least equal to one and a half times the diagonal of the impression." It will be noted that the present results support this rule except for soft copper and soft brass.

(B) *Tests at Constant Load.*

(1) *Copper and Brass.*—The method used in the constant load diamond pyramid tests on copper and brass was as follows. A flat uniform test-sheet was lightly polished on one side, and several diamond pyramid tests were made on this face of the sheet, all the tests being

carried out at the same load. A thin layer of metal was then ground from the *back* of the sheet using very light cuts, another series of exactly

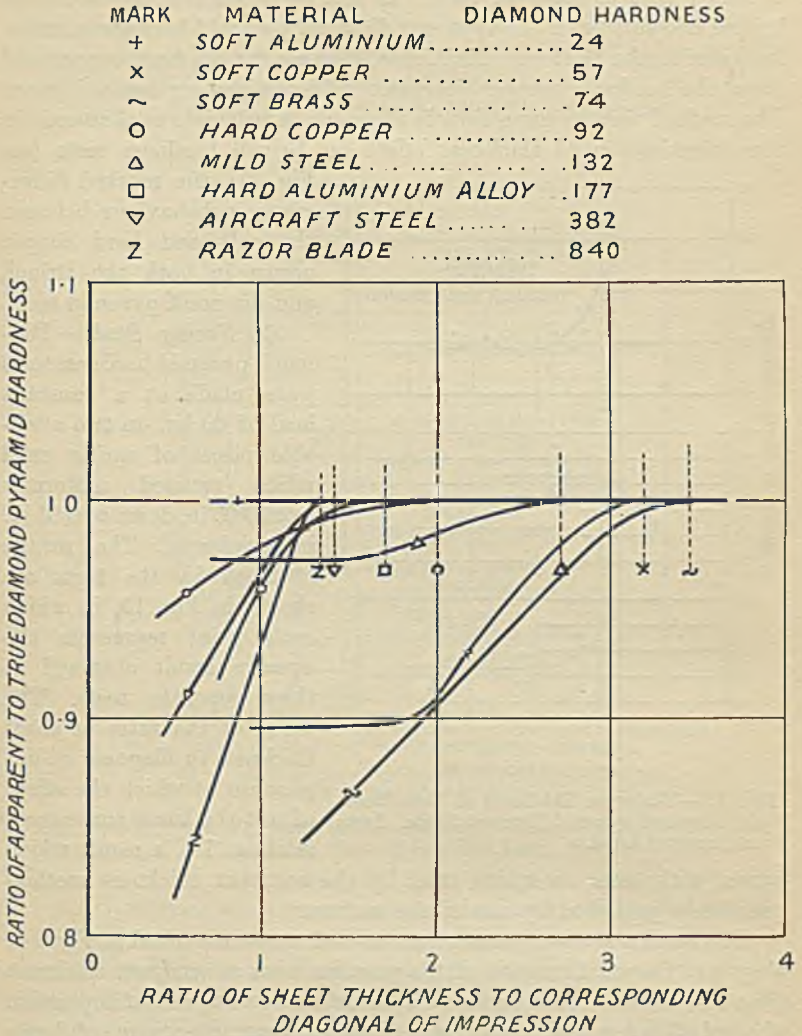


Fig. 11.—Minimum Thickness of Test-Sheets for Diamond Pyramid Hardness Tests. Tests at Constant Sheet Thickness. Summary of Results.

similar diamond pyramid tests being then made on the original test face of the sheet. This procedure was repeated several times, so that a number of results were obtained on the same sheet but at different test thicknesses. The results obtained in the work are shown in Figs. 12 and 13, in which each point represents the average value obtained from at least six tests. It will be noted that for both soft copper and soft brass the apparent diamond pyramid hardness number increases as the thickness diminishes, whereas for the hard copper and brass the hardness number decreases with diminishing test thickness. The method used in these tests is the same in principle as that used in the investigation of thickness effect on Brinell hardness tests (see Fig. 7); the marked differences in behaviour between the soft and hard copper occurs in both the Brinell and diamond pyramid tests.

(2) *Spring Steel.*—Diamond pyramid hardness tests were made at a constant load of 60 kg. on two available pieces of spring steel which tapered uniformly from 0·05 in. down to 0·01 in. in thickness. The results obtained in the tests are shown in Fig. 13, in which each point represents the average result obtained in three separate tests. The value of the ratio of sheet thickness to diagonal of impression at which the effect of test thickness commences is about 1·4, a result which agrees with tests on spring steel by the constant thickness method previously published by one of the authors.*

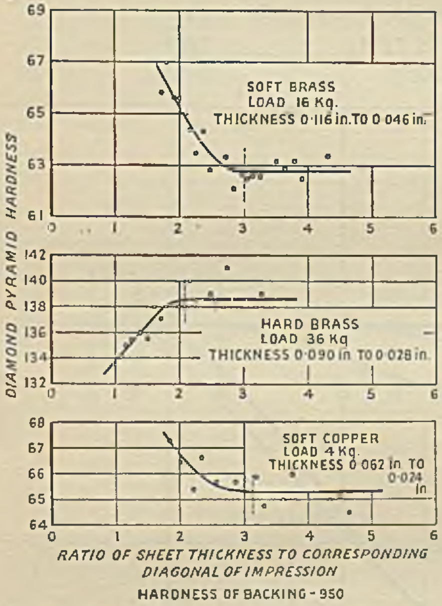


Fig. 12.—Minimum Thickness of Test-Sheets for Diamond Pyramid Hardness Tests. Tests at Constant Load.

The results of the tests at constant load are summarized in Fig. 14; they give fair confirmation of the previous tests at constant thickness (Fig. 11), and show that a ratio of test thickness to diagonal of impression of nearly 3 is required for accurate diamond pyramid tests on soft brass and copper.

Conclusions.

From the results of the investigation it is concluded that:

(1) Provided adequate thickness of test sample is available, the

---

* Letter to the Editor, *Engineering*, 1930, **130**, 324.

width or length of a sample used for a Brinell hardness test should be at least 4½ times the diameter of the test impression when accurate results are required.

(2) No general limiting value of the ratio of thickness of test sample to impression depth can be stated for accurate Brinell hardness tests on all materials; the limiting value of the ratio may vary from about 6 for mild steel to more than 20 for hardened spring steel.

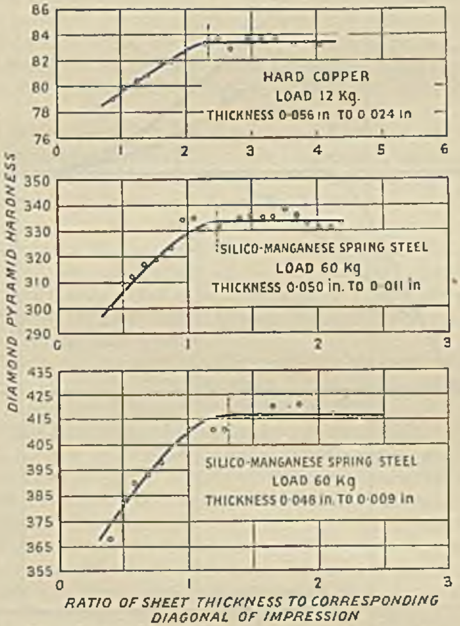


Fig. 13.—Minimum Thickness of Test-Sheets for Diamond Pyramid Hardness Tests. Tests at Constant Load.

(3) In carrying out diamond pyramid hardness tests on thin samples, a limiting value of the ratio of test-sample thickness to impression diagonal of 1½ gives results which are practically independent of test-sample thickness for a number of ferrous and non-ferrous metals. For tests on soft copper and soft brass sheet, however, a higher value of the ratio is necessary if accurate results are required.

(4) With the exception of soft aluminium, the appearance of a bulge or mark on the reverse side of the test sample used for a Brinell or diamond pyramid hardness test, is a rough indication that the test load is too great for the material under test.

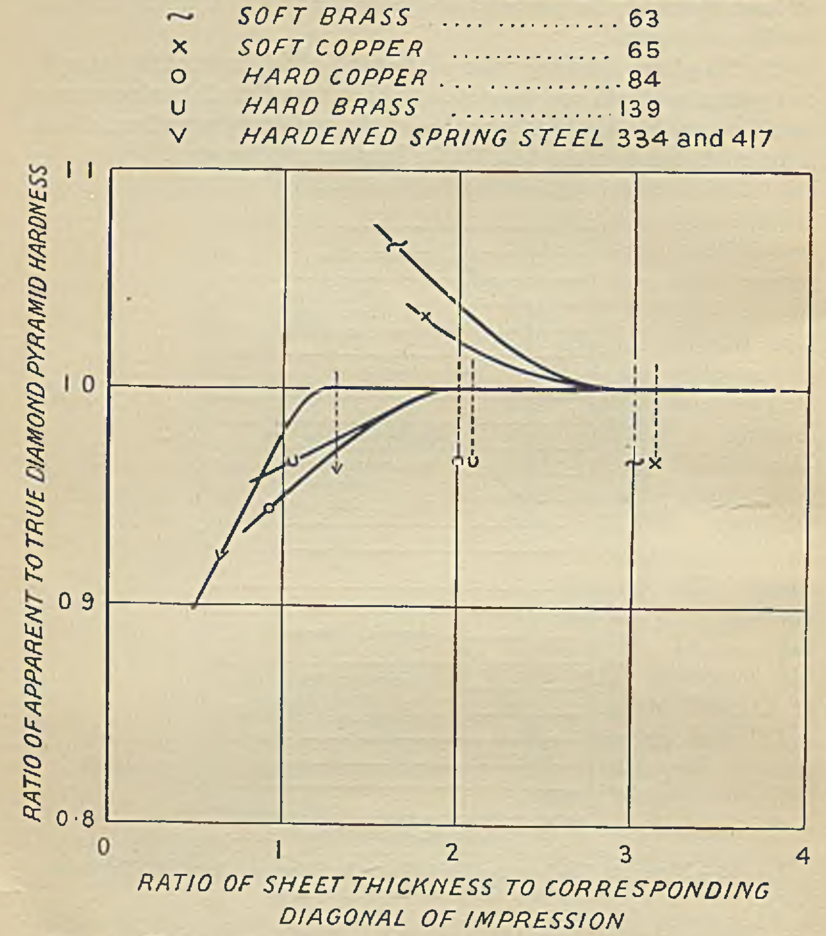


Fig. 14.—Minimum Thickness of Test-Sheets for Diamond Pyramid Hardness Tests. Tests at Constant Load. Summary of Results.

Acknowledgment.

The authors are indebted to the Executive Committee of the National Physical Laboratory for the research facilities provided and for permission to publish the results of the work. They also desire to acknowledge the kindly help and encouragement given by Dr. H. J. Gough, F.R.S., Superintendent, Engineering Department, National Physical Laboratory, during the whole progress of the work.

DISCUSSION.

Dr. Maurice Cook * (Member): Few of the generally recognized testing methods are applicable to thin materials, the testing of which is fraught with many difficulties. While not wishing to compare the relative merits of these tests, it can be said that, for thin metallic materials, hardness tests—and especially indentation hardness tests—are amongst the most satisfactory available; so much is this so that they are being used to a markedly increasing extent. It is singularly unfortunate, therefore, that the authors suggest drastic limitations in the application of these tests, limitations which do not seem to me to be justified by the degree of accuracy which can be reasonably expected in tests of this kind, or warranted by the experimental results put forward. It is hoped, therefore, that those concerned with the testing of thin materials will not feel persuaded to accept as final the conclusions contained in this paper.

As a result of the work which Mr. Larke and I carried out,† we concluded that, so far as copper and copper alloys are concerned, loads of 5 and 10 kg. —which, incidentally, have been standardized—could be used in the diamond pyramid hardness tests on materials down to 0·005 in. in thickness. We did not state or suggest that the results on the very thin material were quite unaffected by the ratio of the thickness of material to diagonal length of impression, but that the magnitude of the variations was negligibly small for ordinary test purposes. Our conclusions were based on a large amount of experimental work and have since been confirmed by further observations in our own and other laboratories.

I propose to limit my remarks to the results obtained with the diamond pyramid tests, since it is with this test that I have been mostly concerned in determining the hardness of thin materials. It will be seen from Fig. 8 of the paper that with aluminium the hardness values obtained are not affected apparently at all by the thickness/diagonal length ratio, and it would have been of interest to have included results of tests at a lower thickness/diagonal length ratio. The experimental results included in the same figure for soft copper are admitted to be unsatisfactory, but they have not been ignored in formulating conclusions. It would appear as if the varying hardness results which have been obtained and are shown on the sloping portions of the curves for soft copper are not true hardness values of the material and that the correct hardness is indicated by the flat portion of the curve, namely, at a diamond pyramid hardness value of about 51, which is more characteristic for the material than the arbitrarily chosen values of 57 in the one case and 59 in the other. Again, in the case of soft brass the value of 74 is abnormally high and suggests that with the light loads the surface condition of the sample influenced the results, the true hardness being probably definitely lower and the suggested limiting thickness/diagonal length ratio too high.

It would be interesting to have the authors' explanation of the diversity of forms shown by the curves in Fig. 9. With the hard copper samples no consistent hardness value of the material has been obtained and the limiting ratio has again been fixed quite arbitrarily; even so, only in one instance do the values given for hard copper and mild steel in Fig. 9 differ from the suggested correct hardness values by more than 5 per cent., a tolerance which Dr. Hankins appeared to suggest as suitable when discussing the paper by Mr. Larke and myself. To attach much significance to percentage differ-

---

* Assistant Research Manager, I.C.I. Metals, Ltd., Witton, Birmingham.

† *J. Inst. Metals*, 1933, **51**, 215–226.

ences of smaller magnitude is splitting hairs, and the ordinates for many of the curves contained in the paper cover a range of hardnesses within this small percentage difference. In the results given for hard copper, 0·027 in. in thickness, in Fig. 9, values within this tolerance of the assumed correct hardness values can be obtained with a thickness/diagonal length ratio as low as 0·48, and in this connection it is of interest to note that the ratio of thickness to diagonal length, as derived from the results given in the paper by Mr. Larke and myself, for hard copper 0·01 in. thick, tested under a load of 10 kg., is 0·6. I do not propose to deal in detail with the other curves in this section of the paper, but it will be seen that results within limits of accuracy of 5 per cent. can be obtained at very much lower ratio values than the authors suggest.

With regard to the results obtained on specimens of varying thickness tested under a constant load, it will be noted that varying thicknesses have been obtained by repeatedly grinding the sample, and with this method of procedure one wonders to what extent the hardness of the metal has been affected. In this series the soft copper is credited with a diamond pyramid hardness of 65, while that of the soft brass is 63. There is also the remarkable anomaly that when the suggested limiting ratio is reached the hardness values increase, whereas in the case of soft copper in Fig. 8 they decrease when the suggested limiting ratio is reached. Similar contradictory results were obtained with the two series of brass samples. These results themselves suggest that the increases shown in the curves for soft brass and soft copper in Fig. 12 are due to the hardening of the thin material by repeated grinding and, if this is so, the suggested limiting ratio of thickness to diagonal length is incorrect.

With reference to percentage error, it may be noted that of the 59 separate values given in Fig. 12 the deviation from the so-called correct values is, except in one isolated case, never greater than 4·4 per cent., the ratio of thickness to diagonal length necessary to obtain values within these limits being much less than the recommended value of 3.

The use of different loads for each material in the tests at constant load is confusing, and it would have been better if standard conditions of loading had been adopted for this series, although with the authors' method the difficulty of obtaining thinner samples to yield the desired ratios can well be appreciated. These several peculiar features shown by many of the results given in the paper make it difficult to accept the conclusions without considerable reservations.

Dr. A. G. C. Gwyer * (Vice-President): I am not altogether in agreement with Dr. Cook with regard to the question of accuracy. Although an accuracy of 5 per cent. may be quite good enough for most purposes, it is most important to know what the limits are, irrespective of the accuracy of the methods. There are members present who are interested in the work of the British Standards Institution, and they would be particularly glad to know at what gauges, and under what conditions, the results depart from the truth, even though the departure may not be great.

With regard to the tests on aluminium, a short time ago we carried out, in collaboration with Dr. Cook, some tests using the Vickers pyramid tester; the results suggested that with a constant load of 5 kg. the so-called "anvil" effect appeared in the case of hard aluminium sheet when the ratio of the thickness to the diagonal of impression fell below 2. In the case of soft sheet, this happened when it fell below 1·6. Brinell tests, on the other hand, showed no evidence of "anvil" effect, even when the ratio fell to 3·5. The

---

* Chief Metallurgist, The British Aluminium Co., Ltd., Warrington.

tests were not sufficiently extensive to enable us to decide whether the effects may not possibly have been fortuitous, and I should be interested to hear, therefore, whether the authors can amplify the data given in the paper with regard to aluminium sheet in both hard and soft tempers; this information would be of great interest because it would now appear that the ratio of 1·5 laid down in the British Standards Institution Specification No. 427, and that of 7 laid down in Specification No. 240 for the Brinell test, can no longer be regarded as universally applicable.

Mr. R. L. SMITH * (Member): From my experience in hardness testing, I believe that the authors' deductions are thoroughly sound in so far as they confirm the minimum width of test-samples as already laid down in the British Standard Specification No. 240 (1926), and they have done well to bring forward the fact that all metals do not require the same minimum thickness of test-piece in relation to depth of impression in order to yield accurate data in hardness testing. I feel, however, that the authors have obtained results which require excessive thickness of specimens, and I suggest that this may be mainly attributable to heterogeneity of the test-pieces.

In the first place, the authors have utilized the very ingenious idea of taking a series of constant-load Brinell impressions on a test-piece of tapered thickness. Unfortunately, however, the test-pieces appear to have been machined with this taper, and such a procedure would, of course, introduce cold-work to the test surface and for some distance below the test surface, not to mention the corresponding conditions which may have resulted from machining the opposite face also. I believe that the hardening effect of machining such soft metals as annealed copper, annealed brass, &c., is not sufficiently appreciated; it undoubtedly has a very deep-rooted effect, and, even when such materials have been machined in an ideal manner, it is necessary to etch a very considerable amount from the surface before the test-piece can be regarded as homogeneous.

In order to illustrate the importance of this point on a basis which could be compared with the authors' investigation, I prepared two test-pieces of soft annealed copper machined from the same bar so as to taper from 0·3 to 0·05 in.; *i.e.*, the same dimensions as shown in the paper. One of these test-pieces was tested at once in the Brinell machine with a 10 mm. ball and a 500 kg. load. The other was re-annealed to remove this cold-work effect of machining, after which it was tested in the same manner. The results obtained with the first-mentioned test-piece are very similar to those shown in Fig. 3 for the soft copper, annealed rolled bar, using the 10 mm. ball. The sample which was re-annealed after machining, however, had a Brinell hardness of 42·9, which remained absolutely steady with decreasing thickness of test-piece right down to a thickness of 0·12 in., after which the hardness developed very rapidly. The ratio of thickness of test-piece to depth of impression in this case becomes little more than 8.

With regard to the peculiar results obtained on silico–manganese spring steel as rolled and after hardening, I have also noticed similar characteristics in special steel plates; the explanation in each case has been traced to chemical heterogeneity. I should like to know whether the authors confirmed the general homogeneity of the steel by microscopic examination, and whether the four sets of curves shown in Fig. 6 are all of material from the same cast. I find it difficult to assume that any steel test-piece requires to be 20 times thicker than the depth of the Brinell impression, unless, of course, the material is not of uniform quality throughout.

Dr. Cook's questions are so similar to those I wished to ask with regard

---

* Consulting Metallurgist, London.

to the diamond pyramid hardness numerals that I need not refer to that matter.

May I say how much I appreciate papers of this kind ? They not only bring forward many points of view with regard to hardness tests, but have the effect of warning us not to specify hardness requirements for sheet metals, &c., without indicating how the tests are to be applied.

Professor D. HANSON,* D.Sc. (Vice-President) : It cannot be denied that an error is introduced in the Brinell test when the thickness of the sample is small in relation to the depth of the impression, but if the Brinell test is to be excluded from use when the readings given are not true readings it will place a very serious limitation on the use of that test. I notice that all these tests were made using an anvil with a Brinell hardness of 950, which greatly exceeds that of the samples used, particularly in the case of the soft materials. I suppose, and I should like the authors' opinion on this, that the limitations of the test are due to the effect of the hard anvil underneath, and I wonder whether the usefulness of this test could be extended in the case of soft material by using an anvil with a hardness approximating that of the sample under test, a brass anvil in the case of brass, an aluminium anvil for aluminium, and so on. Is there any reason to suppose that the results given in testing thin materials would be of greater reliability if the test were modified in this way ? If so, it may be possible to extend the use of Brinell tests to samples of very small thickness without substantial error.

Mr. T. H. TURNER,† M.Sc. (Member) : The authors have dealt with the effect of width and depth of the specimen when a single indentation is made. Many of us make numerous indentations in the surface of a specimen. In recent years I have done this repeatedly, and have developed a routine system. It would be of interest, therefore, if the authors could tell us something of the interference effect of one indentation on the next. They have told us how dangerous it is to run up to the edge of the specimen, and in effect they say that if no bulge is seen at the edge, the test will be accurate.

Practice demands that we shall know the hardness as near the edge as possible in many cases, such, for example, as where there has been notable cold-work or welding or other operations of that kind which will have altered the nature of the material across the section.

As examples have been given of steel, I will quote two : the cross-section of a rail which has been welded on the top and the cross-section of a railway tyre, both of them solid pieces of metal in which mass action and the ordinary segregation effects of the ingot are to be noted. On both of those I have small squares drawn, and a laboratory attendant puts one indentation in each square as a matter of routine, merely writing the hardness figure found for each square; an assistant later colours the diagram so that high spots of hardness stand out, as on a contour map. Systematized in this manner, hardness testing gives a much more intelligible picture of the metal than is obtained with the ordinary large Brinell machine making a few widely spaced indentations.

On reading a paper of this kind I feel that I would rather trust the hardness machine than the metal tested and that when making small indentations with a diamond variations will probably be found in the metal and not in the method of testing.

---

* Professor of Metallurgy, The University, Birmingham.

† Chief Chemist and Metallurgist, London and North-Eastern Railway, Doncaster.

The work-hardening of the specimens has been mentioned, and it is questionable whether the method of preparation may not be sufficient to account for that small 5 per cent. The mere method of casting and rolling may make that difference from place to place; and so, to come back to my first point, I should be interested if the authors could give us some information as to how close we may place the indentations when we want many close together in one surface.

Dr. HANKINS (*in reply*): Although I cannot expect to deal with all the points raised, I will endeavour to reply to those which appear to be the most important, and will deal with the other matters in writing.

Dr. Cook bases his criticism of the paper on a particular diagram, Fig. 8, about which, as is stated in the paper, we ourselves are somewhat doubtful. Because of that doubt the additional tests were made at constant loads, and the results then obtained are much more reliable than can be obtained by the constant thickness method used by Dr. Cook and Mr. Larke in their work and for our results in Fig. 8. It should be realized that in the tests at constant load the successive machining operations were done at the *back* of the sample, and that the test-face was not machined or polished in any way for the different tests. These results show fairly definitely that the two soft materials behave differently from the harder materials.

Dr. Cook's point regarding the accuracy of results has been larely covered by Dr. Gwyer. We do not suggest that it is essential to use the limiting thicknesses put forward in the paper for all routine hardness testing. It depends entirely on the accuracy required in the results; and if the material is known to be lacking in uniformity, for example, it is not essential to impose test conditions which are accurate to a much higher degree than the uniformity of the material. We hope, however, that the results stated in the paper give an indication of the necessary limits when fairly high accuracy is required.

Dr. Gwyer mentioned the question of tests on aluminium, and so confirms a result which at first seemed somewhat surprising. We have no data for Brinell tests on aluminium, but from the diamond pyramid tests we surmise that the limiting thicknesses for some kinds of aluminium may well be less than those required for copper, or perhaps for steel.

In reply to Mr. Smith, it should be understood that we endeavoured to minimize any machining effects as far as we reasonably could. Soft copper appears to be particularly susceptible to the effects of machining, and it must be admitted that the soft copper used for the Brinell tests was not as uniform, perhaps, as we should have desired. The spring steels (Fig. 6) were all from the same cast of uniform high-grade steel.

Professor Hanson's suggestion of using a soft anvil is interesting; as I see it, for the hardness test to be unaffected in such cases, the complete stress and strain distribution under the impression during the test must be the same for the material when in the form of two or more sheets as it is for a thick solid sheet; or, put another way, there must be no relative movement between the contact faces of the layers as a consequence of the test on the top layer. Presumably, the coefficient of friction between the sheets (which is usually less with hard metals than with soft metals) would be of importance. I am rather doubtful whether the method would be of much use with hard metals, but it might be worth investigation for soft metals.

In reply to Mr. Turner, we have no definite information as to the interference effect of impressions close together, but there is little doubt that a higher value would be obtained if a particular test-impression were made very close to previous existing impressions. Our normal procedure at the National Physical Laboratory when making hardness examinations is to space impressions so that the centres are distant from one another by not less than 5 times the impression diameters.

The PRESIDENT: I welcome the renewed interest now being shown in this complex question. In my opinion the last word has not been said and still further work is required.

CORRESPONDENCE.

MR. ALDOUS * (*in further reply to the discussion at the meeting*): I thank those who have taken part in this discussion for their helpful criticism, and in particular for their useful data on practical testing.

In reply to Dr. Gwyer I have particulars of some pyramid tests made at low ratios of test thickness to impression diagonal on the actual samples of aluminium illustrated in Fig. 8, using both the anvil of hardness 950 and an anvil of dead soft aluminium of hardness 24. Tests made at a ratio of 0·3 on the hard anvil gave values of 23·8 and 22·6, respectively, for the upper and lower sheets in Fig. 8, and indicate a slight fall from the straight-line values of 24·5 and 23·6 given in the figure. Tests made at the same ratio on the sheet of thickness 0·078 in. supported on the aluminium anvil gave an apparent hardness of only 21·5, and produced large impressions in the anvil itself. If the value of 21·5 be plotted on Fig. 8, it is clear that a falling curve is obtained for this sheet and that a true limiting ratio might be determined by tests on a soft backing. The actual marks on the back of this sample at the higher test ratios indicate that the limit is above 1·5, but for practical purposes samples can be tested on a hard backing down to a ratio of 0·5. With regard to an aluminium sheet of hardness 50, the same straight line value of hardness has been obtained down to a ratio of 0·6, but further tests below this ratio have not been made. Here again markings under the sheet indicate a limiting ratio above 1·5. I consider that the general form of curve for hardness tests on an anvil harder than the test sheet has a second flat portion, corresponding with that for spring steel of hardness 275 in Fig. 7 and with that for mild steel in Fig. 9, and representing a flow at constant stress as the bulge under the test-piece flows out on to the anvil. Aluminium appears to be a special case in which the material flows so easily that the two flat portions of the curve coincide. In the case of mild steel, illustrated in Fig. 5, definite bulge marks occurred at thicknesses below 0·33 in., but flow at constant stress seems to have continued down to a thickness of 0·2 in.

With regard to Mr. Smith's remarks on his tests on annealed copper, it is possible that his curve corresponds with that for mild steel, and that a limiting ratio is better disclosed when the under-surface of a test-piece is left work-hardened. In the latter case the curve, as obtained by the authors, apparently rises sharply as the flow beneath the impression meets the work-hardened material formed in the machining of the wedge.

Dr. Cook raised the question of tests on brass and copper in which there is a surface hardness greater than the body of the material. In this case the upper flat portion of the general curve becomes a slope as for the copper sheet illustrated in Fig. 8. If this slope be produced below the ratio of three, the sudden drop in the curve is more clearly shown, and, in my opinion, is the point at which material begins to flow at the under surface of the sheet. The

---

* Dr. Hankins has not, owing to serious illness, been able to participate in this reply.

straight-line portion of the curve at a hardness of 51 has been further developed to ratios of 0·5 and 0·3 and appears to correspond with a constant stress less than the true hardness of the sheet. The value at the limiting ratio is not necessarily the true hardness of the sheet if the load is small, the probable hardness of the sheet being less than this value, but greater than 51. Tests made on a ½ in. bar. of annealed copper using a large steel pyramid loaded up to as much as 3 tons produced the same type of curve as for copper 0·078 in. in thickness, namely a slope due to surface hardness from 38·5 to 37·4, a limiting ratio of 3, and a constant stress line at a hardness of 36·3 below a ratio of 2·1. In the case of the soft brass sheet of Fig. 12, the increase in hardness below the limiting ratio appears to have been due to the flowing material under the impression meeting a highly work-hardened surface which was not a surface of separation, and did not allow the same flow as in the case of the hard anvil under the copper sheet of Fig. 8. The upper surface of the brass sheet had been initially polished and carefully protected by a sheet of paper during all grinding operations on the back of the test sheet.

Professor ALBERT PORTEVIN * (Member): The authors have presented a very interesting and useful contribution to a problem which frequently occurs in practice and which we have studied from two aspects, namely, minimum size and minimum thickness of the samples, on two occasions; first during the War for the control of manufactures to ascertain the conditions under which hardness and impact tests could be made on the same specimen, *i.e.*, to find the minimum size of specimen for the normal Brinell test, and recently for the study of the hardness of thin electrolytic deposits to ascertain the minimum thickness at which it is possible to determine the hardness by the various standard methods and apparatus.

It may be of interest to give some indications of the scope of this work and of the results obtained.

1. *Minimum Size of the Test-Pieces for the Normal Brinell Test.*

Crankshafts and forged aeronautical parts were controlled during the War by the ordinary Brinell test (10 mm. ball and 3000 kg. load) and by the Mesnager impact test on specimens with a cross-section of 10 × 10 mm. It was therefore of value to carry out both tests on the same test-piece, and hence of importance to know the maximum error possible as well as the minimum size which would give a correct ball impression.

On heat-treated nickel–chromium steels giving normal impressions of 4 and 3·8 mm. errors on the 10 mm. specimens of + 0·10 and + 0·11 mm. were observed accompanied by a lateral bulging of the specimens by 0·11 and 0·10 mm. respectively. To ascertain the minimum permissible size specimens were prepared from plates 10 mm. thick, of which the two opposite faces were ground and polished to trapezoids 200 mm. long with a large base of 30 mm. and a small base of 6 mm. Brinell impressions were then made at intervals of 15 mm. along the axis of symmetry of the trapezoid and two diameters were measured to 0·01 mm., one along the axis and one perpendicular thereto. These tests were carried out on 3 steels of different hardness. To ensure the greatest possible homogeneity of hardness it was necessary to heat-treat the specimens in such a way that the transformations were produced in an identical manner throughout the mass of metal, and therefore annealed sheets or self-hardening steels softened to the greatest extent were used. These conditions were obtained with: (*a*) a mild steel (annealed) giving an impression of 5·2 mm.; (*b*) a hard steel (annealed) giving an im-

---

* Professeur Suppléant à l'École Centrale des Arts et Manufactures, Paris.

pression of 4·3 mm.; (*c*) a nickel–chromium steel (self-hardening) giving an impression of 3·5 mm.

The results of these tests are shown in Figs. A, B, and C, the points marked with a dot representing the diameter of the impression along the axis of symmetry and those with a cross representing the diameter at right angles to this. The curves show that: for (*a*) when the width of the test-piece is less than 15 mm. visible deformations occur on the lateral faces and the diameter of the impression exceeds the limit of 5·22 ± 0·05 mm. conformed to by impressions in the wider region; for (*b*) this critical width is 12 mm. and the standard impression is 4·32 ± 0·05 mm.; and (*c*) for the normal impression is 3·46 ± 0·05 mm. and the critical width 10 mm.

Fig. A.

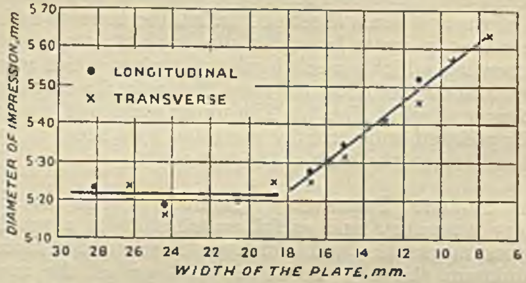


Fig. B.

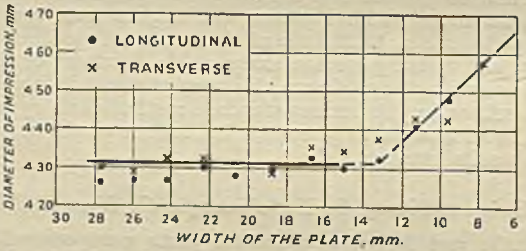
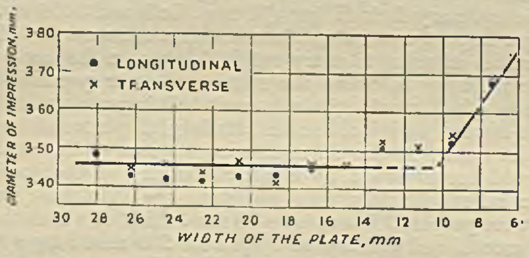


Fig. C.



Figs. A–C.—Influence of Width of Test-Piece on the Diameter of the Ball Impression; 10 mm. ball; 3000 kg. load.

At the time this work was done we came to the conclusion that for a works' test in which the impression is measured to ± 0·05 mm. the width of the specimen should be 3·5 times the diameter of the impression, but for very accurate work it should be at least 4 times this diameter. This conclusion is in agreement with that since adopted in British Standard Specifications and that arrived at by Messrs. Hankins and Aldous.

2. *Minimum Thickness for Thin Electrolytic Deposits.*

The hardness of thin electrolytic deposits is very little known since their thickness of only a few tenths or hundredths of a millimetre makes it impossible to ignore the factors which affect this hardness; it is certain, however, that the hardness of electrolytic deposits of nickel and chromium is greater than that of the metals in their usual forms. The hardness must be determined on the deposit *in situ* since it cannot be removed from the supporting metal without damage.

In collaboration with M. Cymboliste, I have studied the hardness of these deposits, and in this work it was necessary to know beforehand the minimum thickness necessary to obtain a satisfactory value. This problem gave rise to special experimental difficulties since we were ignorant of whether the hardness of the deposit remained constant as its thickness increased and whether the hardness of the basis metal was modified by the electrolysis. The thickness of the deposit cannot be reduced by grinding the back, as Messrs. Hankins and Aldous did with their specimens, since the metal support would first have to be removed and the thinness of the deposit renders this impossible. Finally, electrodeposits are never of regular thickness (throwing-power of the plating baths).

Under these conditions the programme of experiments now being carried out is as follows: using $\frac{1}{16}$-in. balls of steel and tungsten carbide and diamond pyramids and cones (some determinations will also be made with the pendulum hardness tester) we are finding the minimum thickness by the following methods: (1) observations of the progressive penetration of the pyramids or cones under increasing load; (2) examination of the variation of apparent hardness as a function of the thickness using thicker and thicker deposits produced under constant conditions of electrolysis on various basis metals of different hardness. By graphical methods the thickness at which the hardness becomes independent of the basis metal can then readily be found, and, since the apparent hardness is really the resultant of the hardness of the deposit and that of the basis metal, the actual hardness can be obtained for thinner deposits the nearer it is to the hardness of the basis metal. This is shown by the curves in Fig. D which represent the variation in the apparent hardness as a function of the thickness of the deposit for the 3 metals, copper, nickel, and chromium plated on to a mild steel (Brinell hardness 150) and on to a hard steel (Brinell hardness 350). The hardness of the copper deposit is lower than that of either steel, that of the nickel deposit is intermediate between those of the 2 steels, and that of the chromium deposit is much greater than that of either steel. Under these conditions it appears that the actual hardness of nickel deposits is obtained when they are 0·2 mm. thick, whereas that of chromium deposits is obtained only at a thickness of 0·6–0·7 mm. Thus the hardness of electrolytic deposits can be obtained for thinner layers the softer is the deposit and the nearer its hardness to that of the basis metal. This can be readily understood: the impression produces around itself a deformed zone which should not reach the lower face of the deposit if the dimensions of the impression are not to be affected, or with an equal impression the extent of this zone increases with the plasticity of the metal, *i.e.*, inversely with the hardness, but on the other hand it tends to increase with the mean pressure applied to the metal, *i.e.*, with the hardness, which is the same expression as this mean pressure. It can thus be deduced that the relation:

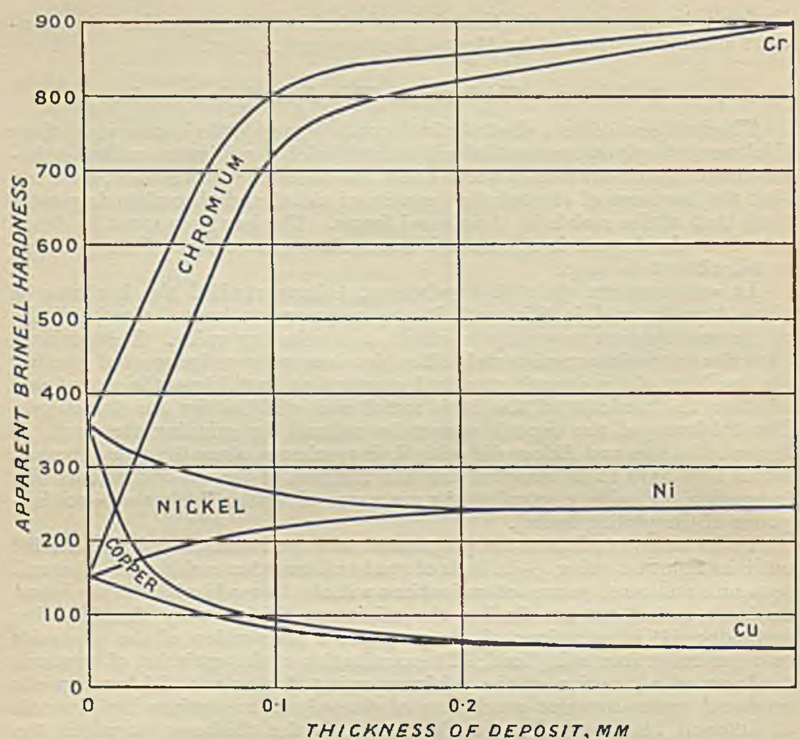


FIG. D.

$$\frac{e}{h} = \frac{\text{minimum thickness}}{\text{depth of impression}}$$

should increase with the hardness Δ.

From the results of Messrs. Hankins and Aldous for mild steels the following expression is approximately correct for the Brinell test: $\frac{e}{h} = \frac{\Delta}{8}\left(1 - \frac{1}{800}\right)$. Moore's rule (Congrès des Méthodes d'Essais de Copenhague en 1908) according to which $\frac{e}{h} > 7$ is insufficient.

The AUTHORS (*in reply*): We thank Professor Portevin for confirmation of the tests on the width of bars for Brinell tests and for the interesting results on deposited materials.

TRANSVERSE TESTS ON SAND-CAST ALUMINIUM ALLOY BARS.*

By C. E. PHILLIPS,† A.C.G.I., D.I.C., and J. D. GROGAN,‡ B.A., MEMBER.

SYNOPSIS.

This investigation was carried out to determine the value of the transverse test in the measurement of the ductility of alloys of low elongation. From the results obtained the transverse test does not seem to yield any information concerning ductility which is not obtained equally readily from the tensile test when a high degree of accuracy of measurement is available; in fact the tensile test appears to be preferable to the bend test.

INTRODUCTION.

MANY of the aluminium alloys at present employed in industry possess, particularly in the sand-cast state, so little ductility that measurements of elongation made on broken tensile test-pieces are of but small value. It has been suggested recently that a bend test such as is already employed in the testing of cast iron might prove to be of greater value. The investigation described in this paper was carried out to examine this point.

RANGE OF INVESTIGATION.

The beam test-bar employed was 8 in. long × 1 in. in diameter, cast in sand in accordance with the British Standards Institution specification for sand-cast test-bars and tested by single-point loading. This bar is the longest light alloy sand-cast bar for which detailed information on casting conditions is available. A range of alloys was employed varying in elongation from a very low value to 12 per cent. Bars were tested unmachined and also machined to a uniform diameter of $\frac{7}{8}$ in. Full tensile tests were also made on machined test-pieces of 0·25 in.^{2} in effective cross-sectional area.

---

* Manuscript received January 2, 1934. Presented at the Annual General Meeting, London, March 8, 1934.

† Engineering Department, National Physical Laboratory, Teddington.

‡ Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

ALLOYS EMPLOYED.

Alloys were selected to provide a series covering a range of ductility. The alloys were made from commercial aluminium containing slightly more than 0·2 per cent. iron and slightly less than 0·2 per cent. silicon. All the casts were analyzed, and in every case composition agreed satisfactorily with that intended. The metal was melted in Salamander crucibles in a gas-fired furnace and was treated with carbon tetrachloride and raw nitrogen to remove dissolved gases. The metal was poured (generally at 680° C.) in green-sand moulds, surface dried, 8·5 in. long × 1 in. in diameter, provided with a feeding head.

The density of each bar was determined after removal of the feeding head, but before machining. Satisfactory agreement among different bars of the same composition was obtained. Where necessary the material was heat-treated to give the required ductility. Table I gives the alloys employed, in order of increasing ductility as measured by elongation in tension, and the heat-treatment used to develop the ductility. The heat-treated material was allowed to age at room temperature prior to testing.

TABLE I.

Batch Mark.	Composition.	Heat-Treatment.
A	" Y " alloy	6 hrs. at 520° C. Quenched in boiling water; reheated for ½ hr. at 250° C.
B	,,	6 hrs. at 520° C. Quenched in boiling water.
C	Copper 4%, Silicon, 3%	6 hrs. at 520° C. Quenched in cold water: reheated for 48 hrs. at 150° C.
D	,,	6 hrs. at 520° C. Quenched in cold water.
E	Copper 4%	As cast.
F	,,	6 hrs. at 520° C. Quenched in cold water.
G	,,	48 hrs. at 520° C. Quenched in cold water.

METHODS OF TEST.

Tensile Tests.

Each bar employed for tensile test was machined to give a test-piece of 0·25 in.² effective cross-sectional area and 2·25 in. parallel length, the test-length being finished by polishing with grade " 00 " emery cloth. The tests were carried out in a 10-ton single-lever testing machine, a Martens-type mirror extensometer being used to measure extension on a gauge-length of 2 in. If the test-piece extended beyond the range of the extensometer, scratch marks were made with a 2-in. gauge, and afterwards measured by means of a microscope. Load–extension observations were made up to fracture in each test, and at regular increments of load the permanent elongation of the specimen was determined by removal of the load.

The load–extension and load–permanent elongation curves were plotted for each specimen, and from them an estimate was obtained of the permanent elongation at fracture. From the plotted observations the modulus of elasticity, the 0·1 per cent. proof stress, and the ratio of permanent elongation at fracture to the total extension at fracture, were determined. The elongation of each test-piece was also determined in the usual manner after fracture, and the diameter at fracture was measured.

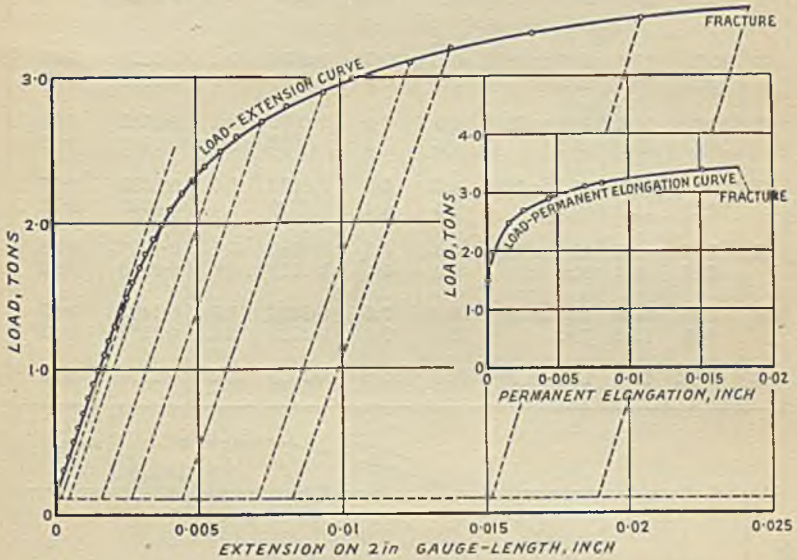


Fig. 1.—Tensile Test on Material D. Diameter of Specimen 0·564 in.

The tensile tests were made in duplicate on each material, except material G, and the results are given in Table II. Representative load–extension and load–permanent elongation curves are given in Fig. 1.

Bend Tests.

Transverse bend tests were made in duplicate on each material, except material G, in the form of bars unmachined, and bars machined to $\frac{7}{8}$ in. in diameter, the surface being finished by polishing with grade "00" emery cloth. The tests were carried out in a 5-ton multiple-lever, gear-driven testing machine at a constant rate of deflection of 0·013 in. per minute. Each specimen was centrally loaded on a 6-in. span; the supports had a radius of 0·75 in. and the load was applied

Table II.—*Results of Tensile Tests.*

Material.	0·1% Proof Stress, Tons/in.^{2}.	Ultimate Stress, Tons/in.^{2}.	Modulus of Elasticity, Lb./in.^{2}.	Approximate Reduction of Area at Fracture, Per Cent.	Elongation on 2-In. Gauge Length (from Specimen after Fracture), Per Cent.	From Load–Extension Curve.			Ratio: Permanent Elongation at Fracture/Total Extension at Fracture.
						Permanent Elongation at Fracture, Inch.	Permanent Elongation at Fracture, Per Cent.	Total Extension at Fracture, Inch.	
A	...	16·3	10·6 × 10^6	VS	VS	0·0003	0·02	0·0072	0·04
	...	15·8	10·2	VS	VS	0·0003	0·02	0·0082	0·03
B	15·7	17·4	10·5 × 10^6	about 0·1	0·5	0·0056	0·3	0·0128	0·43
	15·3	16·7	10·5	0·2	0·5	0·0051	0·3	0·0111	0·37
C	14·3	16·2	10·1 × 10^6	0·5	0·6	0·0072	0·4	0·0142	0·50
	13·8	16·0	10·1	0·5	0·5	0·0082	0·4	0·0149	0·52
D	10·3	13·9	10·3 × 10^6	1·5	1·3	0·0190	1·0	0·0239	0·77
	10·2	14·3	10·2	1·5	1·4	0·0190	1·0	0·0263	0·72
E	7·67	8·1	10·4 × 10^6	6·5	5·5	0·1010	5·1	0·1060	0·95
	7·95	8·5	10·5	6·0	5·0	0·0912	4·6	0·0950	0·96
F	6·23	13·9	10·3 × 10^6	10·0	7·5	0·1332	6·7	0·1402	0·95
	6·20	15·2	10·2	12·0	9·8	0·1910	9·6	0·1979	0·97
G	6·02	16·0	10·3 × 10^6	13·0	12·0	0·2325	11·6	0·2374	0·98

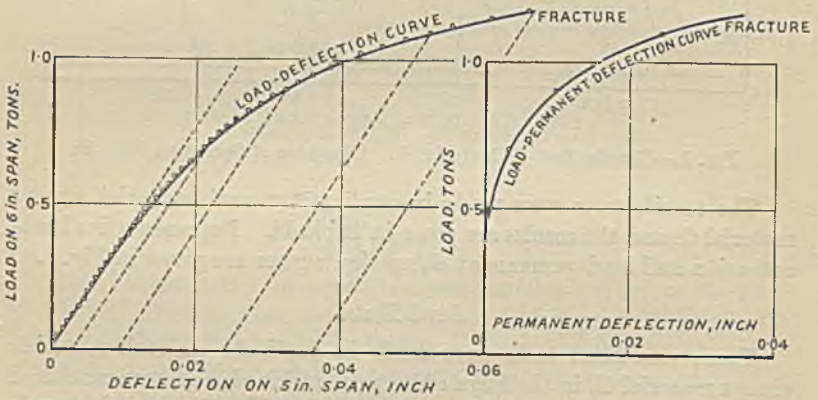


Fig. 2.—Bend Test on Material D (Machined). Central Load on 6-in. Span. Diameter of Specimen, 0·875 in.

through a 1·5-in. diameter steel rod. Deflection measurements were made on a central span of 5 in. by means of the instrument described below. In each test load–deflection observations were made up to fracture; at intervals of loading the permanent deflection was determined by removing the load.

The load–total deflection and load–permanent deflection curves were plotted, and from these an estimate was made of the permanent deflection of each specimen at fracture. The value of the modulus of elasticity was obtained from the plotted observations.

The results of the bend tests are given in Table III, and representative load–total deflection and load–permanent deflection curves of machined and unmachined specimens are given in Figs. 2 and 3, respectively.

TABLE III.—*Results of Bend Tests.*

Material.	Condition of Surface of Specimen.	Diameter of Specimen, Inch.	Maximum Load on 6-in. Span, Tons.	Modulus of Rupture, Tons/in.^{2}.	Modulus of Elasticity, Lb/in.^{2}.	From Load-Deflection Curve.		Ratio: Permanent Deflection at Fracture/Total Deflection at Fracture.
						Permanent Deflection at Fracture, Inch.	Total Deflection at Fracture, Inch.	
A	Machined	0·874	1·11	25·5	10·5 × 10^6	$0\cdot001_1$	0·029	0·04
	,,	0·875	1·10	25·2	10·4	$0\cdot001_3$	0·028	0·05
	As cast	1·062	1·87	23·9	10·6	$0\cdot001_1$	0·022	0·05
	,,	1·067	1·60	20·1	10·5	$0\cdot000_6$	0·019	0·03
B	Machined	0·875	1·235	28·2	10·6 × 10^6	$0\cdot007_8$	0·038	0·21
	,,	0·874	1·295	29·6	10·5	$0\cdot009_8$	0·040	0·25
	As cast	1·066	2·10	26·5	10·3	$0\cdot004_5$	0·029	0·15
	,,	1·064	2·02	25·6	10·3	0·005	0·030	0·17
C	Machined	0·875	1·39	31·7	10·5 × 10^6	0·021	0·059	0·36
	,,	0·874	1·24	28·4	10·2	0·014	0·047	0·31
	As cast	1·066	2·25	28·4	10·3	0·010	0·036	0·28
	,,	1·070	2·10	26·2	10·3	$0\cdot007_6$	0·033	0·24
D	Machined	0·874	1·16	26·7	10·3 × 10^6	0·041	0·080	0·52
	,,	0·875	1·175	26·8	10·3	0·038	0·066	0·57
	As cast	1·070	2·17	27·0	10·3	0·036	0·061	0·59
	,,	1·074	2·00	24·7	10·1	0·019	0·042	0·45
E	Machined	0·875	0·765	17·4	10·3 × 10^6	0·208	0·228	0·91
	,,	0·875	0·835	19·0	10·3	0·246	0·265	0·93
	As cast	1·058	1·22	15·8	10·3	0·132	0·149	0·89
	,,	1·060	1·33	17·1	10·4	0·175	0·191	0·92
F	Machined	0·876	1·50	34·1	10·3 × 10^6	0·550	0·575	0·96
	,,	0·876	1·60	36·3	10·3	0·640	0·675	0·95
	As cast	1·062	2·37	30·2	10·3	0·233	0·260	0·90
	,,	1·062	2·41	30·8	10·3	0·307	0·333	0·92
G	Machined	0·875	1·51	34·5	10·3 × 10^6	0·470	0·508	0·92
	As cast	1·063	2·49	31·6	10·6	0·314	0·341	0·92
	,,	1·062	3·02	38·5	10·1	0·512	0·542	0·95

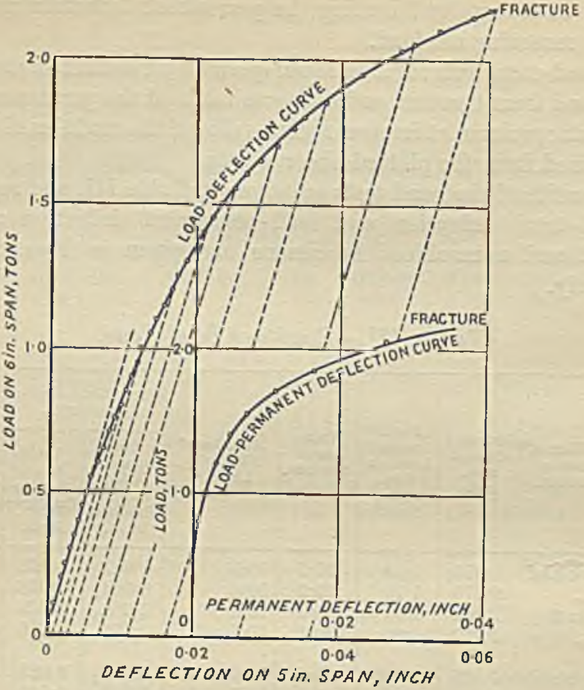


Fig. 3.—Bend Test on Material D (Unmachined). Central Load on 6-in. Span. Diameter of Specimen, 1·070 in.

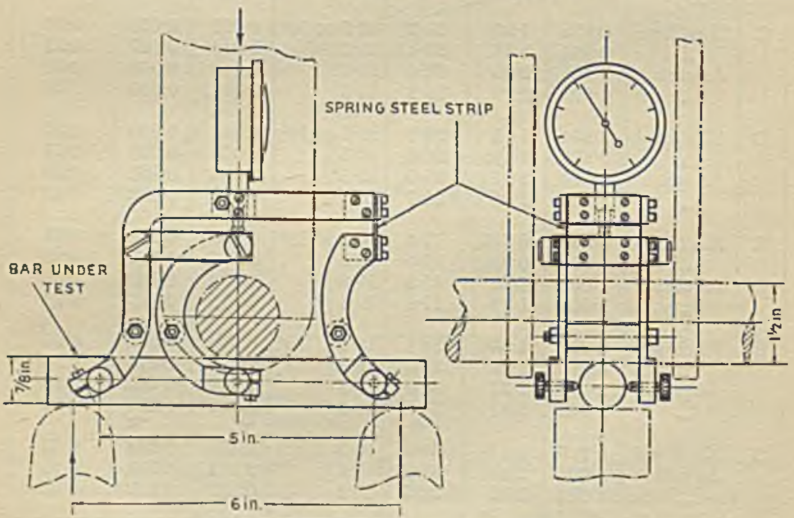


Fig. 4.—Deflectometer for Bend Tests.

In the case of the more ductile materials, errors were introduced into the load observations by the rounded supports of the testing apparatus shown in Fig. 4. At a deflection of 0·5 in, the loading span had decreased to about 5·5 in.; this undoubtedly gives large errors in the determinations of the maximum load and modulus of rupture of materials F and G, and probably accounts for the low values obtained for the ratio of permanent deflection to total deflection at fracture in the materials of high ductility.

A summary of the results of the tests is given in Table IV, and the

TABLE IV.—*Summary of Results.*

Material.	True Elongation on 2-in. Gauge Length in Tensile Tests (from Curve), Per Cent.	Tensile Tests (2-in. Gauge Length).			Bend Tests (6 in. Span).		
		Permanent Elongation at Fracture, Inch.	Total Extension at Fracture, Inch.	Ratio : Permanent Elongation at Fracture/ Total Extension at Fracture.	Permanent Deflection at Fracture. Inch.	Total Deflection at Fracture. Inch.	Ratio : Permanent Deflection at Fracture/ Total Deflection at Fracture.
A	0·02	0·0003	0·0072	0·04	0·001$_1$	0·029	0·04
	0·02	0·0003	0·0082	0·03	0·001$_3$	0·028	0·05
					0·001$_1$	0·022	0·05
					0·000$_6$	0·019	0·03
B	0·3	0·0056	0·0128	0·43	0·007$_8$	0·038	0·21
	0·3	0·0051	0·0111	0·37	0·009$_8$	0·040	0·25
					0·004$_5$	0·029	0·15
					0·005	0·030	0·17
C	0·4	0·0072	0·0142	0·50	0·021	0·059	0·36
	0·4	0·0082	0·0149	0·52	0·014	0·047	0·31
					0·010	0·036	0·28
					0·007$_8$	0·033	0·24
D	1·0	0·0190	0·0239	0·77	0·041	0·080	0·52
	1·0	0·0190	0·0263	0·72	0·038	0·066	0·57
					0·036	0·061	0·59
					0·019	0·042	0·45
E	5·1	0·1010	0·1060	0·95	0·208	0·228	0·91
	4·6	0·0912	0·0950	0·96	0·246	0·265	0·93
					0·132	0·149	0·89
					0·175	0·191	0·92
F	6·7	0·133	0·140	0·95	0·550	0·575	0·96
	9·6	0·191	0·198	0·97	0·640	0·675	0·95
					0·233	0·260	0·90
					0·307	0·333	0·92
G	11·6	0·233	0·237	0·98	0·470	0·508	0·92
					...	...	...
					0·314	0·341	0·92
					0·512	0·542	0·95

ratio of permanent deformation to total deformation at fracture is plotted against the elongation in tension for each method of test in Fig. 5.

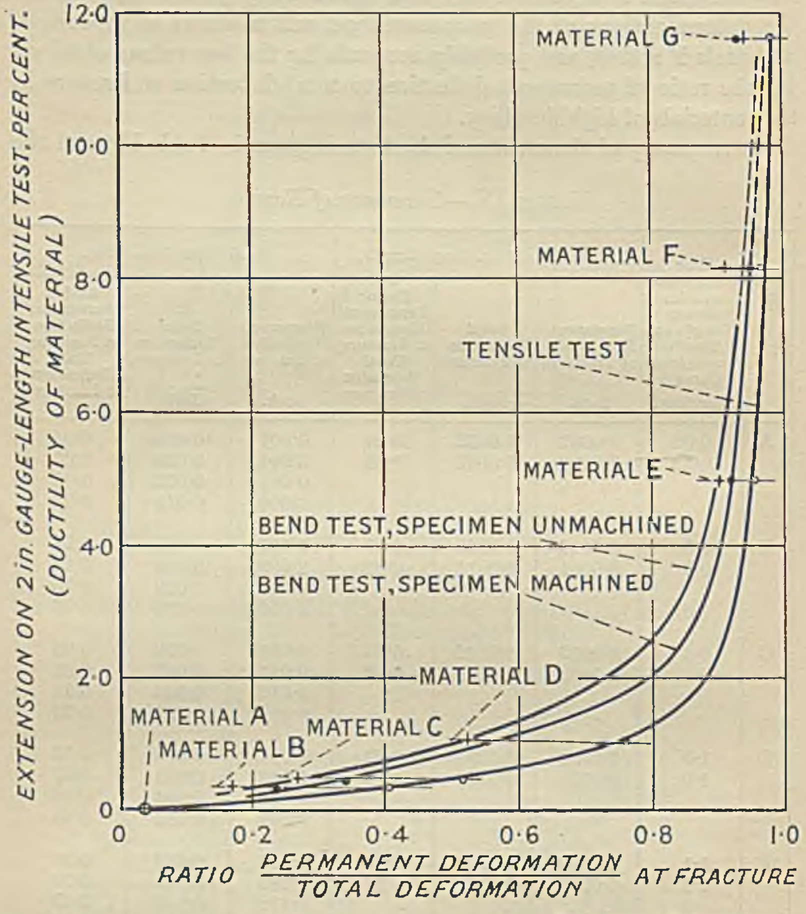


FIG. 5.—Curves Showing the Variation of the Ratio $\frac{\text{Permanent Deformation}}{\text{Total Deformation}}$ at Fracture with the Ductility of the Material as Measured in a Tensile Test.

DEFLECTOMETER USED IN THE BEND TESTS.

The instrument used for determining the deflections of the specimens used in the transverse bend tests is shown diagrammatically in Fig. 4. It was designed at the Royal Aircraft Establishment, South Farnborough, and was constructed in the Engineering Department of the National Physical Laboratory.

The deflectometer incorporates an Ames dial indicator, calibrated in thousandths of an inch, and is arranged so that the specimen under test recedes from the indicator, thus obviating damage to the latter on fracture of the specimen. In use the instrument is lightly fixed to the specimen by three pairs of pointed screws; the deflection of the centre of a 5-in. span is recorded on the dial directly, without a multiplying device. Errors in the readings due to the deformation of the specimen at the points of loading and support are eliminated by mounting the deflectometer on the neutral plane of the specimen. The shape of the deflectometer is such that it can be used for central loading tests on a 6-in. span, and for four-point loading tests on a greater span, deflection measurements being made in each case on a 5-in. span. Over the range of deflections obtained in the tests made the errors due to the method of measurement were negligible.

DISCUSSION OF RESULTS.

Tensile Tests.

Table II gives the mechanical properties determined by the tensile tests. The ratio of permanent elongation to total extension at fracture is plotted against percentage elongation in Fig. 5. The ratio is zero for completely non-ductile material and rises to unity in completely ductile material. The plotted curve consists of two nearly straight lines joined by a short portion of high curvature which corresponds with a permanent elongation of about 2–3 per cent. The values of elongation measured on the broken test-pieces are all definitely higher than those obtained from the load–extension curves.

Bend Tests.

Table III gives the mechanical properties determined by the bend tests on machined and unmachined bars. The ratio of permanent deflection to total deflection at fracture is plotted against percentage elongation from the tensile test in Fig. 5. The curves are of the same form as that obtained from the tensile tests. Very satisfactory agreement was obtained on tests made in duplicate on unmachined bars.

Comparison of the Two Methods.

In this investigation the permanent deformation measured on the tensile test-piece was, in general, approximately one-half of that measured on the bend test-piece. In the tensile tests measurements were made on a 2-in. gauge length; the bend tests involved measurements on a 5-in. span, the loading span being 6 in. There was thus little difference in the order of measurement between the two tests. With either method of test it is possible to compute, with a fair degree of accuracy, the plastic deformation from observations of breaking stress and total deformation immediately prior to fracture, if it is assumed that the ratio of the load to elastic strain is unaltered by the plastic deformation of the material. From the results obtained this assumption appears to be justified in the case of material of very low ductility.

The test-pieces of the dimensions employed in the investigation show the ratio of permanent deformation at fracture to the total deformation at fracture to be higher in the case of the tensile test than in the bend test, and for this reason the tensile test is superior to the bend test for the measurement of ductility. It is not possible to state, from the results obtained, that this ratio is independent of the dimensions of the test-pieces.

SUMMARY.

(1) So far as this investigation extends, the bend test applied to sand-cast aluminium alloy bars has yielded no information concerning ductility which is not obtained from the tensile test.

(2) On the test-pieces employed in this investigation the ratio of plastic deformation to total deformation of a test-piece loaded to the breaking point is higher in the tensile test than in the bend test, particularly when the plastic deformation is small. Consequently the tensile test is preferable to the bend test for the measurement of ductility.

(3) Bend tests on machined and unmachined bars have given very satisfactory agreement.

(4) Measurements of elongation on broken tensile test-pieces have given values higher than those obtained from complete load–extension curves.

ACKNOWLEDGMENTS.

The work described above has been financed by the Department of Scientific and Industrial Research, and carried out at the National Physical Laboratory under the general supervision of the Aeronautical Research Committee; the authors' thanks are due to these bodies for permission to publish this paper; also to Mr. H. Sutton, M.Sc., of the Royal Aircraft Establishment, Farnborough, for assistance in drawing up the programme of work, to that Establishment for the design of the deflectometer employed in the bend tests, to Dr. H. Gough, M.B.E., F.R.S., Superintendent of the Engineering Department, National Physical Laboratory, and to Mr. R. G. Batson, A.K.C., M.Inst.C.E., M.I.Mech.E., who collaborated in drawing up the programme of work and was associated with the earlier stages of the experimental work.

DISCUSSION.

Dr. A. G. C. Gwyer * (Vice-President): This investigation demonstrates, in the most authoritative way possible, that the transverse test as applied to sand-cast aluminium alloys—and quite a wide range have been studied—offers no advantage over the tensile test. This is of importance because, until comparatively recently, the British Standards Institution specified tensile tests for cast aluminium alloys on chill-cast bars, and then, for reasons which were, I think, sound, it decided to abandon the chill-cast test-bars in favour of sand-cast bars. A difficulty arose with regard to elongation, because in the case of the sand-cast bars the values for this property were usually too small to be suitable for incorporation in specifications, and for this reason the suggestion was made that possible deflection tests of the type studied by the authors might be of value. It is therefore all the more unfortunate that this work should have proved so conclusively that the transverse test is of no real value from any point of view.

Mr. H. Sutton,† M.Sc. (Member): Like the authors, I had hoped that the bend test might have proved of considerable value in dealing with these alloys which do not show very large elongation. I think that most of those who have some experience in dealing with numerous tensile tests of the acceptance type realize that there is considerable variation in elongation values, and that is perhaps easily explainable by the curious way in which just a small block of crystals will sometimes rise up during the final failure and prevent the fractured surfaces from being brought together afterwards to form a close fit. This can, however, be catered for by a judicious selection of an appropriate elongation figure in the usual tensile test when drawing up the specification.

On the whole, as the deflections in the beam test on short bars in the rather brittle or harder alloys are so small, I feel that the authors' conclusions are fully justified by their results.

Mr. G. Meikle,‡ B.Sc.: I am afraid that my remarks will be somewhat contrary to those made by Dr. Gwyer. Dr. Gwyer indicated that he does not think that the transverse test is going to be any good whatever from a specification point of view, and that happens to be the particular point in which I am interested. The authors have shown conclusively that the ductility as shown by the bend test is comparable with the ductility shown by the tensile test. My point is that when elongation values of the order of 3 or 4 per cent. are obtained they are almost useless, because of the difficulty which Mr. Sutton mentioned of putting the test-pieces together again. From a specification point of view I consider that the transverse bend test is going to be easier to carry out and more reliable.

I should like the authors' opinion on that point, because I believe that this work was originally suggested at a meeting of the Committee of the British Standards Institution which is dealing with light alloys for aircraft. I think that it would be advisable to go over to the bend test for ductility rather than the tensile test, as is done at present with cast iron. The trans-

---

* Chief Metallurgist, The British Aluminium Co., Ltd., Warrington.

† Senior Scientific Officer and Head of the Metallurgical Department, Royal Aircraft Establishment, South Farnborough.

‡ Farnborough.

verse test is always used to measure the ductility of cast iron, and in that connection I should like to ask the authors if they think that the results would be very different if they used a longer test-bar—a 12-in. bar, as used for cast iron. In the paper they state that they cannot tell whether an alteration in dimensions would mean a big alteration in the results, but I should be glad of an opinion on the 12-in. test-bar.

The PRESIDENT: This paper deals with a method of testing. Had the particular medium used happened to be cast iron, the paper would have gone to another Institute, although essentially it is a method of testing which is considered. That directs my attention to two points. We have no body in this country which is specifically concerned with methods of testing, and a paper dealing with methods of testing of metallic materials may be presented to any one of half a dozen different institutions, very much according to chance. That points, it would seem, not only to some overlapping but also to a gap in the edifice of institutions which deal with scientific and technical subjects.

The other point is this. I think that the paper has proved fairly conclusively that this test is not very suitable for aluminium alloys, but why does it persist for cast iron? The transverse bend test is used very largely for cast iron, and I see little sign of it being abandoned. Presumably it has advantages over the tensile test in the case of cast iron, and, if that is so, are they confined to cast iron?

Mr. GROGAN (*in reply*): The only criticism came from the President and from Mr. Meikle, and is, I think, quite simply answered. The question is one of scale. In these tests two types of deformation are involved, plastic deformation, with which we are concerned, and elastic deformation, which intrudes itself during the test. In the case of the tensile test, the elastic deformation is not greatly affected by scale; it is proportional to the gauge-length and independent of cross-section. In the transverse bend test, however, the position is very different. We worked it out, and, whilst I cannot remember the actual figures, I think that in the case of the transverse test-piece the elastic deformation at fracture is in proportion to a power of the length, and also depends on the cross-sectional area; that is to say, using the bend test it is possible, by altering the dimensions, to alter very appreciably the total deflection that is measured at fracture. That does not mean, however, that the plastic deformation is also altered; it means that to obtain the plastic deformation from the total deformation a very much bigger correction may have to be applied in the bend test than in the tensile test. Our view is that it is better to increase the accuracy of measurement than to increase the dimensions of the measurement made and at the same time increase the percentage correction that has to be applied to the observed deformation in order to obtain the plastic deformation.

Mr. Meikle raised the question of putting together a fractured test-piece to obtain the plastic deformation. Our impression is that if the material is very brittle, little loosened pieces appear in the fracture, which prevent the two parts being put together again accurately, but we think that, as the ductility increases, that tendency to break up decreases, and that measurements of elongation from a broken test-piece are probably absolutely more accurate when the elongation is say 5 or 6 per cent. than when it is 0·5 to 1 per cent. When the ductility exceeds 5 or 6 per cent. as measured in the tensile test, the transverse test becomes valueless for the measurement of ductility owing to the deformation of the test-piece at the points of loading; it is essential, in such cases, to employ the tensile test.

The PRESIDENT: Would you express an opinion as to whether the transverse bend test is likely to be any use for any purpose—whether there is a case for retaining it for any material?

Mr. GROGAN: It would be an *obiter dictum* of my own, but before I answer that I should like to say that so far as aluminium alloys are concerned it is difficult to cast a bar more than 8 in. in length. It could not, I think, be moulded in the simple way that the ordinary tensile test-bar is moulded, and that introduces an item of expense in preparing the test-piece. Where equipment is not available for the making of tests of high accuracy the bend test *may*—I will not say more than may—have value as compared with the tensile test; but, if the measurements can be sufficiently accurately made, I believe that the tensile test is undoubtedly superior.

CORRESPONDENCE.

MR. J. G. PEARCE,* M.Sc. (Member): This paper is of considerable interest in view of the wide use of the transverse test for cast iron. Alloys A, B, and C have elongations comparable with those of grey irons of varying qualities; D is comparable with austenitic cast iron and E, F, and G with malleable cast iron. The test is important for grey iron, in which strength varies to some extent with section, because it is virtually the only test that can be made on any section cast. The span used for cast iron is usually greater, being 15 diameters on a standard 1·2 in. diameter bar, and hence deflection and set readings are more readily made. The results obtained confirm experience with cast iron in that modulus of rupture and deflection are higher on a skin-machined bar than on a bar tested as cast. The ratio of modulus of rupture to tensile strength covers a range similar to that found in grey iron, and the ratio appears to change in a similar way; for average cast irons it varies from 1·8 to 2. The purely elastic deflection at fracture varies very little from alloy to alloy, the permanent set, as in cast iron, increasing markedly with ductility.

The conclusion arrived at by the authors is of great importance, because I believe that for works and routine laboratory use, the transverse test lends itself better to reasonably accurate observation than the tensile test, and partly for this reason I have recently suggested † that the tangent method of determining the elastic modulus should be replaced by a calculation based on elastic deflection at fracture. The curve of elastic deflection is usually a straight line directly proportional to the load, and this method overcomes all difficulties arising from the use of stress–strain relationships which curve towards the strain axis. In cast alloys of low ductility, fracture would thus be regarded in the same way as the limit of proportionality in the ductile alloys. The same treatment could be applied to the tensile test. In the case of cast iron the tangent method has been found inaccurate because, even at low deflections, there is some permanent set present, in spite of the straightness of the load–deflection curve. I should be glad if the authors would state what method was adopted to ascertain the permanent deflection at fracture, as this cannot, of course, be obtained by direct observation, which requires removal of the load on an unbroken bar; and also whether the resilience or energy of rupture of the bars places them in order of toughness or resistance to impact.

---

* Director, British Cast-Iron Research Association, Birmingham.

† "The Elasticity, Deflection, and Resilience of Cast Iron," *J. Iron, Steel Inst.*, 1934, 129 (Advance copy).

The AUTHORS (*in further reply to the discussion at the meeting*): In the case of materials of low ductility the elastic elongation at fracture of a tensile test-piece is proportional to Wl, where W is the breaking load and l the gauge-length: in the beam test the elastic deflection is proportional to Wl^2/d. Correction must be applied to the observed deformation at fracture in order to obtain the plastic deformation. This correction involves the strength of the material as well as the dimensions of the test-piece, as W is directly proportional to the ultimate stress, or modulus of rupture of the material.

The AUTHORS (*in reply*): We thank Mr. Pearce for his interesting communication on the value of the transverse test in the determination of properties other than that of ductility. The method employed by us to determine the permanent deformation at fracture was that of loading the bar and measuring the permanent deformation when the load was removed. In this way a load–permanent deformation curve was obtained which was then extrapolated to give the permanent deformation at fracture. .

We have made no measurements of the resistance to impact of the materials employed in the beam test.

NOTE ON THE INFLUENCE OF GASES IN AN 8 PER CENT. COPPER–ALUMINIUM ALLOY ON NORMAL AND INVERSE SEGREGATION.*

By I. G. SLATER†, M.Sc., Ph.D., Member.

Synopsis.

The relationship between gas content and segregation in an 8 per cent. copper–aluminium alloy has been determined. In a sand-cast ingot, 3-in. in diameter by 3 in., segregation was found to be inverse with very gassy melts but to be normal with degassed melts.

The influence of dissolved gases in alloy melts, which on solidification are liable to show inverse segregation, has been noted by several observers. The significance of dissolved gases and the manner in which they may affect the mechanism of solidification so that inverse segregation phenomena result, has been a matter of keen controversy and of much speculation. Whilst the rival merits of the many theories advanced have received great attention in academic discussions, practically no experimental work has been directed towards a correlation of the exact gas content of the melt and the nature of the segregation in the resulting ingots.

Studies made during recent years, of gas equilibria in solid and liquid metals, have established the necessary technique for the production of melts having controlled gas contents. The relationship, if such exists, between gas content and segregation can therefore be determined. A few experiments which have been made in this connection with an 8 per cent. copper–aluminium alloy, are reported on in this paper.

Experimental.

A series of " 3L11 " aluminium–copper alloy ingots having various gas contents was examined. The ingots were all from the same batch of metal with the exception of No. 1, which had a lower copper content.

---

* Manuscript received December 27, 1933. Presented at the Annual General Meeting, London, March 7, 1934.

† The University, Birmingham.

The gas content of the ingots ranged from a maximum, obtained by thoroughly saturating the melt by poling with damp green wood, to a minimum produced by various de-gassing processes. In each case, the melt was cast at 700° C. into a skin-dried green-sand mould, 3 in. in diameter by 3 in., with an open top and without subsequent feeding. During solidification, large quantities of gas were given off from No. 1 ingot; No. 2 ingot showed little gas, and the others remained quite tranquil. Sections of the five ingots were examined for the visual appearance of pinholes, and these are recorded in Table I.

Two sets of drillings for analysis were taken from each block; from the outer circumference and from the "heat centre," that is, the area at which the last portions solidify. For purpose of comparison of gas content, the total volume of cavities in each ingot has been calculated from density determinations:

$$\text{volume of cavities, per cent.} = \left[1 - \frac{\rho'}{\rho''}\right] 100$$

where ρ' = observed density of ingot, and
ρ'' = optimum density of gas-free metal.

The value of ρ'' for ingots Nos. 2–5 was taken as 2·870, the optimum density recorded on a portion of a sand-cast block, 3 in. by 3 in. in diameter, which had been poured from a completely de-gassed melt. For ingot No. 1, ρ'' was 2·850. The total volume of cavities is not exactly equal to the volume of gas retained in the ingot, since the pressure of the gas in the pinholes is unknown and there is a slight effect due to liquid shrinkage (ingot No. 5 showed traces of shrinkage at the "heat centre"); the comparison requires a relative modification in each instance.

The observations made are summarized in Table I.

TABLE I.

Ingot No.	Density.	Visual Appearance of Polished Half-Section.	Volume of Cavities, Per Cent.	Copper, Per Cent.	
				Edge.	Centre.
1	2·758	Very many pinholes	3·3	7·6	7·0
2	2·802	Moderate number of pinholes	2·4	8·3	8·1
3	2·819	Few pinholes	1·8	8·0	8·1
4	2·842	Sound	1·0	8·0	8·5
5	2·861	No pinholes, trace shrinkage at the centre	0·3	7·7	8·7

The relationship between the percentage volume of cavities and the type and amount of segregation is shown graphically in Fig. 1.

In the experimental conditions employed, it is seen that the amount of gas present in the melt determines the character of segregation in the ingot. The influence of this factor in determining the segregation with other rates of solidification, remains to be established.

A further ingot (No. 6) having the same gas content as No. 2 was prepared by allowing the melt to solidify under a pressure of nitrogen at 200 lb./in.^{2}. This ingot had a density of 2·866 and was quite free from pinholes. Determinations of the copper content were made as before, and the results were identical with those obtained for the No. 2 ingot. An external gaseous pressure therefore does not influence the extent of segregation to which the alloy is normally liable.

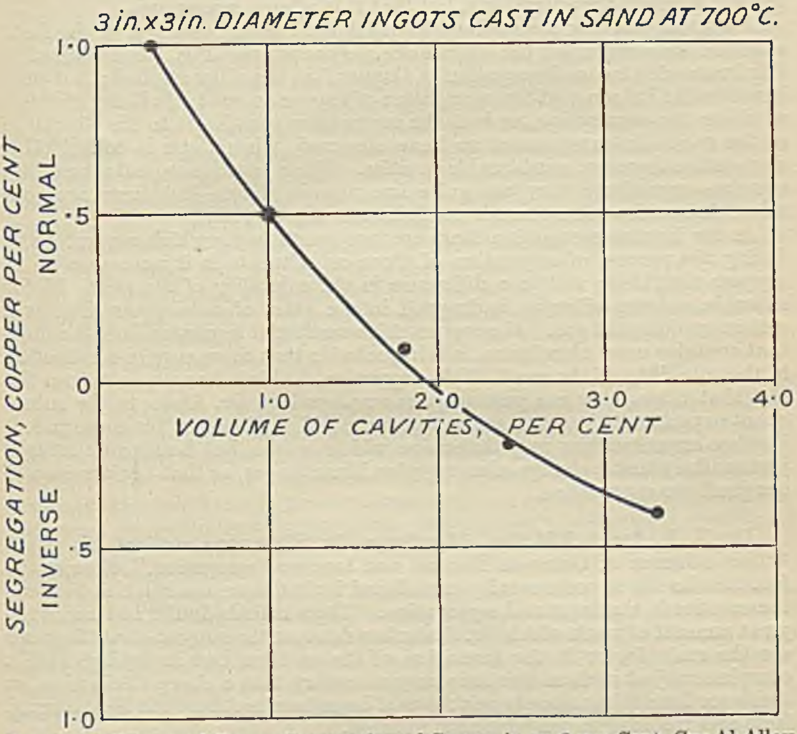


Fig. 1.—Influence of Gas on Segregation of Copper in an 8 per Cent. Cu : Al Alloy.

A discussion of the results now obtained in the light of the several theories of inverse segregation current will not be attempted. It is intended that they should indicate a very profitable line of investigation.

DISCUSSION.

Professor T. Turner,* M.Sc., A.R.S.M. (Past-President): I am pleased that Dr. Slater has investigated the subject of gases and inverse segregation. There is an idea in many places that the gas present in the alloy during solidification is the cause of inverse segregation. It is important in the first place to collect facts, but I used always to impress on my students the need for distinguishing between facts and explanations. I used to tell them that there is a reason for everything, but that it is often a wrong one.

I wonder whether the explanation that Mr. Slater has given of the facts which he has observed is the correct one. For instance, Fig. 1 is described as "Influence of Gas on Segregation of Copper," in the alloy studied; but may it not be the influence of the segregation of copper on gas? Is it the gas that produces the segregation, or is it the segregation that leads to the liberation of the gas? In many cases we have observed, when there is considerable segregation there are considerable cavities. These cavities are not necessarily circular—sometimes they are quite irregular in shape—but there are considerable cavities when there is much inverse segregation.

In the inverse segregation there are two constituents which separate, and during the process of separation of those constituents is it unreasonable to suppose that there will be a difference in the solubility of the gas? If, for example, a lump of sugar is dropped into a glass of soda-water there is a violent evolution of gas. If a copper-rich constituent separates from the mass that contains more aluminium, is it improbable that there may be a reduction in the solubility of the gas? This suggestion, I think, has support from the fact that when more gas pressure was employed by Dr. Slater in the subsequent experiment the increased gas pressure did not increase the segregation. Further experimenters may determine which is true, but I suggest that it is just as likely that a change of segregation liberates gas, as that the presence of gas produces segregation.

Dr. N. P. Allen,† M.Met. (Member): Dr. Slater has entitled his paper "The Influence of Gases on Normal and Inverse Segregation," whereas the fact that he has experimentally established is that there is a relation between the cavities in the ingot and segregation. There is little doubt, in view of the great amount of work which Dr. Slater has done on the subject, that the gases are the main factor in the formation of the cavities, but in dealing with a complex subject such as this it is very necessary that a sharp distinction, as Professor Turner has already said, should be maintained between the observed facts and the conclusions which are inferred.

In a paper which I presented at the last meeting of this Institute,‡ the relation I observed was also a relation between the cavities in the ingot and the segregation, and, although the conditions in my experiment were very different (I used a heavily chilled sample, and Dr. Slater's samples were sand-cast), the two investigations separately do establish that there is some connection between inverse segregation and the production of cavities in an ingot. It is reasonable to suppose, therefore, that, whatever the explanation of these phenomena may be, no explanation can be considered perfectly satisfactory which, while it explains the inverse segregation, does not at the same time explain the production of the cavities.

---

* Leatherhead.

† Lecturer in Metallurgy, The University, Birmingham.

‡ *J. Inst. Metals*, 1933, 52, 193.

Dr. R. Genders,* M.B.E. (Member): There is no doubt whatever that considerable interest will be taken in this small conundrum, without answer, which Dr. Slater has submitted, and this convenient scheme might well be followed in future papers where difficulty arises and where a good discussion is required.

In this paper there are, apparently, two contradictory pieces of evidence. First of all we are provided with a curve which shows very convincingly a relation between the type of segregation and the amount of cavities in the ingot, and this is followed by a further single experimental result which from some points of view does not agree with the previous evidence. Personally, I feel strongly disposed to be cautious regarding that single result. Single experiments are frequently misleading, and, if one looks further into this particular example, it is seen that the alloy showed little segregation of any kind, a matter of 2 per cent., as against a possible experimental error of 1 per cent., and therefore it would not be expected that any large effect would be shown by the application of external gas pressure. Ignoring, then, to some extent that single result, and returning to the sand-cast ingots, it should be borne in mind that the density values given, expressing the porosity of the sand-cast ingots, mean only that a certain amount of the gas evolved was entrapped in the ingot and was available to set up pressure in the interior. The figures have no relation whatever to the actual gas content of the liquid metal, and I think that that should be made clear.

On the whole, the evidence put forward is support for what might be termed the "gas theory" of inverse segregation, and it is of interest in this connection that recent work by Höhne on tin-bronze ingots,† has given evidence of a similar character.

Dr. C. H. Desch,‡ F.R.S. (Vice-President): Some of the criticisms offered in regard to this paper do not seem to me to be entirely deserved. I think that the paper is important, in that it does afford evidence for the view, which I believe to be the only acceptable one at present, that inverse segregation is usually the result of the pressure from gas. In an ingot entirely free from gas, what we call normal segregation, resulting from differential freezing, is the one which occurs; inverse segregation must be produced by an internal pressure of some kind.

In this paper the method for determining the volume of cavities is not a method for determining the amount of gas there; it is a secondary effect of the gas, but it does show in a rough way a relation between the amount of gas present and the extent of the segregation, direct or inverse. It is not, however, the quantity of gas as a whole that matters, but the way in which that gas is liberated at the moment of freezing. That is not elaborated here, but, as it is the determining factor, I see nothing contradictory in the result obtained when the external pressure of nitrogen was put on. I do not see why that should have altered the extent of the segregation, because it is the method by which the gas is liberated, and not its total quantity, which counts. Although this paper is short and contains a limited number of facts, it has an important bearing on the problem of segregation in general.

Professor D. Hanson,§ D.Sc. (Vice-President): I should like to support what Dr. Desch has said. The first two speakers rather suggested that

---

* Research Department, Woolwich.

† *Giesserei*, 1933, **20**, 523.

‡ Superintendent, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

§ Professor of Metallurgy, The University, Birmingham.

this paper is a much bigger thing than it is; actually it is a very small note directing attention to differences in the type of segregation which occur in certain aluminium alloys of varying gas content, and, although the gas content is represented in the diagram as volume of cavities, we know from an intensive study of these alloys for other purposes that in point of fact the different samples had variations in gas content in the direction indicated. The paper does very little more than that, but it contains evidence which does seem to me to make it quite certain that the evolution of gases has an important influence on inverse segregation. I have welcomed that theory since Dr. Genders put it forward. There are certain cases in which it seems to me self-evident, because the evolution of gases sometimes forces a eutectic from the normal position to the surface of the ingot and makes it exude outside the normal chill-cast surface. Moreover, the same sort of thing happens in these 8 per cent. copper alloys, because the gas cavities, when the amount of gas is not too large, are situated in those places where the eutectic will normally be. If the gas replaces the eutectic and forces it right out of the alloy or to portions nearer to the surface, it must set up inverse segregation, because where there is gas instead of the eutectic there is bound to be a deficiency in copper content. I welcome this paper, therefore, as emphasizing what seemed fairly obvious before, that there are many cases in which gas is a very important factor in controlling inverse segregation. Whether it will be found to be the only factor I do not know; it seems to me that normal shrinkage effects might have the same influence. As Dr. Slater points out, here is a line of investigation which has not yet been pursued, and it seems to be one which will lead to very fruitful results.

Mr. G. L. Bailey,* M.Sc. (Member): I should like to support Professor Hanson in agreeing with the author that gas is undoubtedly a factor in inverse segregation, but I would suggest that other factors are probably also involved. I have in mind an experiment by Mr. S. L. Archbutt to which he referred in discussing Dr. Genders' paper on this subject some years ago. Mr. Archbutt showed that serious inverse segregation has occurred in a 3-in. diameter chill-cast bar of aluminium alloy containing 12 per cent. copper, when only a ¼ in. of metal had solidified and the liquid interior had then been poured out. In chill-casting there are probably several factors tending to produce inverse segregation, but there seems no doubt that dissolved gases constitute one of these.

The exudation of the tin-rich eutectic at a late stage of solidification of a "gassy" gun-metal is not an uncommon occurrence, and is generally recognized to be due to dissolved gases. I would, however, point out that a tin-bronze which does not contain sufficient dissolved gas to cause actual exudation of the tin-rich eutectic, and which does not show inverse segregation in a sand-cast bar, will frequently show inverse segregation if chill-cast. The problem is much more complicated than would be the case if dissolved gases alone were concerned, but at the same time it is important to recognize that dissolved gases can exert this effect.

Dr. S. W. Smith,† C.B.E., A.R.S.M. (Member): The point which has arisen is that the inclusion of gases, or at any rate the occurrence of porosity, may undoubtedly occur in metal which also shows inverse segregation. Two of Professor Turner's students, Reader and Iokibe, had shown that many years ago but they did not attempt to associate the two phenomena. As has been

---

* Development Officer, British Non-Ferrous Metals Research Association, London.

† The Royal Mint, London.

said by a previous speaker, it is not quite correct to take porosity, as determined by solid densities, as a measure of the relative amounts of gases which were present in the metal in the liquid state, that state being, of course, the only state in which gas could possibly affect inverse segregation.

The author has not, I think, chosen the happiest method for investigating this phenomenon. Casting in a sand mould is notoriously a procedure which does not give such marked inverse segregation as casting in chill moulds, and when this problem is investigated I think that that procedure should be adopted which accentuates the effects as much as possible. On the question of sampling these small flat slabs, the author speaks of taking drillings from the circumference and from what he calls the "heat centre." I am not sure how he has satisfied himself entirely about the "heat centre," in arriving at the figures in Table I. Dr. Genders has referred to the observation which the author gives later on, when he says: "a further ingot (No. 6) having the same gas content as No. 2 was prepared by allowing the melt to solidify under a pressure of nitrogen at 200 lb./in.^{2}." The author goes on to say that that ingot had a density of 2·866 (which is higher than any of those appearing in Table I), and that it was quite free from pinholes, so presumably there was a minimum gas effect in that case; and yet he says: "determinations of the copper content were made as before, and the results were identical with those obtained for the No. 2 ingot," that is to say of one which showed inverse segregation. Dr. Genders was inclined to disregard that single observation, but I should prefer to regard it as a true representation of what takes place; that is to say, that alloys of this composition, whether they are gas-free or not, will be found to show inverse segregation.

Mr. S. L. ARCHBUTT* (Member): I should like to refer to the experiment, mentioned by Mr. Bailey, that I made with Dr. Rosenhain some years ago. That experiment was made in 1927 after we received preprints of Dr. Genders' paper on the mechanism of inverse segregation in alloys. We poured an ingot, 3 in. in diameter, of 12 per cent. copper–aluminium alloy, and when the wall thickness was ¼ to ½ in. thick we poured out the liquid and on analyzing the hollow shell found inverse segregation in the wall. This appeared serious evidence against Dr. Genders' theory of pressure, due to gases liberated from the liquid near the end of solidification of castings, as the cause of inverse segregation. This further evidence that we now have from Dr. Slater seems to make it positive that gases in solution can produce inverse segregation. It is interesting that it should be found in the thin shell of the ingot as well as in the ingot completely solidified.

The PRESIDENT: This little paper on a big subject has given rise to a most interesting discussion. There is a strong case for the "gas" explanation, but it seems difficult to account for *all* cases of inverse segregation as due to the effect of gas, because in a number of binary alloys containing only a small percentage of one of the two metals, inverse segregation seems to be the usual and ordinary type of segregation, whatever the conditions in which the alloy is cast.

The AUTHOR (*in reply*): Regarding the questions raised as to the significance of gas in the general phenomena of inverse segregation, and more particularly the point as to whether gas is the only cause of inverse segregation, I should like to refer to some work by Masing who summarizes the present position regarding the published literature on this subject, and classifies the possible

---

* Principal Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, The National Physical Laboratory, Teddington.

causes of inverse segregation into four sections: (1) the pressure in the melt due to gas set free on solidification, or gas pressure; (2) volume contraction by solidification of the outside layers; (3) contraction pressure of the first partly solidified and hence porous outer region of the ingot; (4) expansion of the solidifying outer zone by the mutual pushing apart of the growing primary crystals, or pressure of crystallization.

CORRESPONDENCE.

The Author (*in further reply to the discussion at the meeting*): Reference to the text immediately preceding Table I should make it clear that the relationships between the percentage volume of cavities observed, the gas content of the melt, and the amount of gas retained in the cavities in ingots, is no more than roughly qualitative. Dr. Desch has more clearly defined how the actual mechanism of gas evolution on solidification is a determining factor in influencing the extent and type of segregation. Modifications in this mechanism produced by variations of the total amount of gas evolved are to be expected. In this connection, the secondary effect—the formation of cavities—is of great importance, and I am in complete agreement with Dr. Allen that no satisfactory explanation of segregation phenomena, due to these influences can be satisfactory without adequate explanation of the production of the cavities.

With regard to the ingot solidified under an extraneous gaseous pressure of 200 lb./in.^{2}, a possible reason for the results observed is suggested in the following:—

Experiments show that by heating the ingot to a temperature above the solidus, but below the liquidus, cavities appear at areas coincident with the eutectic at grain boundaries. With the pressure-cast ingot, the normal growth of gas-filled cavities is inhibited, so that there is a decreased tendency towards inverse segregation. At the same time, due to the extraneous pressure, the values of factors 2 and 3 given in my verbal reply will be increased, resulting in an increased tendency towards inverse segregation. In the present instance, the two causes appear to balance out.

THE VISCOUS PROPERTIES OF EXTRUDED EUTECTIC ALLOYS OF LEAD–TIN AND BISMUTH–TIN.*

By C. E. PEARSON,† M.Met., MEMBER.

SYNOPSIS.

The eutectic alloys of lead–tin and bismuth–tin, when in the extruded condition, can be deformed in a viscous manner. Elongations up to 2000 per cent. have been obtained in tensile tests employing prolonged loading. By the use of an apparatus designed to maintain a constant stress on the test-piece during extension, it has been shown that deformation takes place at a uniform rate which is greatest in freshly extruded rods and decreases with age or on annealing. The viscosity possessed by the alloys is not that of simple liquids, but resembles that shown by some disperse systems in which the viscosity coefficient is a function of the stress causing flow. The locus of viscous flow is found to be at the intercrystalline boundaries. It is particularly pronounced in these extruded alloys owing to the persistence of a very small grain-size after recrystallization. Measurements have been made which appear to relate the decrease in the viscous property on ageing or annealing with an increase in the grain-size.

INTRODUCTION.

DURING the course of experimental work on the extrusion properties of eutectic alloys with low melting points, the author observed that when the extruded rods were loaded slowly in tension, or stressed continuously under a small load, they showed deformation, apparently of a viscous character, to an extent greatly in excess of their normal plastic behaviour under rapidly applied stress in either the cast or extruded condition. One alloy, the bismuth–tin eutectic, showed almost complete absence of ordinary plasticity, and pieces dropped on a hard floor broke easily in a brittle manner, yet extruded rods could be slowly elongated by several hundred per cent.

The ternary eutectic of zinc, aluminium, and copper, after rolling at 250° C., the properties of which have been described by Rosenhain, Haughton, and Bingham,[1] affords a similar instance in which the tensile strength and ductility are dependent on the time factor in loading. These authors considered the alloy to have viscous properties

---

* Manuscript received October 31, 1933. Presented at the Annual General Meeting, London, March 7, 1934.

† Lecturer in Metallurgy, Armstrong College, Newcastle-upon-Tyne.

between those of glass and pitch, and attributed its behaviour to the partial conversion of the metal, by rolling, into an amorphous condition. Jeffries and Archer,[2] commenting on this, suggested that the resemblance to amorphous substances might be due to its possessing a small grain-size at temperatures normally in the recrystallization range, which would accentuate the effect of the properties of the grain boundary. Jenkins [3] has shown that rolled eutectic alloys of cadmium–zinc and lead–tin give variable tensile tests depending on the rate and duration of loading. The latter alloy gave an elongation of 400 per cent. under prolonged loading, and could be slowly stretched under a load less than 100 lb./in.^{2}. Hargreaves [4] and Hargreaves and Hills [5] have demonstrated that the Brinell hardness of eutectic alloys with low melting point is decreased very greatly by hammering. This is due to the capacity possessed by the worked material to undergo time-flow, which brings about rapid enlargement of the Brinell impressions during the time of application of the load. The change in diameter d with time t is given by the expression $d = ct^s$. Of the constants c and s, the latter is regarded by Hargreaves as a measure of the rate of flow or creep of the material. He concluded that ". . . the extraordinary softening is partly the result of the retention of the individual phases in a quasi-viscous condition and partly interphase action."

MATERIALS.

The experiments described in this paper were carried out on the eutectic alloys of lead and tin (37 per cent. lead) and bismuth and tin (44 per cent. tin). The metals from which these alloys were prepared were of a high degree of purity. Billets for extrusion, 3 in. in length and 1·25 in. in diameter, were made by casting the alloys, at a temperature 20° C. above their melting points, into the body of the extrusion press, which was first heated to 60° C. The ends of the billets were dressed, and they were then extruded into rods 0·25 in. in diameter by the inverted method, it having been shown previously [6] that the deformation produced by this method is extremely uniform. As a further precaution to ensure uniformity, 10 per cent. was rejected from each end of the extruded rod. Preliminary tests indicated that time-flow under stress took place most readily in rods extruded at low temperatures, and extrusion temperatures of 18° C. for the lead–tin alloy, and 30° C. for the bismuth–tin alloy were adopted; the latter temperature was the lowest that could be used without the occurrence of cracking in the extruded rod.

POLITECHNIKI

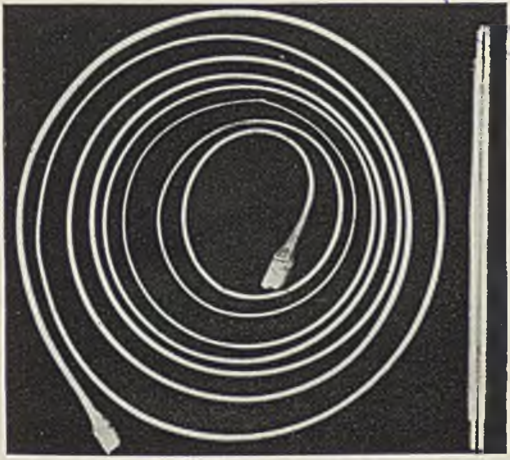


FIG. 1.—Tensile Test-Piece of Extruded Bismuth–Tin Eutectic Alloy. Elongation 1950 per cent. × ½.

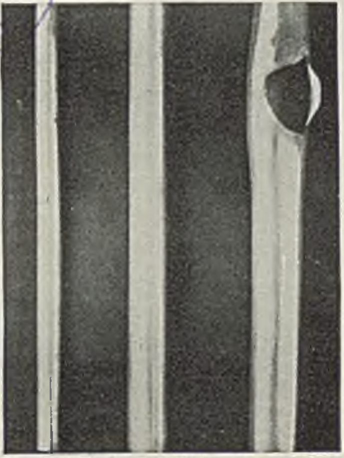


FIG. 2.—Extruded Tubes of Lead–Tin Eutectic Alloy, Deformed under Internal Pressure of 300 lb./in.^{2}. × ⅓.

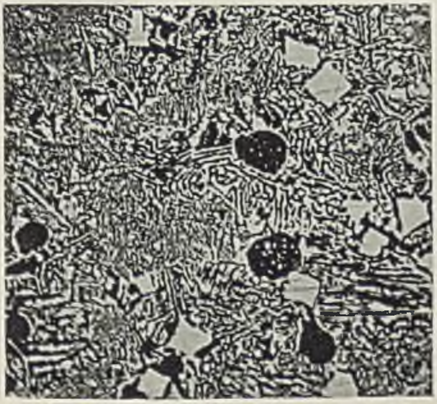


FIG. 5.—Cast Structure in Bismuth–Tin Alloy. Etched with Ferric Chloride. × 100.

FIG. 6.—Longitudinal Section from Extruded Bismuth–Tin Alloy. Etched with Ferric Chloride. × 100.

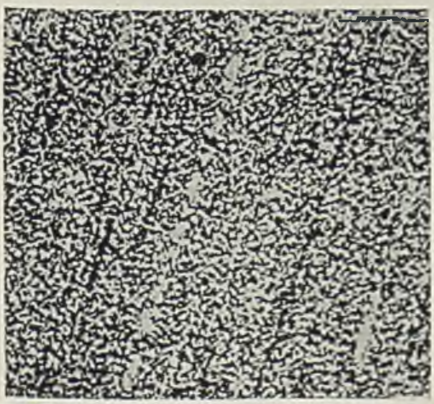


FIG. 7.—Extruded Bismuth–Tin Alloy, slowly Elongated by 150 per cent. Etched with Ferric Chloride. × 100.

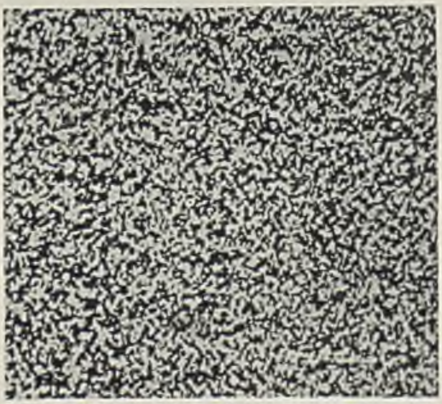


FIG. 8.—Extruded Bismuth–Tin Alloy, slowly Elongated by 600 per cent. Etched with Ferric Chloride. × 100.

[*To face p.* 112.

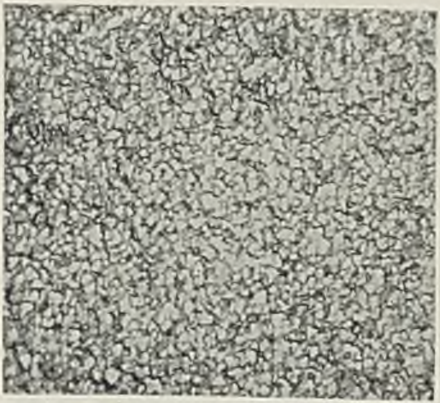


FIG. 9.—Extruded Lead–Tin Eutectic, Aged ½ hr. Structure Developed by Straining. Elongation about 50 per cent. Unetched. × 1000.

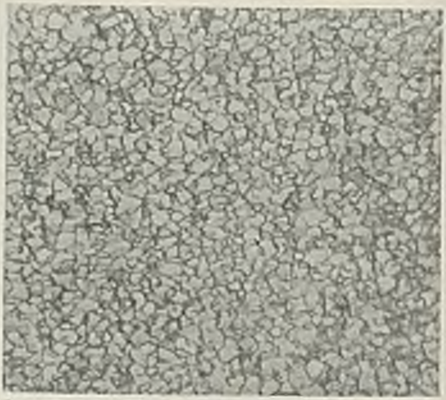


FIG. 10.—As Fig. 9, but Aged One Day before Straining. Unetched. × 1000.

FIG. 11.—As Fig. 9, but Annealed 5 hrs. at 100° C. before Straining. Unetched. × 1000.

FIG. 12.—As Fig. 9, but Annealed 2 hrs. at 175° C. before Straining. Unetched. × 1000.

FIG. 13.—Extruded Bismuth–Tin Eutectic Alloy, Aged ¼ hr. before Straining. Subsequently Etched with Dilute Ferric Chloride. Dark Constituent Tin. × 1000.

FIG. 14.—Extruded Lead–Tin Eutectic Alloy, Annealed 5 hrs. at 100° C. Strained Rapidly. Unetched. × 1000.

PROLONGED LOADING TESTS.

Rods of the extruded bismuth–tin alloy, both in the freshly extruded condition and also after ageing and annealing treatments, were subjected to prolonged loading in tension. Test-pieces for this, 4 in. in length, were prepared by machining the rod to 0·2 in. in diameter over a gauge-length of 2 in., screw threads being provided on the ends of the test-pieces for gripping. For comparative purposes, test-pieces in the cast condition were made from rods formed by drawing the molten alloy into glass tubes. In addition to the long duration tests, ordinary rapid tensile tests were also carried out.

TABLE I.—*Prolonged Loading and Rapid Tensile Tests on Bismuth–Tin Eutectic Alloy in the Extruded and Cast Conditions.*

Condition.	Load, Lb./in.^{2}.	Time to Fracture, Hours.	Elongation, Per Cent. on 2 in.	Remarks.
20 hrs. after extrusion.	1,075	2·0	652	Long tapering fracture. No necking.
7 days after extrusion	1,075	3·1	572	,, ,, ,,
Annealed 3 hrs. at 100° C.	1,075	20·5	400	,, ,, ,,
Cast specimen.	1,075	1944	18	Necked in two places.
3 days after extrusion.	11,150 max.	approx. 1 minute	35	Ordinary tensile test.
Cast specimen.	10,300 max.	approx. 1 minute	5	,, ,, ,,

The figures in Table I show that, while the extruded alloy has a rapid test strength slightly in excess of that of the cast alloy, it possesses far greater capacity for deformation and extraordinary ductility under a moderate load. The readiness to flow and the total elongation are reduced by ageing at room temperature or by annealing. A cathetometer was used to follow the progress of the extension in the prolonged loading tests, and it was found that up to 150–200 per cent. it was almost uniformly distributed along the gauge-length; slight differences in the section of the test-pieces developed during further elongation, and they eventually became tapered to the point of fracture. The rate of extension increased during each test, becoming very rapid in the later stages owing to increase in the stress as the cross-sectional area diminished.

Similar tests to the above made on the lead–tin alloy gave comparable results which need not be detailed. Some experiments made on this alloy, in which constant rates of straining with reference to the original gauge-length were used, are given in Table II. They are of interest as showing that when the alloy is in the newly extruded condition it possesses great ductility even at comparatively high rates of deformation; lower rates of straining are required to obtain high elongations in the aged or annealed specimens.

As an example of the elongation attainable in the alloys under suitable conditions, test-pieces of each were loaded initially at 250 lb./in.^{2}; the stress was then maintained approximately constant by decreasing the load at intervals during stretching. Table III shows the final lengths reached by each original inch of the respective gauge-lengths. The broken test-piece of bismuth–tin after this test was coiled so that it could be photographed conveniently, and is shown in Fig. 1 (Plate IV).

Table II.—*The Influence of the Rate of Straining on the Tensile Properties of Extruded Lead–Tin Eutectic.*

	Rate of Straining, Per Cent. per Minute on 2-in. Gauge-Length.							
	25.		50.		150.		300.	
	Elongation, Per Cent.	Max. Load, Lb./in.^{2}.	Elongation, Per Cent.	Max. Load, Lb./in.^{2}.	Elongation, Per Cent.	Max. Load, Lb./in.^{2}.	Elongation, Per Cent.	Max. Load, Lb./in.^{2}.
½ hr. after extrusion . .	...	...	1122	3270	637	5620	575	7,620
1 day after extrusion . .	...	...	1025	4370	350	6270	110	9,090
3 days after extrusion . .	...	...	517	5440	128	7168	42	10,530
Annealed 5 hrs. at 100° C. after extrusion . .	360	5630	47	6340	27	8620	...	...
70 days after extrusion . .	25	5980	25	6900	...	...	...	...

Table III.

	Final Lengths of Each Inch of Original Test-Piece.				Total, Inches.	Elongation, Per Cent. on 4 in.
	1.	2.	3.	4.		
Bismuth–tin alloy aged 7 days after extrusion .	15·2	21·6	26·8	18·5	82·1	1950
Lead–tin alloy aged 40 days after extrusion .	14·5	15·8	14·9	19·2	64·2	1505

The resemblance which deformation in the alloys bears to the viscous flow of substances like glass is exemplified by the expansion of tubes under internal pressure. Fig. 2 (Plate IV) shows pieces of tube extruded from a billet of lead–tin eutectic; the left-hand tube is as extruded, the other two have been subjected to a pressure of 300 lb./in.^{2}. The expansion took place at first more or less uniformly over the whole length of the tube, as may be seen from the centre specimen in Fig. 2; later a bulge formed, and the tube eventually burst, after the pressure had been applied for 50 minutes. The cubic capacity of a 12-in. length of the burst tube was 9·1 times that of an equal length of the original tube.

Flow in the Extruded Alloys under Constant Stress.

The study of the deformation which occurs in metals with time under conditions of prolonged loading, is complicated by the increase in stress which takes place as the sectional area of the test-piece is reduced. Where the deformation during the test is large, as in the present case, some method of stress compensation becomes essential. An apparatus has been devised on the principle of a watch fusee by means of which it is possible to maintain constant stress on a test-piece during a total elongation of 150 per cent. A sketch of the apparatus is shown in Fig. 3. It consists of a truncated hyperbolic cone with a pulley attached at one end, which is mounted horizontally on a central axle supported on ball bearings. The test-piece hangs vertically from a frame, and is attached at its lower end by means of a fine wire cable to the pulley, the circumference of which is 4·2 in., and is equal to the effective stretching length of the test-piece. A track cut in the surface on the cone, of uniform pitch, extends for 1½ complete turns, and serves as a guide for a second wire cable, which is secured at one end to a stud on the narrow end of the cone, and at the other to a weight. This weight hangs at the beginning of a test from the end of the track at the wide end of the cone, and exerts stress on the test-piece. As the test-piece elongates, the cone revolves on its axis and causes the cable bearing the weight to become unwound from its track, thus causing a reduction in the moment of the load which is proportional to the reduction in cross-sectional area of the test-piece.

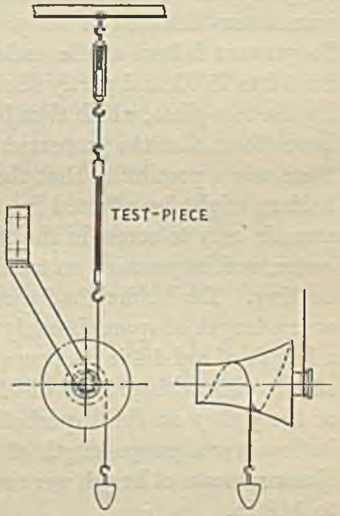


Fig. 3.

A series of weights was used to give various stresses. This method of compensation is dependent on the elongation taking place uniformly along the test-piece. That this is so within narrow limits is shown by the following figures, which represent the final lengths of individual inches of a test-piece after it had undergone considerable elongation: 2·41, 2·42, 2·39, 2·36 in. The apparatus proved entirely satisfactory in use. Some difficulty was experienced in finding a suitable form of test-piece and method of securing it. It is necessary with this apparatus to ensure that the extension is confined to a definite gauge-length, and for this the ordinary form of test-piece with reduced central portion in unsuitable, since in these alloys some deformation always occurs in the shoulders. In addition, accurate machining in the case of the lead–tin alloy was very difficult, owing to its softness—the Brinell hardness of the extruded rod is just over 1. The method finally adopted was to use unmachined lengths of the extruded rods, which were screw-threaded at the ends and screwed into light brass holders. To prevent failure at the ends of the screw threads, the holders were heated to 75° C. and partly filled with molten Wood's alloy, before inserting the test-piece, which thus became firmly soldered in. Previous tests have shown that the properties of the alloys are changed by heating, and there was a possibility that the portions of the test-piece nearest to the holders might be affected by this method of securing. It took a few seconds only to screw in the test-piece, after which it was immersed in water, and in practice no trouble arose as the result of the slight local heating. The holders had a certain supporting effect on the test-piece over a length of approximately 0·2 in. at each end, and it was found that a length of rod 4·4 in. between the holders was necessary to provide an effective stretching length of 4·2 in. corresponding with the circumference of the pulley on the hyperbolic cone. Test-pieces were marked off in inches over a gauge-length of 4 in. by means of finely scratched lines. Measurements of length were made with a cathetometer reading directly to 0·01 in.

A large number of tests has been made on both alloys with this apparatus. The stresses used in the case of the lead–tin alloy were from 200 to 1600 lb./in.^{2}, and for the bismuth–tin alloy from 400 to 2400 lb./in.^{2}. It was not possible, within the limits of accuracy of measurement used, to detect any immediate change in length on applying the load. With the exception of those tested within a few hours after extrusion, all the test-pieces stretched at a uniform rate per unit length from the beginning of the test. Typical series of measurements are given in Table IV.

It will be observed that the length does not increase by the same

TABLE IV.

	Time, Minutes.	Length, Inches.		Time, Hours.	Length, Inches.
Lead–tin eutectic, 24 hrs. after extrusion. Stressed at 1000 lb./in.^{2}.	0	4·02	Lead–tin eutectic annealed 5 hrs. at 100° C. Stressed at 400 lb./in.^{2}.	0	4·01
	10	4·63		4	4·47
	20	5·36		8	4·96
	30	6·12		12	5·53
	40	7·04		16	...
	50	8·05		20	6·78
	60	9·18		24	7·56

amount after each time interval. This is obviously brought about by the increase with time in the length of rod which is flowing at any moment. For the flow to be viscous in character, the lengths observed at regular time intervals should be in geometrical progression, and this is actually the case. The expression for flow of this kind is given by $l = l_0 . e . ^{kt}$, where l_0 is the original length, l the new length after time t, and k is a constant giving a measure of the viscosity.

The above result is strikingly similar to that obtained for pure metals by Andrade,[7] who found that the flow occurring with time under constant stress is given by the equation $l = l_0 \, (1 + \beta t^{\frac{1}{3}}) . e . ^{kt}$, where β and k are constants, l is the length after time t, and l_0 is the length immediately after the application of the stress. The time flow is of two kinds: an initial flow which decreases and finally disappears, the expression for which is $l = l_0 \, (1 + \beta t^{\frac{1}{3}})$, designated the β flow, and a purely viscous flow, taking place at constant rate throughout the extension, given by $l = l_0 . e . ^{kt}$. In "fuse wire," a lead–tin alloy, close to the eutectic composition also used by Andrade, the β flow was negligible, and the viscous flow occurred with great readiness. It did not, however, fit the equation for viscous flow given above.

The rates of flow for different stresses, in rods of lead–tin alloy after various treatments, are given in Table V.

TABLE V.—*Rates of Flow of Extruded Lead–Tin Eutectic at Constant Stress.*

Stress, Lb./in.^{2}.	Rate of Extension, Inch per inch per minute.			
	Aged 1 day after Extrusion.	Aged 7 days after Extrusion.	Annealed 5 hrs. at 100° C.	Aged 37 days after Extrusion.
200	...	...	0·00007	0·00005
400	...	0·00075	0·00045	0·00035
600	0·0040	0·0024	0·0013	...
1000	0·0148	0·0071	0·0040	0·00235
1200	0·0235	0·0105	0·0059	0·0034
1600	...	0·0202	0·0108	0·0064

In the majority of tests the rates were measured during an extension of 120–150 per cent., but this was reduced to 50 per cent. where the rates were very low. The rate of flow remained constant whether the test occupied ½ hr. or several days. No particular effort was made to maintain a constant temperature during the tests, which were carried out at 21° C. ± 2°. There was one exception to the general behaviour. Rods tested within a few hours after extrusion stretched at a decreasing rate. This was not very marked when, using a high stress, the test was completed quickly, but became more apparent in lengthier tests at low stresses. The decrease was found to be due to a change in the viscous properties of the alloys on standing after extrusion, which is very rapid at first. The curves in Fig. 4 show this ageing effect and the influence of annealing. It will also be seen that the rate of flow is not proportional to the stress, but increases more rapidly. The significance of this is discussed in a later section.

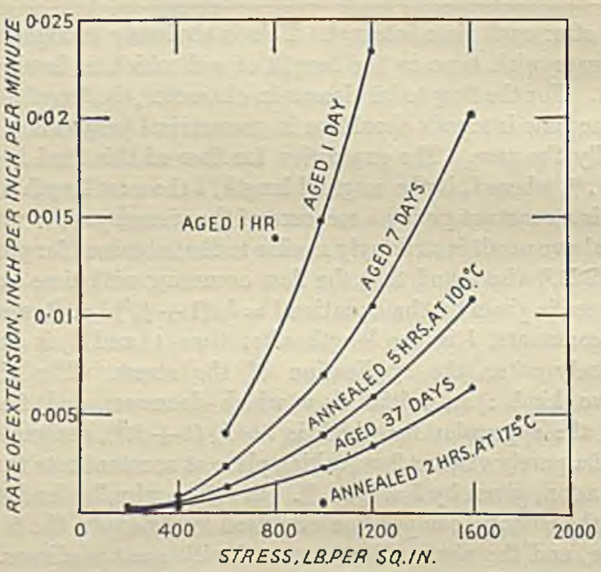


FIG. 4.

Accurate determinations of the rates of flow at stresses less than 200 lb./in.^{2} have not been attempted. It can be asserted, however, that continuous deformation occurs in test-pieces of the lead–tin alloy at stresses as low as 20 lb./in.^{2}.

THE MICROSTRUCTURE OF THE EXTRUDED ALLOYS.

The mechanism of deformation in the alloys has been studied microscopically. Some examples of the structures found in the bismuth–tin alloy in the cast and extruded conditions, and in the extruded rods after elongation under prolonged loading, are shown in Figs. 5–8 (Plate IV). The photomicrographs of the worked specimens were all taken from longitudinal sections. In the cast alloy (Fig. 5) portions of idiomorphic crystals can be seen in addition to the eutectic structure. These were invariably present in billets of this alloy, probably as the result of supercooling during freezing. On extrusion, the constituents have become elongated parallel to the axis of the extruded rod (Fig. 6). During the subsequent stretching of the rod there is no further elongation of the constituents; on the contrary, after an elongation of 600 per cent. the structure has ceased to show directional features (Figs. 7 and 8, Plate IV). During this stage, the remnants of the idiomorphic crystals, after separation into smaller pieces, become completely dispersed. It is obvious that the modes of deformation during extrusion and slow stretching have been quite different. The elongation of the constituents during extrusion suggests that deformation has been largely by ordinary plastic flow in each phase of the alloy, probably accompanied by recrystallization, since at 30° C. both metals recrystallize readily. On earlier consideration, it had appeared possible that the flow in the alloys under prolonged loading might be explained by a process of slip with simultaneous recrystallization in each phase of the eutectic, but such a process would cause the areas of each constituent to be drawn down still further in the direction of flow.

New light on the problem was obtained by observing the progress of stretching under stress by means of the strain effects produced on smooth surfaces of the extruded alloys. Excellent surfaces for the purpose were prepared by pressing rods immediately after extrusion between two polished steel plates so as to form narrow flat areas on the rods. It appeared unlikely that the slight additional deformation which this involved would alter appreciably the structure or properties of the extruded material, and this has been confirmed by tests in which the rate of flow of rod so treated was found to be the same as that in the plain rod. Test-pieces of both alloys, prepared in this way, were allowed to stand for periods from ½ hr. to 30 days, and others were annealed at various temperatures. They were then loaded in the constant stress apparatus, being removed at intervals during their elongation for microscopic examination. In each case there developed gradually a granular appearance which was extremely fine and could be resolved only under high magnification. The size of the grains was not similar in the different specimens, being smallest in the freshly extruded rod and becoming larger the longer the period of standing or the higher the annealing temperature used prior to the straining. Examples of these structures are shown in Figs. 9–12 (Plate V). With continued straining the boundaries became more marked and, using oblique illumination, it could be seen that they represented differences in the level of adjacent grains. Finally, when the elongation exceeded 100 per cent., simultaneous focussing of the grains became difficult, and some of them appeared to have become tilted to the original surface. It is important to note that even after this amount of deformation, the shape of the grains was apparently unchanged, and they were free from slip-bands.

It seems reasonable to conclude that the granular boundaries brought up by straining are those of the crystal grain constituting the alloy after recrystallization following extrusion, and that the increase in the size of the grains which takes place after standing at room temperature, or after annealing, is the normal process of grain-growth. The grains are much smaller than those usually found in recrystallized metals, possibly owing to the obstruction to grain-growth offered by two closely intermingled phases. The relation which the granular structure bears to the distribution of the two phases present in each alloy was revealed by etching a previously strained surface. Fig. 13 (Plate V) is taken from a specimen of the bismuth–tin alloy treated in this way. A uniform fine-grained structure resembling that seen in Fig. 9 (Plate V) was first produced by straining a smooth surface of the alloy 30 minutes after it had been extruded. The strained surface was then etched with dilute ferric chloride, which darkened the tin constituent. After this treatment the granular structure can still be seen in the bismuth areas, but is obliterated in the tin areas. It is evident that each phase consists, soon after extrusion, of a large number of grains, and that there is opportunity for grain-growth to occur within the individual areas of each. It is perhaps a little surprising that etching should have been necessary to distinguish the distribution of two phases, for it might have been expected that the interphase boundaries would have developed more prominently on straining than those between similar grains, but this was not the case. The grain-size was uniform over the whole of each of the strained surfaces and the boundaries were evenly developed.

It is interesting to compare the strain structures just described with those formed when the straining is done rapidly. Fig 14 (Plate V) shows the strain structure near to the fractured edge of a specimen of lead–tin alloy broken rapidly in tension. The grains are again made evident, but in this case they have an elongated appearance which was never seen in the slowly strained specimens. The test-piece became elongated by 29 per cent., most of which occurred in forming a well-marked neck. The distorted grains did not show slip-bands, and it may be noted that Hanson and Wheeler [8] have been able to produce deformation in fine-grained aluminium without the appearance of visible slip-bands, although only when the metal was slowly strained.

The evidence put forward strongly suggests that the viscous type of deformation shown by the alloys under prolonged loading is due solely to flow taking place at the boundaries of the crystal grains. Support for this view is to be found in the constancy in the rate of flow throughout a particular test, and in the fact that the rate is highest when the grain-size is smallest. There is no reason to believe that flow is readiest at interphase boundaries. It is well known that intergranular boundaries in metals may be the seat of deformation occurring in a viscous manner, and that relative displacement of crystals may occur as the result of long-continued stress at appropriate temperatures. In worked metals as a rule, however, the temperature at which such flow can occur readily promotes the formation of grains of comparatively large size, and the total deformation which can be brought about in this way is thereby reduced. On these grounds, the readiness and extent of deformation in the extruded eutectic alloys may be attributed to the persistence of extremely small grains at a temperature sufficiently high for intergranular flow.

THE RELATION BETWEEN GRAIN-SIZE AND VISCOSITY.

The relation between the rate of flow under constant stress and the grain-size, already observed in a general way in preceding tests, has been made the subject of a few careful determinations. Rods of the lead–tin alloy, from one extrusion, were made up into test-pieces having smooth flats extending over a gauge length of 4 in., so that rates of flow could be measured and the granular structures developed on specimens which had received identical treatment. These were treated in pairs as follows, so as to produce different grain-sizes: (*a*) aged one day; (*b*) annealed 5 hrs. at 100° C.; (*c*) annealed 2 hrs. at 175° C. One of each pair was then stressed at 1000 lb./in.^{2} and the rates of flow were determined; the remainder were elongated by 30 per cent. under the same stress, and their strain structures were photographed at a magnification of 1000 diameters. Grain counts were made in the usual manner from the number of grains enclosed and cut by a circle 1 in. in diameter. From these, assuming the grains to be cubic in shape, there has been calculated the number of grains per unit volume and the total grain surface per unit volume in the alloy. Although this method involves certain errors, it is satisfactory for comparative purposes.

It will be seen from Fig. 15 that the rate of flow diminishes very rapidly as the number of grains, or the total grain surface, becomes less. The relation is not linear in either case. Although only three points have been obtained in plotting each of these curves, the results have been confirmed by a duplicate series of experiments on another set of test-pieces.

It is interesting to observe with reference to Fig. 15 that whereas a normal worked metal in the recrystallized condition rarely contains more than 10^9 grains per in.^{3}, in the lead–tin alloy, one day after extrusion, there are about 5000 times as many. The disparity is much greater with cast metals.

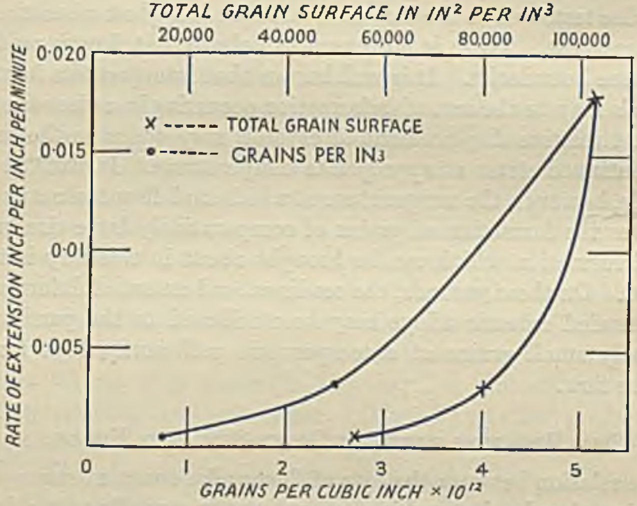


Fig. 15.—Lead–Tin Alloy. Comparison of Rates of Flow at 1000 lb./in.^{2} and Grain-Size.

General Considerations regarding the Viscosity of the Alloys.

The viscous properties shown by solid metals do not lend themselves as a rule to comparison with the viscosity of other materials, although their behaviour in this respect is sometimes considered to resemble that of glass or pitch. In most cases where viscous effects are well marked, as for example in experiments on creep, it is difficult to dissociate the purely viscous flow from deformation occurring in other ways. It is not the intention of the author to attempt any general discussion of the phenomenon of viscosity, but it appears to be worth while, in view of the magnitude of the viscous deformation shown by the alloys and the apparent absence of masking effects, to put forward a few relevant considerations.

In liquids which conform to Newton's law, the resistance to shearing stress tending to set up relative motion and expressed by "η" the coefficient of viscosity is constant, so that flow takes place uniformly at a rate which is directly proportional to the stress. This does not hold good in the case of the extruded eutectic alloys, as may be seen from Fig. 4. Their behaviour resembles that of many colloidal solutions and coarser disperse systems, such as suspensions of particles of microscopic size which have been found to have anomalous viscous properties.[9] In such cases the rate of flow is not proportional to the stress, but increases more rapidly, a result which would be produced if η were not constant, but decreased with increasing stress. Some doubt has been expressed whether a resistance to deformation which is a function of the stress can properly be regarded as a viscosity, and a number of alternative terms have been suggested, none of which has yet found acceptance. It may be pointed out that the conclusion that viscous deformation in metals does not conform to the ordinary laws of viscosity is in accordance with the results obtained from torsion tests on copper and steel at high temperatures by Henry,[10] who found that a constant rate of deformation was soon attained at any stress, but that the relation between the rate of deformation and the stress was not linear.

ACKNOWLEDGMENTS.

In conclusion, the author wishes to acknowledge a grant from the Research Committee of Armstrong College. He is indebted to Dr. J. A. Smythe for much helpful criticism, and to his colleagues Dr. E. G. Richardson, Mr. J. F. Wood, M.Sc., and Mr. R. H. Hiscock for valuable advice on various aspects of the work.

REFERENCES.

[1] Rosenhain, Haughton, and Bingham, *J. Inst. Metals*, 1920, **23**, 261.
[2] Jeffries and Archer, "The Science of Metals," 1924, p. 76.
[3] Jenkins, *J. Inst. Metals*, 1928, **40**, 21.
[4] Hargreaves, *J. Inst. Metals*, 1927, **38**, 315; 1928, **39**, 301.
[5] Hargreaves and Hills, *J. Inst. Metals*, 1928, **40**, 41; 1929, **41**, 257.
[6] Pearson and Smythe, *J. Inst. Metals*, 1931, **45**, 345.
[7] Andrade, *Proc. Roy. Soc.*, 1910, [A], **84**, 1; 1914, [A], **90**, 329.
[8] Hanson and Wheeler, *J. Inst. Metals*, 1931, **45**, 229.
[9] Hatschek, "The Viscosity of Liquids," 1928, p. 190.
[10] Henry, *Rev. Mét.*, 1927, **24**, 421.

ADDENDUM.

Since this paper was submitted, Dr. O'Neill has very kindly made an X-ray examination of rods of the lead–tin eutectic. There appeared to be some possibility that preferred orientation might be present in the extruded rod, and that the effect on this of subsequent straining might throw some light on the mechanism of the viscous flow. Tests were made on (*a*) rod as extruded; (*b*) rod extruded and slowly elongated by 400 per cent. in tension. Dr. O'Neill reports that there is no evidence in either case of preferred orientation. The metals appear to have recrystallized.

A NOTE ON SOME FORMULÆ CONCERNING VISCOUS AND PLASTIC FLOW IN SOFT METALS.*

By E. W. FELL,† Dr.-Ing., M.Sc., Member.

Synopsis.

The note deals with a certain type of flow observed in soft metals, eutectics included. In particular, the flow of the metal in a prolonged ball-hardness test is compared with the flow in tensile test-pieces under a constant stress per unit area of cross-section.

A formula concerning the continuous penetration into the metal of a ball under a constant applied load is discussed with particular reference to the constants in the formula. A result is given of the assumption that the change in the diameter of the ball-impression with time is a function of the flow of the metal. A formula concerning the increase in length with time of tensile test-pieces under constant stress is discussed regarding constants. The applicability of the ball and tensile methods is considered, and constants compared. One formula relates to the change in rate of extension with stress and a comparison is made with viscosity.

This note was written as a result of conversation on the meaning of some constants mentioned in a series of papers, one of which was entitled "The Ball-Hardness and the Cold-Working of Soft Metals and Eutectics." ‡ In the discussion on these papers, little was said about the meaning of the constants c and s in the formula described,

$$d = ct^s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where d = diameter of impression, and t = duration of loading after the load on the machine had reached its maximum. The values obtained for these constants varied according to the state of the metal and the mode of carrying out the test. It is hoped that this note may be of value in attempting to discuss the meaning of these constants and in comparing them with some recent work concerning a similar type of flow in metal at room temperatures.

---

* Manuscript received December 29, 1933. Presented at the Annual General Meeting, London, March 7, 1934.

† Recently at St. John's College, Cambridge.

‡ F. Hargreaves, *J. Inst. Metals*, 1928, 39, 301–327; further papers, *ibid.*, 1928, 40, 41–54; 1929, 41, 257–283; 1930, 44, 149–167.

Formula (1) fits the interesting experimental results which were obtained,* since the points representing a single set of observations lie near a straight line when plotted with log t as abscissa and log d as ordinate. It is seen from the formula that at a specified time, the diameter of the impression is dependent on the coefficient c and the index s. The value of log c is the "additive constant" in the equation of the log t–log d curve, and s is the gradient. c and s are found to be constants for a particular metal in a definite state and for prescribed conditions of testing.

It will be noted that formula (1) is determined for a constant load only. Strictly, therefore, it does not seem clear why the rate of application of the load should have little effect on the results obtained when s has a negligible value (see p. 308 of Hargreaves's paper), or that its effect will vary at different stages of the operation of loading when s is not constant for different loads (*ibid.*, p. 309). In passing, it may be noted that the formula does not hold in an interval of time including $t = 0$ and values of t above $t = 0$: there is little to show when d begins to fit the formula. It is possible that, contrary to the formula, the diameter of the impression is not equal to c when $t = 1$. The diameter of the impression when $t = 0$ depends on the metal and on the conditions of testing prior to this time.

The formula shows that the diameter of the impression, which is indirectly a measure of the ease with which the ball penetrates the metal, is dependent on both c and s. For, suppose that the change in the diameter of the impression with time is a function of the flow of the metal, then the increase in d in a small interval of time, δt, is from formula (1) found to be $cst^{s-1} . \delta t$, to the first order. Thus the increase in d is partly dependent on c and s, or, briefly, on the constant (cs). Both c and s appear to vary differently in the experiments, and the influence of c is considerable, as is shown by taking, for example, the lead–tin eutectic, worked, referred to on p. 322 of Hargreaves's paper, Table X, as Material No. 8, where approximately $c = 1{\cdot}92$, $s = 0{\cdot}143$.

t.	t^s.	ct^s.
30	1·62	3·11
270	2·23	4·28
540	2·46	4·72

In a further paper,† mention is made of the "creep factor s," but since

---

* F. Hargreaves, *loc. cit.*

† *J. Inst. Metals*, 1930, 44, 151.

c should be taken into account, this term would not appear permissible. Meyer's formula,

$$L = ad^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where L = maximum load on the ball, d = diameter of impression after a standard time, and a and n are constants, scarcely shows what is taking place as the load is increased from zero to maximum in a test, since strictly the time required for this to happen is generally less than the standard time employed.

The author of the present paper is indebted to Mr. C. E. Pearson, M.Met., for kindly supplying details of a paper on "The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin."* In that paper, rates of extension in tensile tests at constant stress per unit area of cross-section are given, and provided sufficient time after extrusion was allowed for, rate of extension was found to be uniform; Table IV showed the change in original gauge-length with time at constant stress (in passing, it may be mentioned that the relation $\log_{10}$ (time)–$\log_{10}$ (length) is not linear for the two cases described). In the formula mentioned,

$$l = l_0 e^{kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where l = length after time t, l_0 = original gauge-length, the constant k will be found in Table IV to have the following approximate values in in./minute: for lead–tin eutectic, 24 hrs. after extrusion and stressed at 1000 lb./in.^{2}, $k = 0{\cdot}0140$; for lead–tin eutectic, annealed 5 hrs. at 100° C., and stressed at 400 lb./in.^{2}, $k = 0{\cdot}00044$.

It is interesting to compare, as far as is possible, the results of Hargreaves and Pearson with regard to the flow of the metal. The lead–tin eutectic, 75 per cent. reduction by hammering, in Table XVI of Hargreaves's paper, may be compared with the lead–tin eutectic, severely worked by extrusion at room temperatures, in Table V of Pearson's paper. On differentiating in (3) with regard to the time and putting $l_0 = 1$, $t = 0$, the rate of extension $\left(\frac{dl}{dt}\right)$ will be found to be k. Results for k, together with the values for c and s taken from Table XVI, are given in Fig. 1. It will be seen that only c varies in accordance with the curve representing k, whilst s has practically the same value for the three determinations made in the first four days of ageing after working. From these few results it may be deduced that k and s are not comparable.

Why should not the ball method be convenient for measuring this type of flow, provided the metal be more or less isotropic and the points of support of the specimen be at such a distance that reaction effects

---

* This Volume, pp. 111–124.

thereat have negligible influence in the neighbourhood of the ball? It might be expected that the two methods should give comparable values for these constants in homogeneous materials like pitch. Comparable values for the flow in metals may not be obtainable, because they are not in this sense homogeneous, in addition to the alteration of their properties on working. In the ball method the material is pushed away by the penetrating ball, in the tensile method it is pulled out.

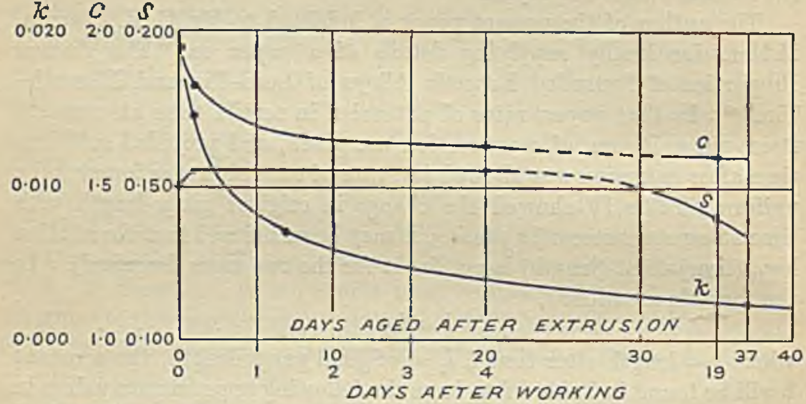


FIG. 1.—Lead–Tin Eutectic. Comparison of the Constants k, c, and s (k for 1000 lb./in.^{2}, c and s for 6·35 mm. ball/40·3 kg.).

In the first method, the contact pressure at a fixed point on the ball varies in magnitude and possibly also in direction with time; in the second method, the pull across a transverse section within the gauge-length may be visualized as constant in magnitude and direction with the passage of time. The experimental conditions are thus simpler in the second method. Such differences as these may account for any variation of results between the two methods, assuming that the metal is initially in the same condition.

Table V has also been used to examine the relationship between the applied stress and the rate of extension k, and Fig. 2 shows log (stress)–log k curves for extruded lead–tin eutectic in the four states mentioned in the table. The curves are not straight lines, they may cease to be straight above a stress of about 600 lb./in.^{2}, and in the absence of systematic experimental error this may suggest that a change occurs in the mode of flow as the stress is increased.

Accordingly, in the range 200–600 lb./in.^{2}, let

$$k = b^{-1}p^{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where k = rate of extension, p = stress, b and m are constants. b will be seen to depend on the state of the metal and possibly on the kind of metal, whilst m ($= 2{\cdot}72$ in c.g.s. units) has the same value for the four curves, since they are parallel, as shown in Fig. 2, and so is practically unaffected by the different states of the metal considered in the figure.

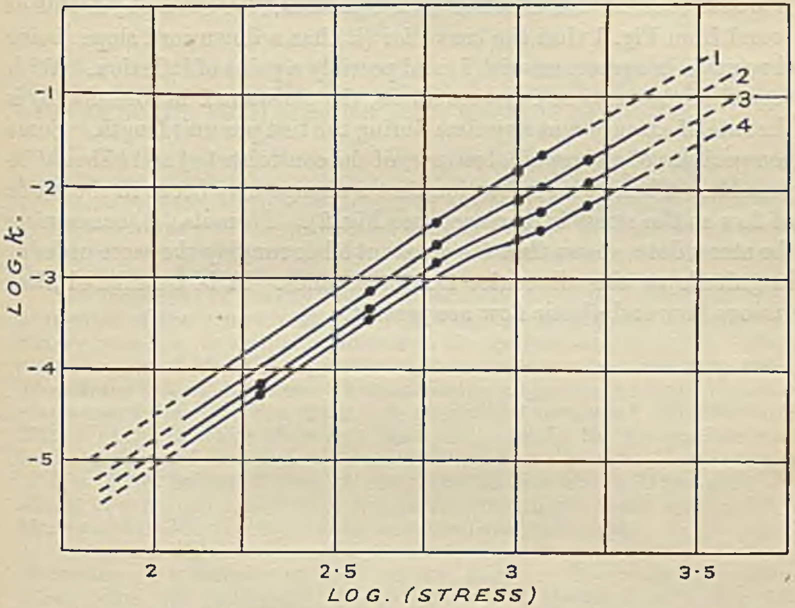


FIG. 2.—Extruded Lead–Tin Eutectic. Variation of k with Stress. (1) Aged 1 Day after Extrusion; (2) Aged 7 Days after Extrusion; (3) Annealed 5 Hrs. at 100° C.; (4) Aged 37 Days after Extrusion.

It will be found in this range that for the extruded lead–tin eutectic the following values for b are obtained :

Aged 1 day after extrusion . . .	$b = 4{\cdot}46 \times 10^{16}$ c.g.s. units
Aged 7 days after extrusion . . .	$b = 7{\cdot}94 \times 10^{16}$,, ,,
Annealed 5 hrs. at 100° C. . . .	$b = 1{\cdot}41 \times 10^{17}$,, ,,
Aged 37 days after extrusion . . .	$b = 2{\cdot}24 \times 10^{17}$ approx.

The tests were made at 21° C. ± 2°. In the figure, the curves have therefore been assumed to consist each of two straight portions, for a lower and a higher range of stress, which have been made clearer by drawing the broken lines. For the higher range of stress above about 1000 lb./in.^{2}, the values for b and m behave as above, being somewhat smaller in magnitude. The only reason for introducing formula (4) is to show that b is roughly of the same order of magnitude as the viscosities for some solids.

CONCLUSION.

The constants c and s require careful use; complex conditions—for example, in the ball method—have been mentioned. It is suggested that the use of the product cs would remove some irregularities, in that it would combine the effect of each constant: for example, it will be found from Fig. 1 that the curve for (cs) has a downward slope (being thus more in agreement with k) and possibly a point of inflexion. With regard to the tests at constant stress, the constant k in formula (3) is the rate of extension at any time during the test per unit length. Some comparison, of an empirical nature, of the constants (cs) and k should be possible. There is an indication that a change may occur in the mode of flow as the stress is increased (see Fig. 2). Formula (4), concerning the stress data, shows that the constant b has roughly the same order of magnitude as the viscosities for some solids. It is considered that viscous flow and plastic flow are present.

JOINT DISCUSSION ON PEARSON'S AND FELL'S PAPERS.

Dr. E. W. Fell, at the request of the President, presented his paper as the first contribution to the discussion of the paper by Mr. C. E. Pearson, on which his (Dr. Fell's) paper was partly based (see pp. 127–130).

Mr. R. Chadwick,* B.A. (Member): Mr. Pearson's investigation adds some further interesting observations on the cold-working of highly dispersed two-phase systems. The work on lead–tin alloys I found especially interesting, and I much admired the photo-micrographs in Figs. 9–12, in which actual grain-growth is shown, similar to, but much slower than, that produced in the annealing of uniform solid solutions.

The properties of heavily deformed eutectics must be a resultant of the properties of the constituent solid solutions, and it is to be regretted that Mr. Pearson has, by confining himself to the consideration of eutectic alloys, rather suggested that these peculiar viscous properties are essentially linked up with the eutectic structure. I found similar properties in heavily deformed zinc which I described in a paper presented to the Institute.† The recrystallization of the zinc took place very much more rapidly, but the same decrease in the property of viscous flow occurred with recrystallization. In the testing of this highly deformed zinc, an elongation of only about 70 per cent. was shown in a normal tensile test, but in the creep tests, under smaller loads, elongations of 300 to 400 per cent. were frequently obtained.

In my investigations into the nature of these creep properties, I related elongation of a loaded test-piece to two factors: (1) viscous elongation, which below the yield-point was proportional to the time of testing, and (2) plastic deformation, which was independent of time. For this reason I regarded the determination of yield-point as of very great importance, and determinations were made with as nearly as possible instantaneous loading. The mechanism of elongation can most easily be explained by the presence of two phases. Below the instantaneous yield-point I suggested that purely viscous elongation occurred in the amorphous phase (I notice that Mr. Pearson is very careful to avoid using the word amorphous), whilst with greater loads plastic deformation of the lattice structure of the remaining crystallites took place. The dual nature of the elongation is clearly shown in Fig. A, similar conditions in extruded lead–tin being shown in Fig. B. This analysis is confirmed by the observation of Dr. Fell that in plotting log k against log stress a straight line was obtained below 600 lb./in.^{2}. The determination of the instantaneous yield-point of freshly extruded solder placed it at about 800 lb./in.^{2}, but it was difficult to get a sufficiently short loading period for an accurate value.

This account of the mechanism of elongation applies necessarily only to small elongations. A short experiment will show this. A test-sample of extruded solder was loaded instantaneously at 1500 lb./in.^{2} and gave 0·7 per cent. elongation. It was then allowed to elongate 20 per cent. under a load of 500 lb./in.^{2}—almost certainly below the instantaneous yield-point—and on again loading with 1500 lb./in.^{2}, a further elongation of 0·5 per cent. was

---

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

† *J. Inst. Metals*, 1933, 51, 93.

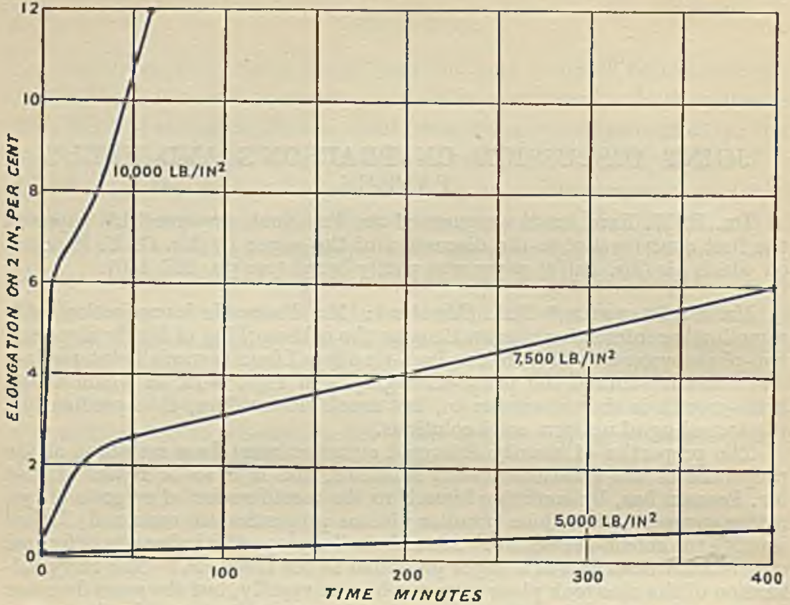


FIG. A.—Elongation of Loaded Test-Pieces of Rolled Electrolytic Zinc Strip.

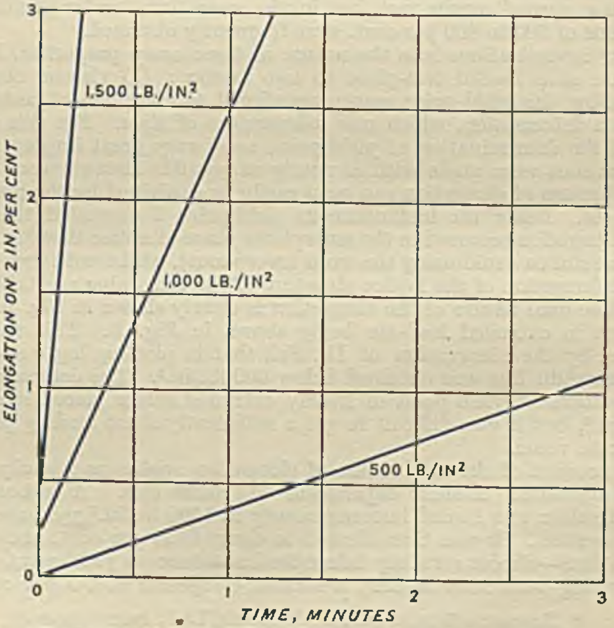


FIG. B.—Elongation of Loaded Test-Pieces of Extruded Lead–Tin Eutectic.

obtained, which indicated that there had been some re-orientation of the crystallites allowing a further distortion with instantaneous loading. In Fig. 14 Mr. Pearson shows elongated grains produced in rapidly strained extruded lead–tin eutectic. I should like to know whether he suggests that in slow straining the grains would simply roll over each other without any distortion. I think that he said that he did not find any distortion, but my own observations on sections from slowly elongated extruded strip certainly gave visible grain distortion with more than 50 per cent. elongation. I would relate only the initial rate of elongation $\frac{dl}{dt}$ at low loads to purely viscous flow in the boundary material, high elongation involving distortion in both phases.

Finally, I would point out that extrusion is by no means the best method to obtain a highly cold-worked viscous condition. The heat evolved in extruding a cold billet was found to be very considerable, the product being at over 100° C. on leaving the die-mouth. It appeared probable that some recrystallization had taken place immediately after the extrusion even when a quenching bath of iced water was employed. A sample of cast solder was carefully cold-rolled to 97 per cent. reduction in thickness * avoiding any appreciable increase of temperature. The strip prepared gave three times the rate of extension and a similar ratio of total extension when compared with extruded strip under the same load. The rate of creep of highly deformed zinc was found to decrease very rapidly immediately after rolling and then at a diminishing rate. This is shown with a similar curve for lead–tin in Fig. C. Under better conditions of cold-working, I think that the lead–tin curve would have commenced from a very much higher creep rate, the short

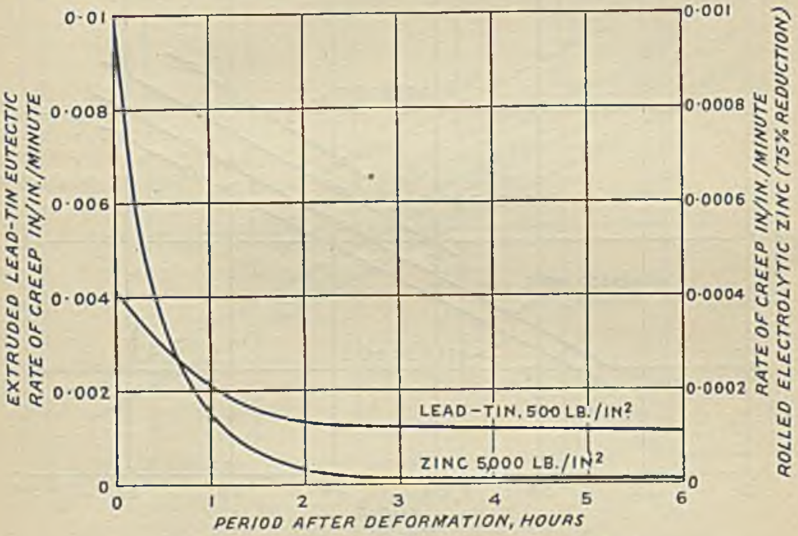


Fig. C.—Effect of Ageing on Viscous Elongation.

---

* It was found that a deformation of well over 90 per cent. was necessary to give material in a similar physical state to the extruded product. It appears doubtful whether the hammered solder dealt with by Dr. Fell on p. 127, was in a condition at all comparable with that of Mr. Pearson's extruded solder.

interval at a high temperature causing as great a change as a much longer period at room temperature.

Professor Gilbert Cook: * The mechanical properties of the lead–tin alloys are most interesting. I do not speak as a metallurgist, but I am keenly interested in the mechanical properties of metals and the laws which govern their flow. It is obvious that the viscosity to which Mr. Pearson and Dr. Fell refer is of a type quite different from that met with in liquids. Like Dr. Fell, I have spent some time in studying Table V of Mr. Pearson's paper, and I, too, have plotted the rates of stress against the rates of flow logarithmically, but I reach quite different conclusions from those of Dr. Fell. I disagree with the way in which Dr. Fell has drawn lines through the points in Fig. 2 of his paper. Dr. Fell says that the curves are not straight lines, but of course a straight line can be drawn through any two points, and I think that he has drawn a straight line through the lowest two points, found that it does not go through the others, and then proceeded to reach what I consider to be rather an improper conclusion. At the bottom of p. 128 he says that the curves cease to be straight above a stress of about 600 lb./in.^{2}, and that therefore a change occurs in the mode of flow as the stress is increased. In Fig. D the observations are replotted to the same scales as in Fig. 2, p. 129, and it is evident that if a linear relation be assumed, it is at the lower values of the stress that the deviation occurs, and not at the upper. This is very significant, and it seems to me to indicate the existence of plasticity as well as viscosity. A plastic body as distinct from a purely viscous body is one which possesses a flow limit; that is to say, a shear stress exists below which flow will not take place, and the relation between stress and flow velocity could be expressed by an equation of the type: $s = s_0 + c\phi(v)$. I have examined the data given in Table V carefully on the assumption that

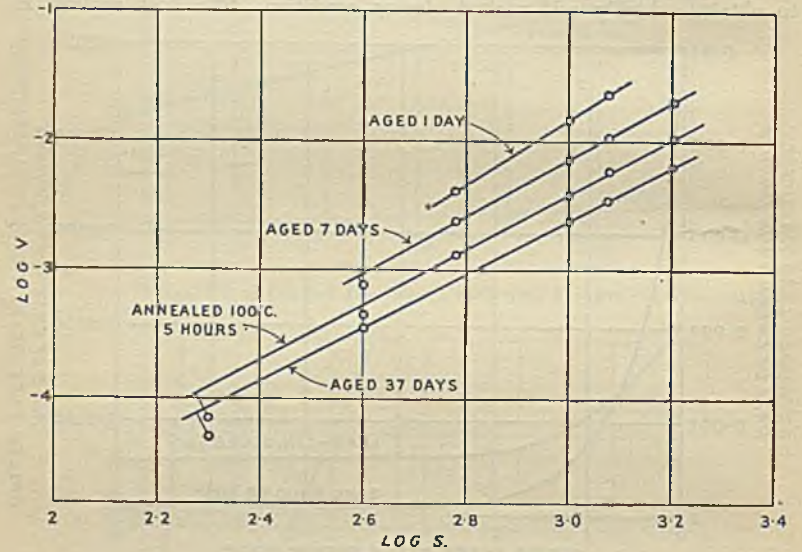


Fig. D.

---

* Professor of Mechanical Engineering, University of London (King's College).

this equation holds, and that $s - s_0 = cv^n$. In this form it is amenable to logarithmic plotting, although somewhat troublesome because s_0 has to be found by trial.

The result is shown in Fig. E. It will be seen that a series of parallel straight lines pass almost identically through the points; and it is most interesting to note that the slope of these straight lines shows that the index of v in all cases is exactly $\frac{1}{2}$. I have heard it said that nature abhors anything except very simple indices, and when I see variables related in this way I feel that there must be something more in it than a mere empirical relation.

With regard to the plastic limit which seems to exist in each case, I am in a difficulty, because Mr. Pearson has pointed out that flow was observed at stresses as low as 20 lb./in.². The lowest value of s_0 in the above equation was 64 lb./in.². It would be most interesting, I think, to have more data with regard to the flow under very low stresses. There must be some sort of limit, or the metal would flow under its own weight like pitch, and I presume that that does not occur.

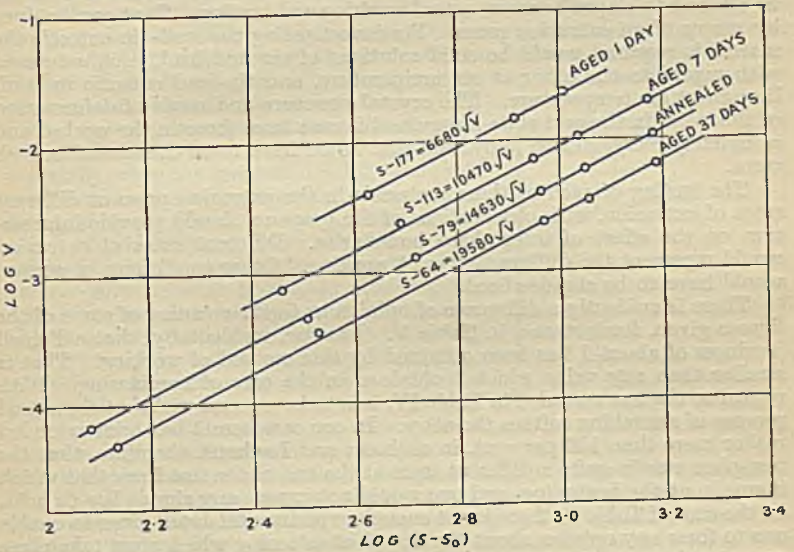


Fig. E.

As to the physical significance of the square root, I am not prepared at the moment to give an opinion, but it does show definitely that the viscosity is not of the same type as that of a liquid. If this law is the right one, the coefficient c in this equation must have the dimensions $ML^{-1}T^{-\frac{3}{2}}$, and I have not discovered any satisfactory way of correlating that with such properties of the material as are likely to have any effect. It would be most interesting to know whether this law would hold for other types of stressing, say in torsion, and whether fluid pressure might affect it. Such pressure, we know, has practically no effect on plastic flow in solids; in the case of soft copper, for instance, a fluid pressure as high as 2500 atmospheres has only a slight effect in impeding the plastic flow. We know, however, that high pressure does increase notably the viscosity of liquids, and it would be of interest to know whether this type of viscosity is susceptible to the same effect.

Mr. F. Hargreaves,* A.R.S.M., D.I.C. (Member): The real question which concerns us with regard to the matter dealt with in these two papers is this: do soft eutectics behave differently, in any fundamental respect, from pure metals and solid solutions? A superficial survey suggests that they do, and in certain ways, particularly with regard to recrystallization after cold-work, they show a great difference. I suggested some years ago that there was a great difference between soft eutectics and pure metals or solid solutions in the duration of the phenomena observed, but neither my own tests nor those of Mr. Pearson touch that particular point. After heavy working these soft eutectics undergo such rapid changes that the Brinell test cannot follow them, and the tensile test certainly cannot. It seems to me, therefore, that to get information on this point testing must be carried out at the same time as the working of the alloys; in other words, no time should be allowed to elapse between actual working and testing. That can be done by means of an extrusion press. For investigating the lead–tin eutectic the materials required would be solid solutions of tin and lead, each saturated with regard to the other at air temperature, and tin–lead eutectic in equilibrium at air temperature. The crystal structure and mode of deformation of the latter in the cast state are quite different from those in the worked and completely recrystallized alloy, and this would have to be considered in such tests.

The testing of each of these materials in the extrusion press at different rates of extrusion, with observations of the pressure, should provide information on the effect of inter-phase boundaries. Different rates of extrusion would represent the different rates of working. Other conditions, of course, would have to be standardized.

There is evidently a difference of opinion as to the meaning of some of the figures given, for instance, in Table V. I notice, incidentally, that a Brinell hardness of about 1 has been obtained by this method of working. That is smaller than any value which I obtained in the case of hammering. With regard to the test recorded in Table IV, it is to be remembered that the actual process of stretching softens the alloy. In one case here it has been extended rather more than 100 per cent. in an hour, and I submit, therefore, that the test-piece was in quite a different state at the end of the test from that which it was in at the beginning, and one would not expect any simple law to hold. In the case of Table V, there is not enough experimental detail given to enable one to form any opinion about the degree of softening which must take place on extensions under stress. I suggest that some of the departure from a linear relation, as pointed out by Dr. Fell, is due to softening during the test. . . .

With regard to flow at inter-phase boundaries, it is not right, I think, to say that there is no evidence that flow is readiest there, as is stated by Mr. Pearson. The development of the eutectic structure by straining is well known, and in my investigation on strain methods it was freely used. It is, of course, realized that the extruded structure is a very different structure from that of the cast alloy.

I do not agree with the suggestion that the rate of flow and the pressure are determined by grain-size; to suggest that is to ignore previous observations. It has been clearly shown, of course, that there is a connection between them, but at the same time I do not think that one is the cause of the other; it is more nearly true to say that they are both results of the same cause. It has been shown in some of my previous work that it is possible to increase the rate of flow under pressure without any small grain formation. In the average lead–tin eutectic sample the tin crystals are relatively very big. Of

---

* Chemist, Southern Railway, Eastleigh.

course, on recrystallization they are very small, as shown by Mr. Pearson, but it is very difficult to make a fine-grained eutectic recrystallize completely. If it is hammered to the extent of reducing it 75 per cent., annealing at within 8° C. of the melting point will often fail to recrystallize it completely.

With regard to Dr. Fell's paper and the factors *s* and *c*, he points out that the product of these would be a better representation of the flow phenomena. He has plotted *c* and it corresponds somewhat to Mr. Pearson's "*k*": but in working eutectics the *s* factor always increases whilst as in the case of the silver–tin eutectic, log *c* may decrease.

Professor B. P. Haigh,* M.B.E., D.Sc. (Member): This paper illustrates clearly how complex is the problem of plastic strain in metals, at any rate in some cases and probably generally. We can recognize, I believe, four distinct actions producing strain in metals, the first of these being the elastic action that affords such a valuable basis for theoretical study. Putting that aside, there appear to be at least three other actions that produce plastic strain. There is the process which, involving slip-bands, work-hardens the metal; and there is the action about which Mr. Pearson has spoken so interestingly, recrystallization, which must have many effects, especially when the recrystallization product is smaller than the amorphous or other matter from which it forms. Lastly, there is the effect of viscosity. I have sometimes been inclined to doubt whether there is such a thing as viscosity in solid bodies, or whether the apparent effect is not simply a combination of slip and recrystallization; and yet it is very difficult to believe that, especially in the light of such considerations as Professor Cook has just put forward.

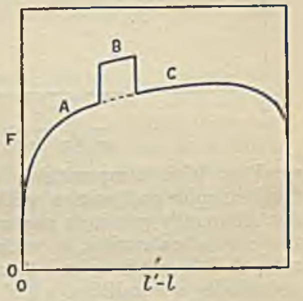


FIG. F.

I should like to show by means of a diagram how measurements may be taken to illustrate the kind of effect that is attributed to viscosity. We will think of an ordinary tensile test, where the force which is applied to the test-piece is shown vertically and the increase of length, $l' - l$, horizontally. The simplest type of diagram, obtained with a constant rate of straining, is as sketched in Fig. F; but if the rate of straining is increased, we get a step as in Fig. G, and can return to the original graph at *A* by returning to the initial rate of straining. The consistent manner in which the graph returns is very difficult to explain unless we assume that there is something which may fairly be described by the name of viscosity.

With the alloys such as the author has described and with many others, *e.g.* tin alloys, this may be done repeatedly, and several intermediate rates of straining may be used to draw intermediate graphs, because the long range of extension available before fracture is amply sufficient to enable the changes to be made repeatedly. Thus the effect of viscosity can be ascertained by tests on a single test-piece.

If that is translated into terms of the diagram which I put before you a year ago, in which one plots not the applied force, but the force divided by the reduced area of the piece on a base representing the reduced area *a* changing from the initial value *A* down to zero, interesting results are obtained which explain why some of the pieces elongate so tremendously and others only very much less. Great elongation is found to depend—not necessarily on abnorm-

---

[*] Professor of Applied Mechanics, Royal Naval College, Greenwich.

ally evident viscosity—but rather, on the work-hardening properties of the metal, being obtained whenever the graph G rises gradually to approach the hyperbolic profile represented by the dotted line H. As faster rates of loading tend to raise the graph without greatly changing its profile, the modified graph G runs tangent to a higher hyperbola H at an earlier stage, giving less distributed elongation before necking leads eventually to fracture.

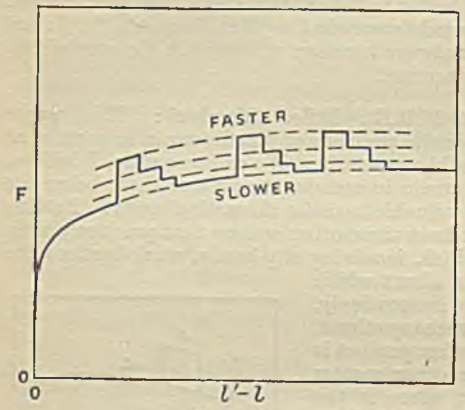


Fig. G.

Dr. N. P. **Allen**,[*] M.Met. (Member): Mr. Pearson's very interesting piece of work has demonstrated some very remarkable phenomena. The most remarkable feature is the great uniformity of the rate of extension in the alloys. In the ordinary way, viscous flow in any metal or alloy becomes uniform with time eventually, but there is a "qualifying" period in most cases characterized by an abnormal rate of flow before uniform flow begins. That is seen in the case of steel at high temperature, where the rate of extension is at first relatively rapid and varies with time, and afterwards becomes uniform. In Mr. Pearson's previous paper he showed the same sort of thing occurring in the case of extrusion, in which with some metals there was an initial slower rate of deformation, and in others an initial faster rate of deformation, but eventually a condition which was reproducible with constant rates of flow was established. The present alloys are immediately in a condition to undergo uniform flow with time. Mr. Pearson seems to relate that difference to the very small grain size in these alloys, and considers the flow due, apparently, to the movement of the crystals over each other. In that connection I should like to raise two points which do not appear to be referred to in the paper. The first is whether he noticed any difference in size between the grains as they appeared in the alloy at the beginning of the deformation and their appearance at the end, and whether he established by any experiments that the grains seen at the beginning of his tests were the same individuals as the grains seen at the end of his test; that is to say, whether he has established that it is not possible that the grains which were seen at first have broken down, recrystallized and been replaced during the progress of the experiment by another complete set.

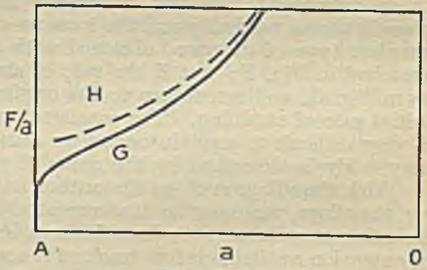


Fig. H.

Even if the grains at the end of the test are established to be the same ones as existed at the beginning, I think that it is doubtful whether we ought

---

[*] Lecturer in Metallurgy, The University, Birmingham.

to conclude that in all cases of viscous flow the movement is due to translation at the crystal boundary. I remember that in some experiments I was carrying out on some zinc-base die-castings I found viscous deformation occurring in alloys in the cast state; and whereas it is quite easy to visualize the grains moving over each other when there are an exceedingly large number of uniform grains, it is not quite so easy to visualize that movement when the grains are comparatively large and dendritic in form, so that they interlock with each other and would apparently be prevented by their shape from any movement relatively to each other, like the various pieces in a jigsaw puzzle.

Another point which bears on that question is the fact established by Professor Hanson and Mr. Wheeler that viscous flow can occur in a single grain. Although Mr. Pearson has placed it beyond doubt that the size of the grain is a very important factor, yet, in view of the fact that viscous flow is such a general phenomenon in metals, and of the general similarities that metals of all kinds show in their behaviour, I think that it is time we recognized that the capacity for viscous flow is a property of the metallic crystal and, just as the crystal is able to flow in a plastic manner, it is also capable of undergoing a different kind of deformation which we call for the present viscous flow, although it certainly seems not to be the same thing as the viscous flow which occurs in liquids.

Professor T. Turner,* M.Sc., A.R.S.M. (Past-President): I have been very interested in the unexpected flow of these eutectic alloys. It is remarkable to see the very great difference between the material which has been allowed to stand for a short time, to age, and that which has been tested immediately after being extruded. If the author's object in these experiments were theoretical it was natural for him to proceed as he has done with the purest materials, to obtain a eutectic, and to study it. If that were the object, the present research is only the first step towards a further series of experiments. There are metals at either end of a series, the eutectic in the middle, and intervening solid solutions. Having shown the unexpected properties of the eutectic, it would be interesting to see whether they differ from those of the solid solutions. That would be a very interesting inquiry, but it would be a wide one.

From the more practical point of view, these alloys are referred to as "eutectic solders"; they are extruded on a fairly considerable scale, I believe, and are articles of commerce; but the eutectic solder which would be employed in the ordinary way would contain some antimony, amounting to something like one-fiftieth part of its weight. The alloys studied were of antimony-free material. One wonders why in small rods and tubes the antimony is omitted. Is it because the material flows more readily during the process of extrusion, or is it because the alloys are used for electrical purposes and that the antimony makes a difference to the conductivity? Another question arising from the practical point of view is: why is it that in the smaller sizes of rods of solder no antimony is added or permitted, whilst in the case of ordinary solders the presence of some antimony is definitely beneficial? In practice the mixture generally contains sufficient antimony, so that it is not necessary to make any addition.

Mr. E. H. Bucknall,† M.Sc. (Member): I am particularly interested in the ageing behaviour of the alloys, particularly in that 5 hrs.' annealing at 100° C. has more effect than 7 days at room temperature but less than 37 days

---

* Leatherhead.

† Junior Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

at room temperature in decreasing the rate of flow, whilst 2 hrs. at 175° C. has more effect than even 37 days at room temperature.

The results given in Table V for the lead–tin eutectic aged at room temperature after extrusion are plotted in Fig. I below.

The experimental points fall on a series of curves which might well converge at some point on the time-scale between 1000 and 10,000 hrs. It would be very interesting if the author, should he continue the work, would investigate the rate of creep after ageing for such periods.

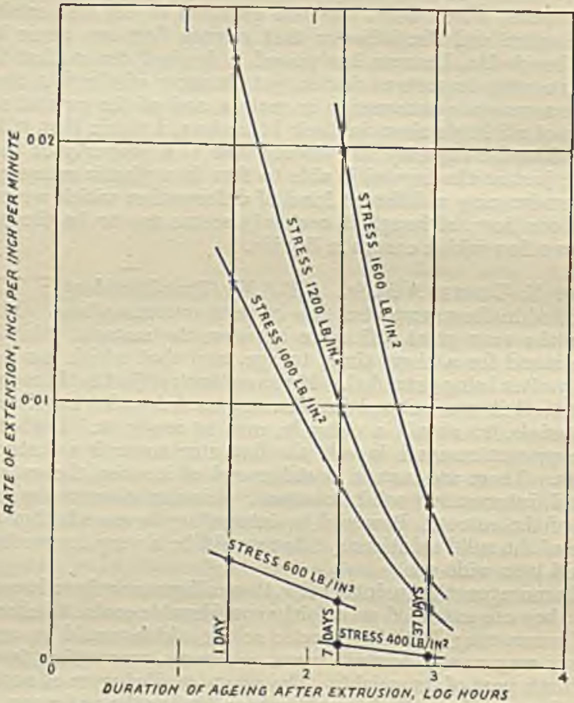


FIG. I.

Dr. C. H. DESCH,* F.R.S. (Vice-President): I have followed with very great interest the work which Mr. Pearson has carried out on these extruded metals on account of the novel methods which he has adopted. I should like to refer here to the work of Andrade, which has been strangely overlooked by so many writers on deformation, but which is actually fundamental. Although many people had carried out experiments on the stretch of specimens under constant load, Andrade was the first to use constant stress, which he achieved by using a hyperbolic weight immersed in water. Mr. Pearson has adopted the very similar plan of using a hyperbolic drum over which his cord is wound.

With regard to the mechanism of the flow, we are dealing here with soft substances, made soft by the process of extrusion, and, although it has been pointed out that the bismuth–tin eutectic is brittle in the cast condition, yet

---

* Superintendent, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

when it is extruded there is this extraordinary amount of ductility. It is very interesting to compare a substance of that kind, which is evidently quite different from a hard metal at the ordinary temperature, with a soft substance of crystalline structure, but yet showing no crystal grains. The substance to which I am referring is baker's dough. In some recent papers by Drs. Schofield * and Blair, of Rothamsted, the mechanical properties of baker's dough have been very carefully studied; and when you find that the work-hardening curves are just like those of metals, and the hysteresis loops are much the same in form, you begin to think that you must be careful about constructing theories of deformation of metals which depend on slip layers, because in baker's dough, although the material is crystalline, the crystals are in the nature of very long fibres, entangled and holding a network of starch crystals between them. If we are to get a theory of plastic viscous flow, we shall have to take into account those materials as well as the metals themselves.

Andrade's distinction between that flow, which he calls the β flow, which comes to rest after a short time, and the viscous flow, which continues with time, is extremely important and sometimes overlooked. One would not expect, of course, to get perfect agreement with a formula for viscous flow in the case of metals, because of the recrystallization which occurs; so one must not be too disappointed if a mathematical formula when applied fails to fit all the results; but the work that has been done by the author, and some of the things which have come out in the discussion have, I think, helped enormously in the study of this particular problem.

Mr. Pearson (*in reply*): Time will not permit me to deal with all the points which have been raised; I will merely try to indicate the replies to some of the main ones, and deal with other points in writing. Referring first of all to Professor Turner's query regarding the object of this work, it arose really in following up work by Dr. Smythe and myself on the extrusion of pure metals. During some experiments on the extrusion of eutectics I came across this remarkable flow property, and the deformation occurring being not of the usual type, it appeared to be worth investigating.

The question of an initial flow has been mentioned. I should point out that the total elongations are very great, and the cathetometer used did not record very small changes in length; but I think that it is true, probably, that there is a very small initial flow in some cases.

Turning to Andrade's work, in addition to work on pure metals, he did some experiments on solder wire, which might be taken to have been extruded, although that is not definitely indicated, and found a very high degree of viscous flow and a very small initial β flow; and that seems to agree with what I have observed.

With regard to the question of size of grain at beginning and end of a given stretching experiment, so far as it was possible to tell, the individual grains were the same at the beginning and the end of the process, although I have not actually made any tests with marked grains. The size is certainly the same, I will not say from the beginning, because they are not visible until a certain amount of elongation has occurred, but they remain the same through the whole of the stretching so far as one can tell, and I think that they are the same individuals; that is to say, there is no continuous recrystallization and reformation. That would certainly be indicated by a change in the grain-size. It is possible, for example, to take a piece of rod which has been annealed at 100° C., and which has therefore reached a certain grain-size and is comparatively free from ageing effect, and to determine the rate of flow during

---

* *Proc. Roy. Soc.*, 1932, [A], 138, 707; 1933, [A], 141, 72.

40 per cent. or so elongation, and then to subject that specimen to a further annealing for some hours at 100° C. and again take the rate of flow, which is found to be almost the same. There is a very small variation in rate sometimes a little more and sometimes a little less. The grain-size is unchanged: in fact, the grain structure developed by the first stretching goes on developing. I think that is clear evidence that there is no recrystallization.

CORRESPONDENCE

Dr. Fell (*in reply*): Concerning Professor Gilbert Cook's welcome contribution to the discussion, it is my opinion that further experimental observations, within and without the range of stress given in Table V of Mr. Pearson's paper, are necessary before the nature of any connection between the individual experimental observations may be understood. Thus the purpose in presenting Fig. 2 (p. 129) was to suggest that a change occurs in the mode of flow of the metal in the range of stress given in Table V; this was supported by the fact that the curves were not linear: the curves are not of the simplest form. At present, it seems this is all that can be said concerning any change, if it exists. On pp. 128 and 129, the curves in Fig. 2 were assumed, for purposes of illustration, to consist each of two straight portions, and in Fig. D, Professor Cook has considered a straight portion corresponding with an upper range of stress. Both the latter method and my own seem admissible, and according to Fig. D, the linear portion for the upper range of stress ceases to fit the points of experimental observation at a lower value of the stress than as in the method adopted in Fig. 2. It is not clear how an indication of the existence of plasticity as well as viscosity may occur as a result of the deviation at the lower values of the stress, and not at the upper, as mentioned by Professor Cook, because all the experimental observations of Table V, from which Figs. 2 and D are prepared, represent flow of the metal according to the formula $l = l_0 e^{kt}$.

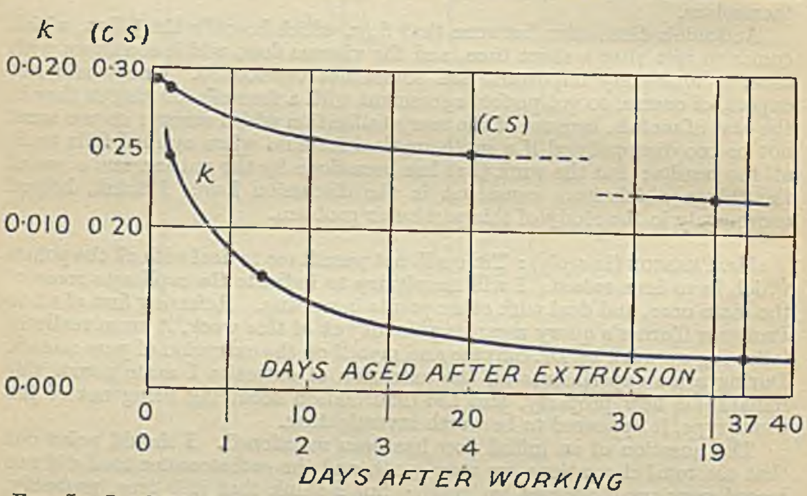


Fig. J.—Lead–Tin Eutectic. Comparison of the Constants k and (cs), making use of the Results in Fig. 1, p. 128.

In connection with Mr. Hargreaves's references to my paper, the curve for (cs), prepared from the results of Fig. 1, p. 128, is shown in Fig. J, including the curve for k for purpose of comparison, and the same general slope of these two curves will be seen.

The constants c and s have in themselves no strict physical meaning, they merely form part of formula (1) on p. 125, and in that way serve a useful purpose. Reference may be made to Figs. 4 and 5 of Mr. Hargreaves's paper "The Ball-Hardness and the Cold-Working of Soft Metals and Eutectics,"*

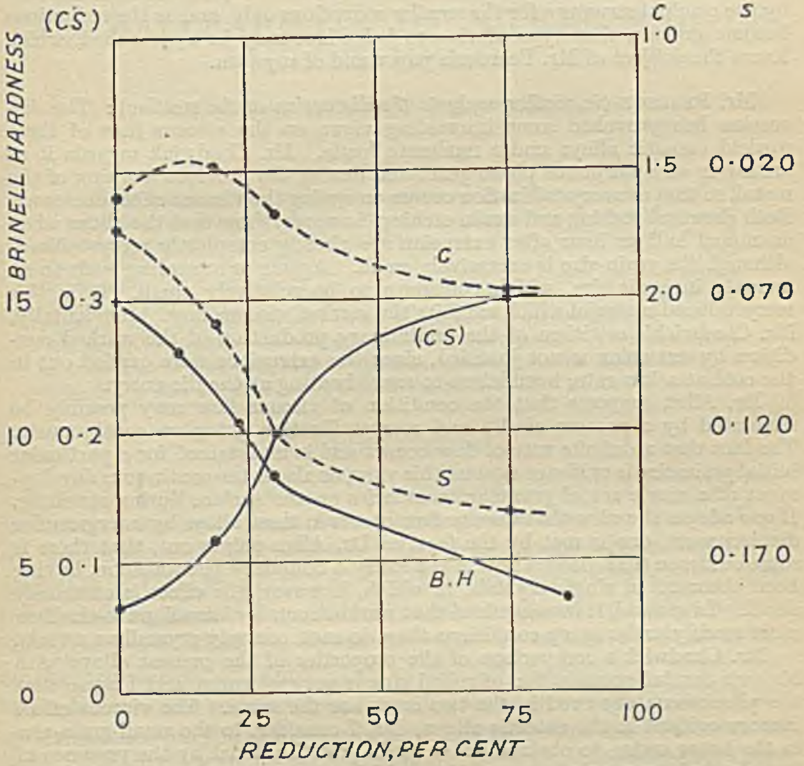


Fig. K.

where it will be seen that as the reduction per cent. of the lead–tin and cadmium–tin eutectics increases, the value of c appears to decrease to a minimum, and then increases, whilst the value for s continually increases; this is interesting. The presence of this minimum may suggest a smaller diameter of the impression near the start of the test than occurs in the case of the neighbouring reductions given in the two Figures, although it would appear impossible to be more precise, since the values of the diameters of the impressions when $t = 1$, and for some seconds after, are lacking.

As a further example of the (cs) method of plotting, the minima in the values for c, indicated in Figs. 4 and 5, become removed on multiplying

---

* *J. Inst. Metals*, 1928, 39, 310, 316.

the value of c by the corresponding value of s, which in the case of Fig. 4 (for lead–tin eutectic) is shown in Fig. K. This figure reveals a correspondence between the curve for Brinell hardness (30 seconds duration of loading) and the curve for (cs); the variation of c and s is shown in the figure by curves in the form of broken lines. The curve for (cs) shows a point of inflexion, and the cause of this is probably related to the greater slope and unevenness (occurring between 0 and roughly 40 per cent. reduction, and during which the original eutectic structure is being removed) in the curves for log c, s, and Brinell hardness in Figs. 4 and 5. Thus the flow of the metal may be more affected by the original structure for the smaller reductions only, and as the reductions become greater, that type of viscous behaviour may be approached, which forms the subject of Mr. Pearson's paper and of my own.

Mr. PEARSON (*in further reply to the discussion at the meeting*): The discussion has provoked some interesting views on the viscous flow of these worked eutectic alloys under moderate loads. Mr. Chadwick regards it as arising in an amorphous phase generated during the previous working of the metal, so that as recrystallization occurs on ageing the viscous effect decreases. Both chemical etching and strain etching, however, show that the alloys when examined half an hour after extrusion are already completely recrystallized, although the grain-size is excessively small. Ageing or annealing leads to an increase in grain-size, which continues to be relatively small. It is this recrystallized material which exhibits the marked viscous flow. Incidentally, Mr. Chadwick's criticism of the preliminary production of the worked condition by extrusion is not justified, since the extrusions were carried out in the cold at a low rate, insufficient to cause heating at the die entry.

Dr. Allen suggests that the condition of viscous flow may possibly be simulated by a process of slip and recrystallization going on continuously. The fact that a definite rate of flow occurs and is maintained for a particular initial grain-size is evidence against this view, as also is the continuous development of a single set of granular boundaries on the surface during straining. If one adopts the view that viscous flow occurs in these alloys by intergranular displacement, one is met by the fact, as Dr. Allen points out, that there is some evidence that viscous flow is not solely a boundary phenomenon, having been observed in single crystals, in which, however, the effect is extremely small. In general, it is recognized that worked metals of small grain-size flow more readily under creep conditions than do cast, coarsely crystalline metals.

Mr. Chadwick's comparison of the properties of the present alloys with his own careful examination of rolled zinc is very welcome, and I agree that the phenomena observed in the two cases are the same. The viscous effect is more evident in the eutectic alloys, due, I consider, to the small grain-size in the latter owing to obstruction to grain growth offered by the presence of two closely intermingled phases. It would be of great importance if a limiting stress for flow, as suggested by Professor Cook's examination of the data, could be established. At present I can only affirm that flow is continuous at stresses below 64 lb./in.^{2}, which he has deduced as a possible limit. Dr. Desch's reference to the similarity in the behaviour of baker's dough and metals is of great interest, and serves to remind one that many difficulties have yet to be overcome in providing a complete explanation which must cover the process of deformation of such diverse substances.

THE MALLEABILITY OF NICKEL AND OF MONEL METAL.*

By OWEN W. ELLIS, M.Sc.,† Member.

Synopsis.

A brief review of the literature is followed by a discussion of the effect of annealing temperature on the hardness of two rods—½ in. and 1 in. in diameter, respectively—of cold-drawn nickel, which were the subject of malleability tests at temperatures varying from 250° to 1100° C. The relationship between energy of blow and percentage reduction in height of normal ½-in. samples is demonstrated, as is the influence of the initial hardness of the same material on its resistance to deformation at 750° C. The paper concludes with a description of experiments: (1) on the effect of annealing normal samples of the 1-in. material on its malleability at 800°, 900°, and 1000° C., and (2) on the malleability of Monel metal.

I.—Introduction.

The effects of temperature on the mechanical properties of nickel and of Monel metal have been the subject of considerable investigation. As Crawford and Worthington[1] have so completely covered the literature in their recent paper, "Nickel and Nickel Alloys other than the Nickel–Chromium–Iron Group," it is unnecessary to review it here. Some reference, however, should be made to papers by Sauerwald[2] on the dependence on temperature of the drop-hardness of nickel, and by Robin[3] on the resistance of steels to plastic deformation, which are both missing from the bibliography given by Crawford and Worthington at the end of their paper, and which are both of importance to those interested in the malleability of nickel, if not of Monel metal. Attention should also be directed to the recent work of Ransley and Smithells.[4]

Sauerwald's paper, which dealt with the work of Frischnich and Neuendorff on the drop-hardness of pure nickel (*Reinnickel*), may well be referred to first. The nickel employed in their experiments was of unstated composition. It had a Brinell hardness number of 87 (applied load not mentioned) and had been rolled and fully annealed. The

---

* Manuscript received August 3. Presented at the Annual General Meeting, London, March 8, 1934.

† Director of Metallurgical Research, Ontario Research Foundation, Toronto, Canada.

samples used in the drop hardness test were cylinders 13 mm. high and 13 mm. in diameter. They were heated individually, together with a small anvil, in a furnace placed near the testing machine. When sample and anvil had reached a desired temperature, they were removed together from the furnace and placed in the machine, where the sample was tested for hardness by means of a 10-mm. ball integral with a tup which, together with the ball, weighed 1377 kg. Tup and ball were allowed to fall through a height of 444–445 mm. The results of the Frischnich and Neuendorff tests are given in Table I. From these Sauerwald concluded that the sharp fall in the hardness of nickel between 300° and 400° C. was due to the magnetic transformation, whilst the maximum at 450° C. was a phenomenon similar to the blue brittleness of iron. The cause of the increase in hardness at 812° C., Sauerwald considered, was uncertain.

TABLE I.—*Drop-Hardness of Nickel at Various Temperatures.*
(Sauerwald, *loc. cit.*)

Temperature, ° C.	Drop-Hardness.	Temperature, ° C.	Drop-Hardness.
20	262	449	218
113	250	529	208
201	250	610	203
289	245	711	170
329	220	812	175
388	204	914	143

Ransley and Smithells, in their work on the tensile strength of nickel wires of various compositions at different temperatures, found that, no matter what was the composition of the nickel, the tensile strength–temperature curve showed an inflection at 300°–450° C. The inflection was much less pronounced in the curve for some nickel of exceptional purity, which they had prepared. In their paper they suggest that the inversion is practically absent from this curve, although careful examination of the curve itself makes it difficult to accept their view. In none of their curves do inversions appear corresponding with those reported by Sauerwald as occurring at 812° C.

Robin's experiments were carried out on normal samples * cut from 15-mm. (0·591-in.) bars. These samples were forged under a hammer which fell from a height of 2 m. (6·56 ft.). By interpolation Robin estimated the amount of energy required to reduce the sample by 20 per cent. of its initial height. The results of his tests on three types of nickel (referred to respectively as "forgeable nickel," "commercial nickel worked," and "commercial nickel annealed") are given in

---

* Samples of which the heights and diameters are equal.

Table II. It will be seen that Robin's experiments were relatively few; nevertheless, there is sufficient evidence to show that an inversion occurs in the malleability–temperature relationship of nickel in the region 300°–450° C.

Table II.—*Malleability of Nickel of Various Types.*

(Samples tested, 15 mm. × 15 mm.)
(Robin, *loc. cit.*)

Forging Temperature, ° C.	Energy of Blow in Ft.-lb. Required to Produce a 20 Per Cent. Reduction in Height of Sample.		
	A.	B.	C.
15	290	234	...
20	...	...	500
100	257	...	...
200	234	216	445
300	216	209	432
500	198	187	335
700	158	...	189
900	144	...	130

A. Forgeable nickel.
B. Commercial nickel annealed.
C. Commercial nickel worked.

The maximum temperature used by Robin in his experiments was 900° C., a temperature somewhat below that ordinarily employed in the forging of nickel, hence, the author considered that it might be of interest to determine the malleability of nickel at somewhat higher temperatures than those used by Robin, and for this purpose ½-in. and 1-in. rods of cold-drawn nickel were obtained, which were tested by methods described in some detail later in this paper. Chemical analyses, made by Mr. J. R. Gordon, of the Ontario Research Foundation, showed the composition of these rods to be as follows:

	½-In. Bar Per Cent.	1-In. Bar, Per Cent.
Cobalt	0·46	0·44
Manganese	0·20	0·12
Carbon	0·16	0·16
Iron	0·16	0·18
Copper	0·02	0·03
Silicon	0·01	0·01
Nickel	difference	difference

II.—Effect of Annealing Temperature on Hardness of Cold-Drawn Nickel Rod.

To determine the effect of annealing on the hardness of the cold-drawn nickel rod used in the malleability experiments, normal samples were cut from the ½-in. and 1-in. bars. The ½-in. samples were heated to, and held at, the various annealing temperatures during periods of 10 minutes, at the end of which they were quenched in water at about 22° C. The 1-in. samples were similarly treated after a 30-minute anneal (30 minutes from the time of introduction into the furnace to the time of quenching). The ½-in. samples were treated simultaneously with those of the same dimensions used in the forging tests; the 1-in. samples were treated independently. After the samples had been annealed, they were tested for hardness. The tests on the ½-in.

Table III.—*Vickers Hardness Numbers of Annealed Samples of ½-in. Diameter Cold-Drawn Nickel Rod.*

(Original Hardness Number, 235.)

Annealing Temperature, ° C.	Vickers Hardness Number.	Annealing Temperature, ° C.	Vickers Hardness Number.
263	244	803	150
326	241	822	138
459	232	842	137
523	229	878	128
603	228	904	122
629	219	936	123
654	226	946	126
666	227	972	122
705	219	1000	120
728	208	1019	118
750	204	1048	122
772	198	1075	116
790	194	1094	111

(Time of anneal, 10 minutes.)

Table IV.—*Brinell Hardness Numbers of Annealed Samples of 1-in. Diameter Cold-Drawn Nickel Rod.*

(Original Hardness Number, 215.)

Annealing Temperature, ° C.	Brinell Hardness Number.
265	224
358	226
412	216
505	214
541	198
577	206
668	206
692	202
800	163
900	113
1000	108

(Time of anneal, 30 minutes.)

samples were made in a Vickers machine, a load of 50 kg. and a 136° diamond pyramid being used. Those on the 1-in. samples were carried out in a Brinell machine, using a load of 3000 kg. and a 10-mm. Carboloy ball. The results of the hardness tests are given in Tables III and IV and are shown graphically in Fig. 1.

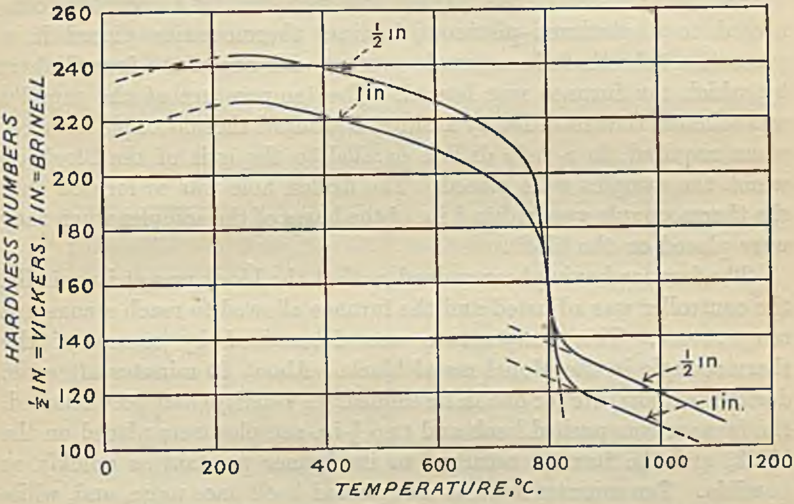


Fig. 1.

Under the conditions imposed in these experiments, the temperature range of softening was much the same for both sizes of bar, the upper limit of the range being about 860° C., both for the ½-in. bar (initial hardness, 235; annealing time, 10 minutes) and for the 1-in. bar (initial hardness, 215; annealing time, 30 minutes). The upper limit of the range was, if anything, slightly higher for the 1-in. bar.

III.—Malleability of Cold-Drawn Nickel Rod at Various Temperatures.

The malleability experiments were carried out on ½-in. and 1-in. normal samples. In most cases, the tests on the ½-in. samples were made simultaneously with the quenching operation described in Section II. To make this possible the following procedure was adopted: the samples were heated for forging and quenching in a horizontal Globar tube furnace fitted with a 1·5-in. I.D. silica tube closed at one end. They were supported, side by side, on the diametrical section of a 1-in. hemicylindrical Monel metal block, which fitted snugly and was firmly secured to one end of a length of stainless steel of semi-annular cross section (a 1-in. I.D. tube bisected along its axis). The other end of the half-tube of stainless steel, supported on a stand outside the furnace, was so arranged that the furnace could be moved backwards and forwards parallel to the axis of the Monel metal block on which the samples were placed with their axes at right angles to that of the furnace.

The temperature of the furnace was regulated by a controller connected to a platinum–platinum/rhodium thermocouple placed in a protection tube that almost made contact with one of the four Globars by which the furnace was heated. The temperature of the samples was taken as that recorded by a Chromel–Alumel thermocouple inserted, when required, in a hole drilled parallel to the axis of the block on which the samples were placed. The drilled hole was so located that the thermocouple was within ⅛ in. of the bases of the samples when they were placed on the block.

The furnace having been moved so that the block was at its middle, the controller was adjusted and the furnace allowed to reach a constant temperature. This temperature was determined by means of the thermocouple in the Monel metal block. About 10 minutes after the desired temperature (or one in its immediate vicinity) had been reached, the furnace was pushed back and two ½-in. samples were placed on the block, and the furnace returned to its former position as quickly as possible. Ten minutes later, it was pushed back once more, and, while one operator quenched one of the samples, another at the same time forged the second sample under the drop hammer. The height of the drop in the experiments on the ½-in. samples was 8½ in., the energy of the blow being 80 ft.-lb.

For the 1-in. samples, a 1-in. normal Monel metal cylinder was drilled axially to a depth of ⅞ in., and was so secured to the stainless steel half-tube already described that the sample to be heated for annealing or forging could be dropped into the space formerly occupied by the hemi-cylindrical Monel metal block used to support the ½-in. samples. In the hole in the Monel metal cylinder was placed, when required, the Chromel–Alumel thermocouple used for determining the temperature of the sample, one end of which was within about ⅛ in. of the cylinder containing the thermocouple. The axis of the sample was, of course, in line with that of the cylinder. Provision was made for the small tongs used in lifting the sample from the furnace to the anvil to grip it without difficulty when heated.

The sequence of operations for the 1-in. samples was as follows: (1) the controller was set to the desired temperature; (2) the furnace was allowed to reach the desired temperature and held there for 10 minutes; (3) the furnace was pushed back as rapidly as possible;

(4) the sample was placed in position next to the Monel metal cylinder containing the recording thermocouple; (5) the furnace was pushed forward as rapidly as possible until the sample was at the centre of the furnace; (6) after 30 minutes, the furnace was pushed back, the sample quickly removed, and quenched or forged; (7) when the sample had cooled, its height was measured.

The results of the forging experiments on the ½-in. and 1-in. samples are given in Tables V and VI, respectively. The malleability–tem-

Table V.—*Malleability of ½-in. Normal Samples Cut from Cold-Drawn Nickel Rod.*

(Malleability of Rod as Received, 5·4 per Cent.)

Forging Temperature, ° C.	Reduction in Height, Per Cent.	Forging Temperature, ° C.	Reduction in Height, Per Cent.
263	6·2	822	17·0
326	6·8	836	17·6
459	7·2	842	17·0
523	8·0	868	17·6
603	8·4	878	17·2
629	8·4	896	18·2
654	9·0	904	19·0
666	9·2	936	19·8
705	9·6	946	20·0
728	10·6	972	20·4
750	11·4	1000	21·0
772	12·0	1019	21·6
790	12·6	1045	22·0
803	13·4	1075	23·2
821	15·6	1094	23·8

Table VI.—*Malleability of 1-in. Normal Samples Cut from Cold-Drawn Nickel Rod.*

Forging Temperature, ° C.	Reduction in Height, Per Cent.
633	7·0
666	7·1
690	7·6
718	8·2
744	8·7
764	9·3
792	10·4
817	13·4
842	15·2
867	15·8
903	16·6
963	18·5
993	19·0
1050	20·9
1106	22·4

perature relationships for both series are shown in Fig. 2. Probably the most interesting features of the curves in Fig. 2 are the sharp inflections which correspond closely with the upper limits of the temperature ranges of softening for both sizes of bar under the conditions imposed on them in these experiments.

Less definite is the lower limit of the temperature range of what might be termed "rapid softening" for the ½-in. bar. This is at about 500° C., where the linear and curved parts of the graph meet.

The experiments carried out within the range 20°–600° C. were insufficient to determine the effect of the 300°–450° C. inversion in mechanical properties on the malleability of the metal, which, however, for all practical purposes may be assumed to increase in direct proportion to temperature from 20° to 600° C., as shown in Fig. 2.

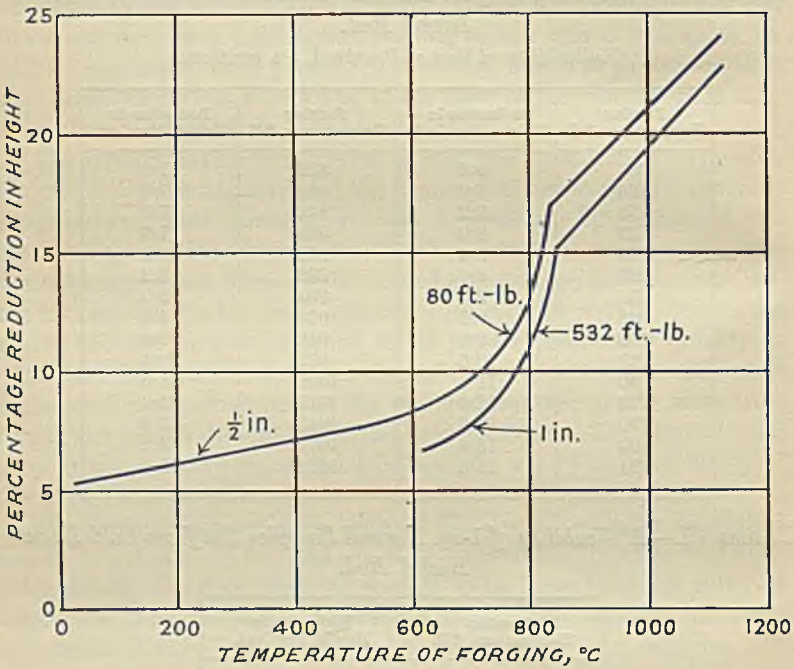


Fig. 2.

IV.—Relationship between Energy of Blow and Percentage Reduction in Height of Sample at Various Temperatures.

A series of experiments was carried out, at six different temperatures, on normal samples cut from the ½-in. rod. These samples were subjected to blows of different energy content, the energy being varied by altering the height of fall of the hammer. The results of these experiments are given in Table VII and are shown graphically in Fig. 3.

TABLE VII.—*Relation between Energy of Blow and Percentage Reduction in Height of ½-in. Normal Samples of Cold-Drawn Nickel Rod Forged at Different Temperatures.*

Temperature, °C.	Percentage Reduction in Height of Sample.				
	80 Ft.-lb.	193 Ft.-lb.	306 Ft.-lb.	419 Ft.-lb.	532 Ft.-lb.
603	8·4	20·2	30·0	36·8	44·4
705	9·6	22·8	33·6	41·8	49·2
790	12·6	27·2	39·2	48·0	55·6
904	19·0	34·6	46·6	55·0	61·2
1000	21·0	38·4	51·2	58·4	65·2
1094	23·8	42·8	55·2	64·2	69·2

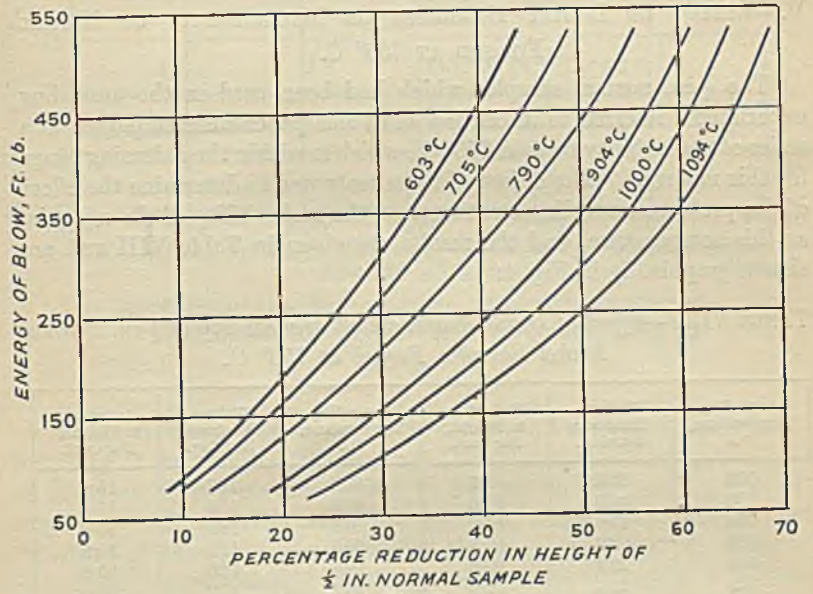


FIG. 3.

The author has up to now been unable to find a satisfactory equation for the graphs in Fig. 3—such, for example, as he found to apply to a somewhat similar series of curves for straight carbon steels.[5] There is a distinct difference, however, between the slopes of the curves for the samples forged (*a*) at temperatures below, and (*b*) at temperatures above, the softening range.

According to Tresca's theorem, the energy required to reduce the height of a 1-in. normal sample by a definite percentage at a given temperature should be eight times that required to deform a ½-in. normal sample under the same conditions. That this is true of the samples investigated by the author can be shown by comparing values presented in Figs. 2 and 3. To produce, for example, a 22 per cent. reduction in the height of a 1-in. normal sample at a temperature of approximately 1095° C. requires 532 ft.-lb. (see Fig. 2). To produce the same reduction in the height of a ½-in. normal sample should require, according to Tresca, 532/8 = 66½ ft.-lb. Reference to Fig. 3 will show that 68 ft.-lb., approximately, were required to reduce a ½-in. normal sample by 22 per cent. in height at 1094° C. One is led to assume, then, that nickel obeys Tresca's law, *viz.*, the energy required to deform similarly-shaped bodies by a certain percentage varies as the volumes of the bodies concerned.

V.—EFFECT OF INITIAL HARDNESS ON MALLEABILITY OF NICKEL FORGED AT 750° C.

The ½-in. normal samples which had been used in the annealing experiments referred to in Section II of this paper were employed in a series of malleability tests at 750° C., which is within the softening range for this material. The object of these tests was to determine the effect of the previous annealing treatment on the malleability of the material at this temperature, and the results are given in Table VIII and are shown graphically in Fig. 4.

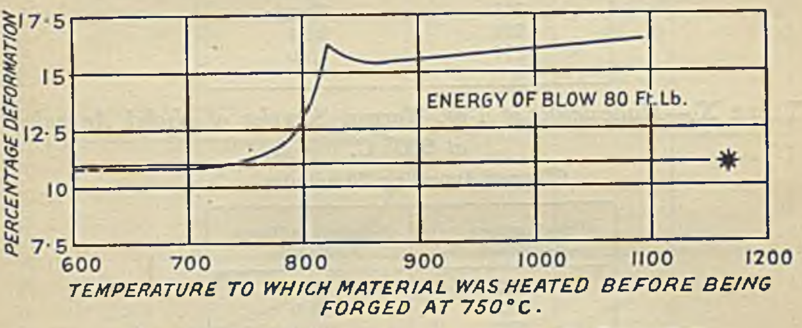
TABLE VIII.—*Effect of Initial Hardness on Malleability of ½-in. Normal Nickel Samples Forged at* 750° *C.*

Annealing Temperature, ° C.	Vickers Hardness Number.	Reduction in Height, Per Cent.	Annealing Temperature, ° C.	Vickers Hardness Number.	Reduction in Height, Per Cent.
603	228	9·8	842	137	15·6
629	219	10·8	878	128	15·6
654	226	10·8	911	122	15·6
666	227	10·8	936	123	15·8
696	219	10·8	946	126	15·8
728	208	11·0	972	122	16·0
750	204	11·2	1000	120	16·1
772	198	11·6	1019	118	16·0
790	194	12·0	1048	122	16·2
803	150	13·9	1075	116	16·4
822	138	16·2	1094	111	16·4

(Time of heating to and holding at 750° C. prior to forging, 10 minutes.)

It appears that the annealing of ½-in. normal samples for 10 minutes (cf. section II) at temperatures *below* 750° C. (the forging temperature) has little or no effect on the malleability of the metal *at* 750° C. When the annealing temperature is raised *above* 750° C., the malleability of the metal *at* 750° C. is profoundly affected; it becomes increasingly malleable as the annealing temperature is increased from about 750° C. to about 820° C. This temperature (820° C.) is about 40° C. below the upper limit of the softening range. It is the temperature at which the precipitous change in hardness due to annealing (represented by the almost vertical portions of the hardness–temperature curves in Fig. 1) is completed.

Annealing at temperatures between 820° and 860° C. increases the resistance of the metal to plastic deformation at 750° C., so that samples which have been annealed at 860° C. are more resistant to deformation at 750° C. than samples which have been annealed at temperatures between 820° and 860° C.



✱ Percentage Deformation of sample forged at 750°C. without previous treatment (cf Fig. 2.)

FIG. 4.

Since the temperature of 750° C. is within, and not above, the softening range of the material, the forging of samples at this temperature has an effect on their structure similar to, but not so profound as, that of forging at temperatures below the softening range (cold-work). The structure of samples annealed within the range 750°–820° C. changes apparently with increasing annealing temperature in such a way that hardening due to cold-work during forging at 750° C. does not affect the continuity of the malleability–annealing temperature curve within this range. The structure of samples annealed within the range 820°–860° C., however, changes relatively so little with increasing temperature that hardening of such samples due to cold-work during forging at 750° C. reduces their malleability below what might be expected, and gives rise, therefore, to the sharp inversion in the malleability–annealing temperature curve at 820° C.

VI.—EFFECT OF ANNEALING COLD-DRAWN NICKEL ON ITS MALLEABILITY AT VARIOUS TEMPERATURES.

Samples cut from the 1-in. rod were annealed for ½ hr. at 800° C., 900° C., and 1000° C., respectively, and were afterwards forged at a series of temperatures. The results of the tests on these samples are given in Tables IX, X, and XI, and are shown graphically in Fig. 5.

TABLE IX.—*Malleability of* 1-*in. Normal Samples of Nickel Annealed at* 800° *C.*

(Time of Annealing, 30 minutes.)

Forging Temperature, ° C.	Reduction in Height, Per Cent.
667	9·3
708	9·5
761	10·4
798	11·4
817	13·0

TABLE X.—*Malleability of* 1-*in. Normal Samples of Nickel Annealed at* 900° *C.*

(Time of Annealing, 30 minutes.)

Forging Temperature, ° C.	Reduction in Height, Per Cent.
667	13·7
692	14·0
722	14·4
749	14·7
778	14·9
806	15·2
838	15·8
868	16·1
902	16·8
919	17·4

TABLE XI.—*Malleability of* 1-*in. Normal Samples of Nickel Annealed at* 1000° *C.*

(Time of Annealing, 30 minutes.)

Forging Temperature, ° C.	Reduction in Height, Per Cent.
676	14·7
724	14·9
774	15·4
826	16·0
865	16·7
922	17·9
971	18·7

In Fig. 5, the continuous, heavy black line is the malleability–temperature relationship for the cold-drawn rod (cf. Fig. 2). The results of the forging tests are indicated by closed and open circles.

It will be noticed from Fig. 5 that annealing at 800° C. for ½ hr. increases the malleability of the metal at all temperatures up to about 800° C., above which the malleability–temperature relationship for both the cold-drawn and the annealed materials is the same. Annealing at 900° C. for ½ hr. increases the malleability of the material at all temperatures up to about 900° C., above which the malleability–temperature relationship for both the cold-drawn and the annealed materials is the same. Annealing of the metal at 1000° C. for ½ hr. is generally similar in its effects to annealing at lower temperatures.

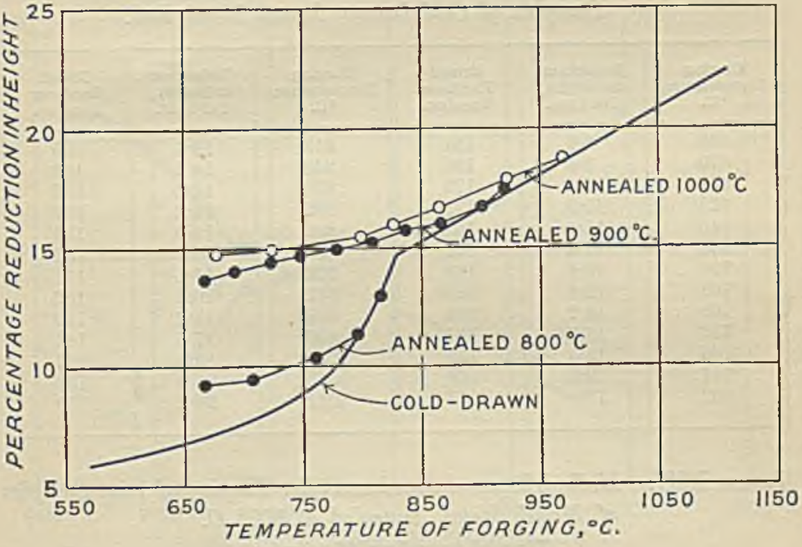


FIG. 5.

It appears that annealing at any temperature above the lower limit of the softening range increases the malleability of the metal at all forging temperatures up to the temperature of annealing, beyond which the malleability–temperature relationship for both the cold-drawn and the annealed materials is the same.

VII.—MALLEABILITY OF MONEL METAL.

The forging experiments on the Monel metal were made on 1-in. round samples of cold-drawn stock, having a Brinell hardness number of 231. The methods of heating, forging, &c., were those adopted for the 1-in. nickel samples. The material was of the following composition :

	Per Cent.
Nickel	67·59
Manganese	1·26
Iron	1·05
Silicon	0·05
Copper	difference

TABLE XII.—*Malleability and Hardness after Forging of* 1-*in. Normal Samples of Cold-Drawn Monel Metal Rod.*

Forging Temperature, ° C.	Reduction in Height, Per Cent.	Brinell Hardness Number.	Forging Temperature, ° C.	Reduction in Height, Per Cent.	Brinell Hardness Number.
648	8·6	181	818	14·1	155
670	8·6	181	848	14·5	152
699	9·3	173	850	14·6	152
723	10·9	171	865	14·8	157
745	11·8	169	880	15·0	153
753	12·7	161	890	15·2	152
758	13·1	163	909	15·1	151
761	12·6	163	942	16·2	152
768	13·2	163	979	17·0	140
772	13·5	161	993	17·6	146
785	13·5	155	1038	18·8	137
791	13·8	160	1076	20·0	134
802	13·9	157	1087	20·2	130

TABLE XIII.—*Malleability and Hardness after Forging of* 1-*in. Samples of Monel Metal Annealed at* 900° *C.*

(Time of Annealing, 30 minutes.)

Forging Temperature, ° C.	Reduction in Height, Per Cent.	Brinell Hardness Number.
652	12·5	171
702	12·7	168
730	13·3	166
753	13·4	156
778	13·6	163
801	13·9	162
812	14·1	164
845	14·8	163
853	14·9	154
892	15·6	161
921	15·8	161
945	16·6	154
967	16·5	161
993	17·2	146
1046	18·8	147

The results of the malleability tests are given in Table XII, together with the Brinell hardness numbers of the samples after forging at various temperatures. The author is not satisfied that these hardness numbers can be considered as representing the hardness of the samples as a whole, but the values are given for what they are worth.

Table XIII shows the results of the malleability and hardness tests on samples which had been annealed at 900° C. for ½ hr. before forging.

All these results are shown graphically in Fig. 6, in which the continuous curves are the malleability–temperature and hardness-after-forging–temperature relationships for the alloy, whilst the closed and open circles represent the individual results of the malleability and hardness tests on samples which had been annealed at 900° C. before forging.

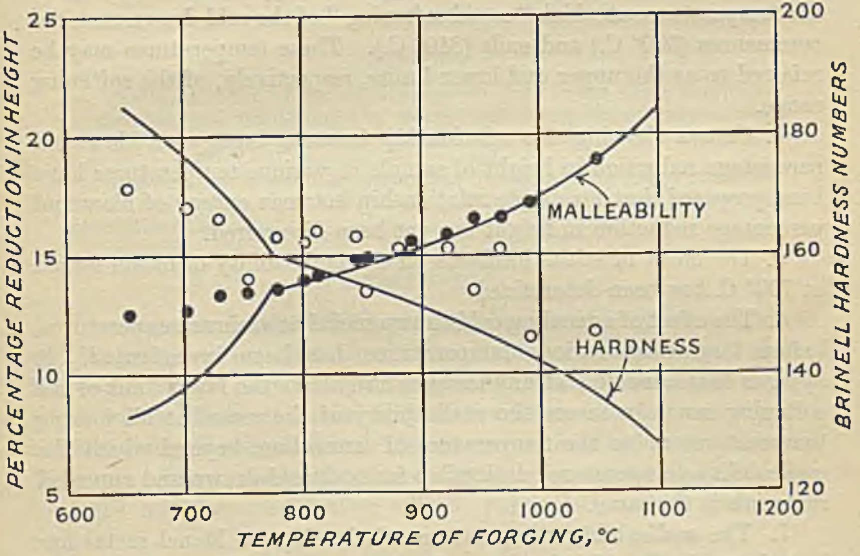


FIG. 6.

The upper limit of the softening range is as clearly defined in the malleability–temperature curve for Monel metal as in that for commercial nickel, the point being somewhat higher for the Monel metal.

It is of interest to note that the malleability of cold-drawn nickel over the range 600°–825° C. is somewhat less than that of cold-drawn Monel metal, but is appreciably greater than that of Monel metal at temperatures above the upper limit of the softening range for the relatively pure material.

SUMMARY.

1. The malleability of samples cut from two cold-drawn nickel rods has been determined over the temperature range 600°–1100° C.

2. The malleability–temperature relationship for the cold-drawn ½-in. material was found to consist of three portions: (*a*) a practically linear relationship over the temperature range 20°–500° C.; (*b*) a curved relationship over the temperature range 500°–840° C.; (*c*) a linear relationship over the range 840°–1100° C.

3. The points of intersection of the linear portions of the malleability–temperature curves with the curved portions appear to coincide with the temperatures at which "rapid softening" of the cold-drawn material commences (500° C.) and ends (840° C.). These temperatures may be referred to as the upper and lower limits, respectively, of the softening range.

4. Curves showing the relationship between energy of blow and percentage reduction in height of sample at various temperatures have been prepared, but no simple relationship between energy of blow and percentage reduction in height has yet been discovered.

5. The effect of initial hardness on the malleability of nickel forged at 750° C. has been determined.

6. The effect of annealing cold-drawn nickel at various temperatures, before forging at various temperatures, has been investigated. It appears that annealing at any temperature above the lower limit of the softening range increases the malleability of the metal at all forging temperatures up to the temperature of annealing, beyond which the malleability–temperature relationship for both cold-drawn and annealed materials is the same.

7. The malleability–temperature relationship for Monel metal has been determined, and it has been shown that malleability–temperature curves exist of the same type as those found for nickel.

ACKNOWLEDGMENTS.

The author wishes to express his appreciation of the assistance rendered him by Mr. J. Barbeau in the conduct of this investigation, and of the interest shown in it by Dr. H. B. Speakman, Director of the Ontario Research Foundation.

REFERENCES.

[1] Crawford and Worthington, *Symposium on Effect of Temperature on Properties of Metals, American Society for Testing Materials and American Society of Mechanical Engineers*, **1931**, 557–585.

[2] Sauerwald, *Z. Metallkunde*, 1928, **20**, 408–409.

[3] Robin, *Carnegie Schol. Mem., Iron Steel Inst.*, 1910, **2**, 70–270.

[4] Ransley and Smithells, *J. Inst. Metals*, 1932, **49**, 287–298.

[5] Ellis, *Metal Progress*, 1932, **22**, (3), 19–23; *Trans. Amer. Soc. Steel Treat.*, 1933, **21**, 673–707.

ALLOYS OF SILVER AND BERYLLIUM.*

By H. A. SLOMAN,† M.A., Member.

Synopsis.

The constitution of the whole range of alloys in the silver–beryllium system has been redetermined by thermal and micrographic analyses, and the results are recorded. Modifications and amplifications of Oesterheld's original constitutional diagram are proposed.

A description is given of new tarnish-resisting silver alloys obtained by the addition to silver and to some "standard" silvers of very small quantities of beryllium.

Introduction.

An investigation of the effects of the addition of beryllium to silver and its alloys was undertaken in the Metallurgy Department of the National Physical Laboratory as part of the work on beryllium and its alloys which has been carried out for the Minor Metals Committee of the Metallurgy Research Board, Department of Scientific and Industrial Research. The investigation was to include the addition of beryllium to high- and low-grade silver alloys, particularly those containing copper.

The results of the work on high-grade alloys are described in Part II of the present paper.

In the case of low-grade silver alloys containing copper, no advantages were found by the introduction of beryllium, but it was observed that within certain ranges of composition separation into two liquid layers occurred. This immiscibility disappeared on the addition of nickel.

These observations, which are collected in Table I, led to an investigation of the constitution of the silver–beryllium system, the results being described in Part I of the present paper.

---

* Manuscript received October 26, 1933. Presented at the Annual General Meeting, London, March 8, 1934.

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

TABLE I.

Number of Alloy.	Composition, by Weight.				Colour.
	Ag.*	Cu.	Be.	Ni.	
ABC1 . . .	50·07	48·91	0·98	...	Yellow
ABC2 . . .	49·83	48·62	1·50	...	Light yellow
†ABC3 Top layer .	33·03	64·50	2·51	...	Yellow (about same as ABC1)
†ABC3 Bottom layer	61·20	37·91	0·92	...	Pale yellow
†ABC4 Top layer .	19·63	75·00	5·33	...	Dark yellow
†ABC4 Bottom layer	76·52	22·81	0·72	...	Very pale yellow
ABCN4 . . .	49·63	42·42	1·66	6·29	,, ,,
ABCN7 . . .	49·88	41·28	2·57	6·31	,, ,,

* All alloys were made up to contain approximately 50 per cent. by weight silver.

† In ABC3 the volumes of the two layers were approximately equal. In ABC4 the volume of the top layer was approximately twice that of the bottom layer.

Various attempts were made to obtain homogeneous castings from ABC3 and ABC4, but without success. The sharpness of demarcation between the two layers is illustrated in Fig. 4 (Plate VI), which shows a typical " meniscus."

PART I.—*The Constitution of the Silver–Beryllium System.*

The unexpected immiscibility found in the case of certain of the ternary alloys of silver, copper, and beryllium led to a critical examination of the constitutions of the three binary systems, silver–copper, copper–beryllium, and silver–beryllium. The following question naturally presented itself. Does this immiscibility occur in one or other of the binary systems, or is it confined to a range of compositions in the ternary series?

The constitution of the silver–copper system has been investigated and confirmed by many workers, whilst Masing and Dahl [1] have recently re-determined the constitution of the copper–beryllium series, particularly in the copper-rich range. Their proposed equilibrium diagram differs from that given by Oesterheld,[2] but the evidence is undoubtedly in favour of the later work of Masing and Dahl.

With regard to the silver–beryllium system, it will be noticed that, in the ternary alloys shown in Table I which exhibited immiscibility, the beryllium content in the silver-rich layers was always very small, suggesting that a peculiarity might exist in the silver–beryllium series. The only available information about this system was contained in the paper by Oesterheld, referred to above, whose work was carried out in 1916 on very small specimens, owing to the scarcity of beryllium at that time. Oesterheld's diagram is reproduced in Fig. 1.

In the region 40–70 atomic per cent. beryllium, the liquidus is comparatively flat. It appeared possible that in this region the true liquidus might be as suggested in Fig. 2, indicating immiscibility in the liquid state, which might persist in the presence of a third metal. Moreover, a more accurate knowledge of the silver-rich alloys of the series was desirable in view of the investigation described in Part II of the present paper.

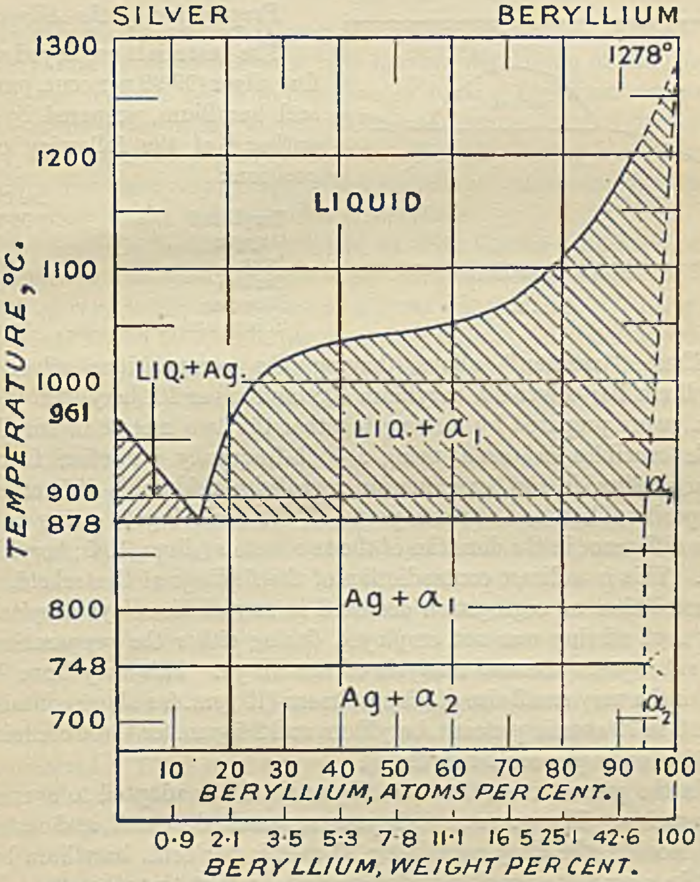


Fig. 1.

The constitution of the whole system was accordingly investigated by thermal and micrographic analyses. Owing to the enormous difference in the atomic weights of the two metals (silver, 108; beryllium, 9), all percentages are given as atomic, as these give a much clearer idea of the true composition of a particular alloy than do the weight percentages. The following formulæ are included to facilitate conversion of one to the other.

$$x = \frac{y}{12 - 0{\cdot}11y}; \quad y = \frac{12x}{1 + 0{\cdot}11x} \quad \text{where } y = \text{atomic per cent. beryllium. and } x = \text{weight per cent. beryllium.}$$

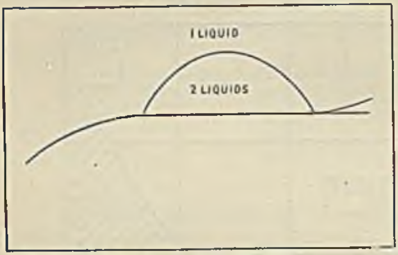


FIG. 2.

Preparation of the Alloys.

The materials employed were fine silver (99·99 per cent. purity) and beryllium, prepared by the author,[3] of the following composition:

	Per Cent.
Beryllium . . .	99·7
Oxygen . . .	0·2
Iron	0·01
Carbon . . .	0·05
Nitrogen . . .	0·005
Silicon and aluminium .	trace

Three "master" alloys, having the compositions silver 90, beryllium 10; silver 40, beryllium 60; and silver 10, beryllium 90 per cent., were prepared by melting together the two metals in beryllium oxide crucibles *in vacuo*, using a high-frequency induction furnace. After cooling, *in situ*, examination revealed considerable differences in composition between various parts of the same ingot, owing to the large difference in the densities of the two metals (silver, 10·5; beryllium, 1·8). This is a direct contradiction of the findings of Oesterheld, who reported that no segregation occurred in any of his alloys despite the fact that stirring was not employed during either the preparation or the subsequent thermal analysis of the alloys. This may have been due to the very small size of his specimens (10 grm. for alloys containing from 0 to 70 atomic per cent. beryllium and 2·5 grm. for those containing 70–90 atomic per cent. beryllium).

In the present case, the following method was adopted to overcome segregation. The "master" alloys were remelted, stirred, and cast into cold moulds, the alloy containing 10 atomic per cent. beryllium being held in a graphite crucible under graphite, whilst the other two alloys were contained in beryllia crucibles under a sodium fluoride–beryllium fluoride flux. The difficulty was, in this way, almost completely overcome, chemical analysis revealing only negligible differences in composition in different parts of individual castings.

The above procedure was adopted for the preparation from the "master" alloys of a series covering the whole composition range, the silver-rich alloys being melted in graphite crucibles under graphite, whilst beryllia crucibles and the flux were employed for those rich in beryllium. The alloys were cast in the form of cylinders about 2 cm. in diameter and 2 cm. in height, the weights varying from about 80 grm. (silver-rich) to about 10 grm. (beryllium-rich).

Thermal Analysis of Alloys.

In general, the relationships in the system are simple. The addition of beryllium to silver causes a very marked depression of the freezing point, the liquidus curve falling steeply until a beryllium content of 10·49 atomic per cent. is reached. This is the composition of the eutectic alloy, and its melting point is 881° C. With increasing beryllium, the liquidus first rises very sharply, then flattens out, and afterwards again rises rapidly to the melting point of beryllium.

The eutectic horizontal (solidus) at 881° C. can be traced on the beryllium side to about 85 atomic per cent. beryllium, where the arrest becomes very feeble and occurs at a lower temperature. It disappears altogether above 90 atomic per cent. beryllium. On the silver side, it was followed down to a beryllium content of about 3 atomic per cent., below which the arrest becomes ill-defined and occurs at a higher temperature.

An interesting observation noted by Oesterheld was confirmed. This is the occurrence in the beryllium-rich alloys of an arrest point at a temperature of 750° C. As one proceeds towards the silver end of the system, this point becomes more and more feeble, and cannot be found experimentally, in spite of many attempts, in alloys containing less than 50 atomic per cent. beryllium (Oesterheld traced it down to 65 atomic per cent. beryllium). In alloys in the range 92–98 atomic per cent. beryllium, this arrest occurs at lower temperatures. It is undoubtedly due to a solid transformation, and will be discussed later.

Attention may be directed to the practical difficulties which were encountered. These were entirely due to the serious effects of segregation. The actual analyses were carried out *in vacuo*, and in most cases it was impossible to obtain consistent results for the liquidus temperatures after the alloys had been twice melted. A very sharp arrest was always given by the first heating curve, and a somewhat diffuse one by the first cooling and second heating curves. By this time segregation had had sufficient opportunity to occur, and the results of the second cooling curve were quite inconsistent. Usually two arrests merging into each other occurred, which corresponded more or less with the true liquidus points of two alloys the compositions of which were one on each side of the particular alloy under consideration. The liquidus temperatures were therefore based on the results given by the first heating and cooling curves. In most cases confirmation was

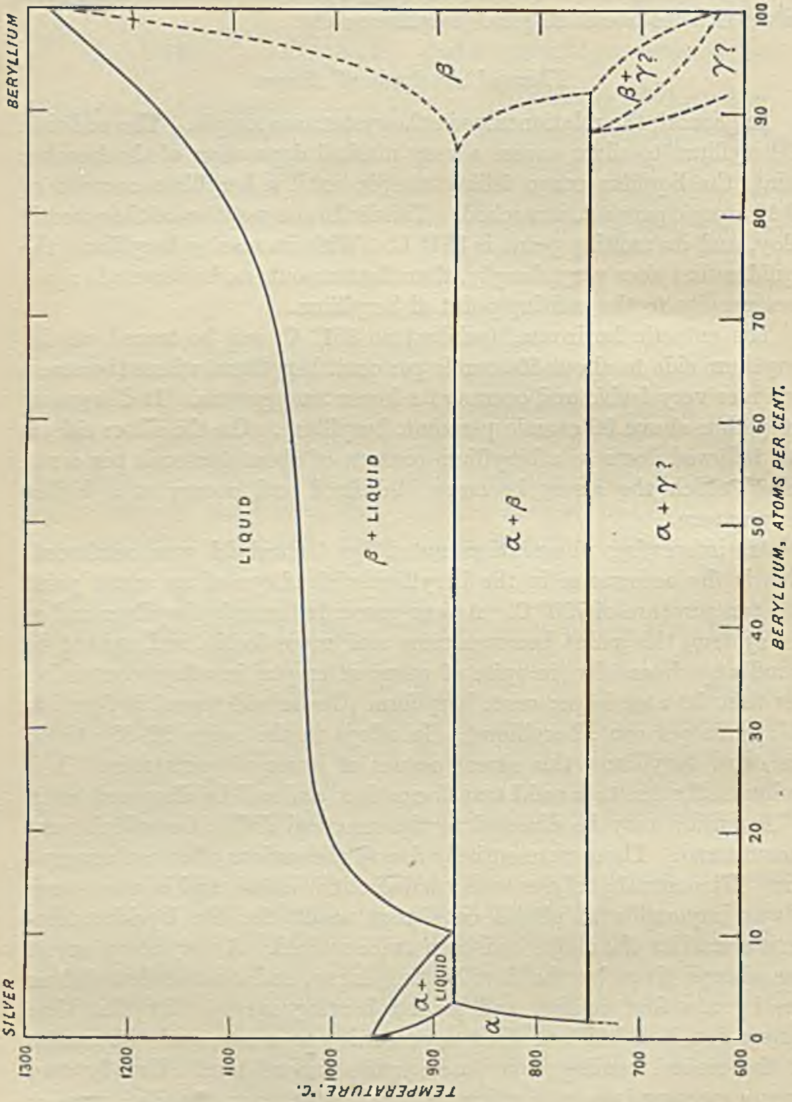

SILVER
BERYLLIUM
LIQUID
β + LIQUID
α + LIQUID
α
α + β
β
β + γ?
γ?
α + γ?
1300
1200
1100
1000
900
800
700
600
TEMPERATURE, °C.
0
10
20
30
40
50
60
70
80
90
100
BERYLLIUM, ATOMS PER CENT.

Fig. 3.

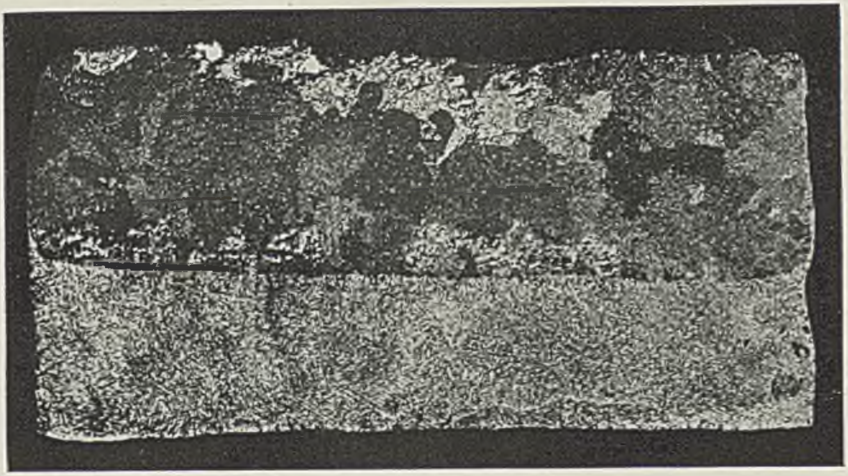


FIG. 4.

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

FIG. 6.—AB 3 (2·45 atomic-% Be). × 100.

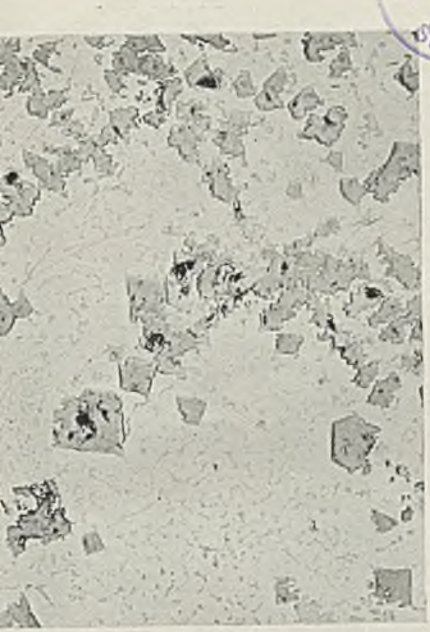
FIG. 7.—AB 5 (3·47 atomic-% Be). × 100.

FIG. 8.—AB 10 (10·49 atomic-% Be). × 50.

FIG. 9.—AB 10 (10·49 atomic-% Be). × 75

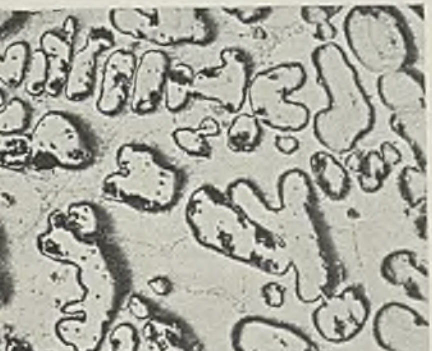
POLITECHNIKI
ŚLAS

PLATE VIII.



IG. 10.—AB 13 (19·94 atomic-% Be). × 75.

FIG. 11.—AB 19 (65·97 atomic-% Be). × 75.



IG. 12.—AB 21 (75·26 atomic-% Be). × 75.

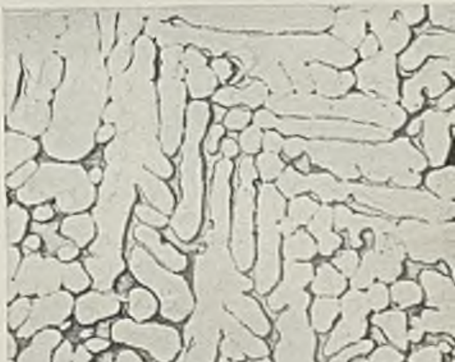
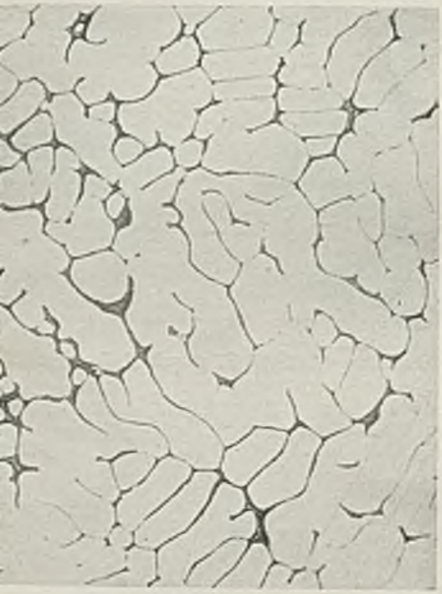


FIG. 13.—AB 24 (86·79 atomic-% Be). × 75.

PLATE IX.



IG. 14.—AB 27 (93·37 atomic-% Be). × 75.

FIG. 15.—AB 3 (2·45 atomic-% Be). Anneale
at 810° C. Quenched. × 100.

obtained by using other specimens of the same composition with which thermal analysis had not up to that time been carried out.

In order to ensure that the incipient segregation, which occurs even on once melting, should not stultify the subsequent chemical analyses, the specimens were sectioned vertically through the centre, and millings were taken from the whole surface thus exposed.

Table II gives the compositions of the alloys investigated, together with the temperatures at which thermal arrests occur. Fig. 3 shows the proposed constitutional diagram.

Micrographic Analysis in the Solid State.

The silver-rich alloys containing less than 10 atomic per cent. beryllium were examined in order to determine the limit of solid solu-

TABLE II.

Number of Alloy.	Percentage, by Weight.		Atomic Percentage Be.	Temperature of		
	Ag.	Be.		Primary Solidification, °C.	Eutectic Solidification, °C.	Solid Transformation, °C.
AB 1	100·00	0·00	0·00	961	...	...
2	99·83	0·13	1·53	955	...	...
3	99·76	0·21	2·45	948	...	...
4	99·72	0·24	2·80	946	890	...
5	99·68	0·30	3·47	941	882	...
6	99·43	0·54	6·10	922	883	...
7	99·32	0·63	7·05	914	881	...
8	99·20	0·77	8·49	900	881	...
9	99·04	0·93	10·09	886	882 *	...
10	98·99	0·97	10·49	...	881	...
11	98·96	1·02	10·97	899	882	...
12	98·47	1·49	15·32	971	881	...
13	97·93	2·04	19·94	1003	880	...
14	97·39	2·59	24·13	1017	881	...
15	95·90	4·07	33·66	1025	881	...
16	94·34	5·65	41·73	1028	883	...
17	92·06	7·91	50·67	1033	881	750
18	88·94	11·03	59·72	1040	880	750
19	86·03	13·95	65·97	1050	880	751
20	83·21	16·76	70·66	1061	882	750
21	79·68	20·28	75·26	1076	880	752
22	78·60	21·37	76·47	1081	881	750
23	68·51	31·47	84·60	1128	880	750
24	64·52	35·46	86·79	1145	878	751
25	60·71	39·26	88·55	1160	873	750
26	51·97	48·00	91·69	1189	...	750
27	45·92	54·06	93·37	1206	...	736
28	26·95	73·03	97·00	1246	...	696
29	24·18	75·80	97·40	1251	...	690
30	0·00	100·00	100·00	1282	...	...

* This point was somewhat vague, overlapping with the initial thermal arrest.

bility of beryllium in silver at various temperatures. The specimens were held at 875° C. for 24 hrs. The temperature was then altered to that required, and maintained for 24 or 48 hrs., after which the specimens were quenched. The maximum solid solubility was then established by micrographic analysis to be 3·5 atomic per cent. beryllium at the temperature of the freezing point of the eutectic. The solubility decreases slowly with decreasing temperature, which was confirmed by slight age-hardening which could be obtained by suitable heat-treatment of these alloys. Investigation of the limit of solubility was not carried out at temperatures below 750° C.

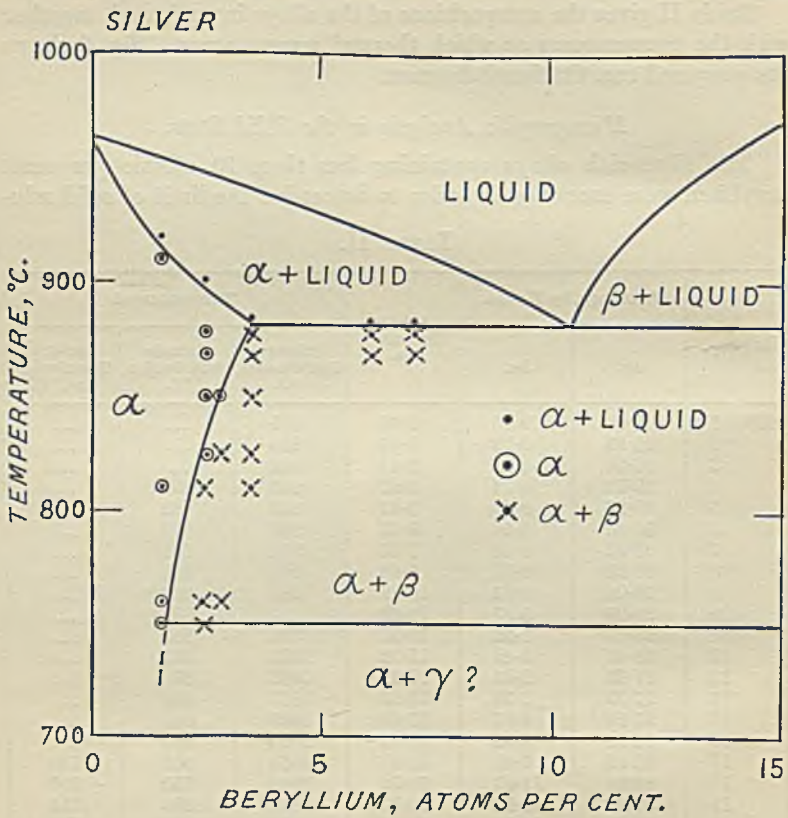


Fig. 5.

Fig. 5 shows this portion of the diagram on a larger scale, whilst Table III gives the results on which Fig. 5 is based. The α-phase is a saturated solid solution of beryllium in silver and the β-phase is a corresponding solution of silver in beryllium.

At the beryllium end of the series, the relationships in the solid state were not so exhaustively investigated, as it was considered that such alloys were unlikely to possess other than a purely academic interest. It was found, however, that in alloys containing more than 90 atomic per cent. beryllium, heat-treatment at temperatures up to 900° C. followed by quenching led to the production of a single-phase alloy (β), and in the absence of other evidence it is suggested that the solidus curve in this portion of the constitutional diagram is as indicated by the dotted line in Fig. 3.

There still remains, however, the consideration of the arrest point found at 750° C. during the thermal analysis of certain alloys in the series. In spite of several attempts, no micrographic, X-ray, or other evidence could be found to confirm or disprove its existence. The author is forced to conclude, with Oesterheld, that it is due to a polymorphic change in the β-phase, and since the thermal effect of the heat of transformation is small, it cannot be detected in the silver-rich alloys of the series containing this phase.

If this explanation be accepted, the logical consequence is that pure beryllium itself must possess a change point occurring at a temperature below 750° C. (In view of the fact that the thermal arrests occur below 750° C. in the range 92–98 atomic per cent. beryllium, it is reasonable to suppose that the transformation temperature in pure beryllium is below

TABLE III.

Number of Alloy.	Structure after Heat-Treating and Quenching from										
	750° C.	760° C.	810° C.	825° C.	850° C.	868° C.	878° C.	883° C.	901° C.	910° C.	920° C.
AB 2	α (traces of β)	α	α	...	...	...	...	...	...	α (traces of liquid)	α + liq.
3	α + β	α + β	α + β	α (traces of β)	α	α	α	...	α + liq.	...	...
4	...	α + β	...	α + β	α (traces of β)	...	...	...	...	...	...
5	...	...	α + β	α + β	α + β	α + β	α + β	α + liq.	...	...	...
6	...	...	...	...	...	α + β	α + β	α + liq.	...	...	...
7	...	...	...	...	...	α + β	α + β	α + liq.	...	...	...

and not above 750° C.) This consideration again raises the question of allotropy in pure beryllium, a question which has already been discussed in a previous publication,[4] in which it was pointed out that although the author and other investigators had found considerable evidence in favour of the existence of allotropy in beryllium, no confirmation could be obtained over the temperature range in question by the use of the most sensitive form of thermal analysis of the pure metal, using a differential thermo-couple. It was stated that "an allotropic change might be more readily found in beryllium-rich alloys than in the pure metal." The present investigation strongly suggests that allotropy does exist in beryllium, but that it is of the type which is largely inhibited in the pure metal, and can thus be detected only by methods which are more sensitive than thermal analysis, and that it is only in the presence of another metal that the transformation proceeds to completion and permits of its ready detection.

The simplest constitution which accords with the ascertained facts is shown in Fig. 3 by the dotted lines which continue at both ends of the horizontal continuous line at 750° C. Allotropy in beryllium is accepted. This is supported by the most recent work of Jaeger,[5] who gives the transition temperature as between 600° and 700° C.

Structure of Alloys.

Except for special purposes, the microstructures of the alloys are quite clearly visible without etching. Figs. 6–14 (Plates VII–IX) illustrate the structure of alloys representative of the whole series. The eutectic alloy, Figs. 8 and 9 (Plate VII) is of interest, as it contains only 10·49 atomic per cent. beryllium, and its structure is typical of eutectics with a large preponderance of one metal over the other.

Figs. 6 (Plate VII) and 15 (Plate IX) are typical of the structures obtained during the determination of the limit of solid solubility of beryllium in silver.

On the beryllium side of the eutectic, it will be seen (Fig. 12, Plate VIII) that the ground mass consists largely, not of the eutectic, but of the pure α-phase. This impoverishment of the eutectic of one of its components is not uncommon. Again, the primary beryllium solid solution (β-phase) is quite different in appearance, depending on the temperature of initial solidification and on the solidification range. In Fig. 10 (Plate VIII), which shows the structure of the alloy in which solidification begins at 1003° C., the crystal boundaries are straight-lined polyhedra. At higher temperatures the surfaces begin to round off as shown in Fig. 11, whilst Fig. 12 illustrates the complete rounding.

The hardness of the alloys increases with the beryllium content, whilst the colour ranges from the white of pure silver to the steel grey of beryllium.

CONCLUSIONS.

In the liquid state, all the alloys of the series are completely miscible, so that the immiscibility noted in the introduction above in certain ternary silver–copper–beryllium alloys cannot be definitely accounted for by peculiarities in any one of the three binary systems involved. It appears probable, however, that the almost horizontal central portion of the liquidus curve in the silver–beryllium series is an indication that, in these alloys, the maximum temperature at which liquid immiscibility can exist is only slightly lower than the temperature at which they become solid; that is to say, were it possible to supercool them, liquid immiscibility would occur. This cannot be achieved directly, but its effects can be obtained by the addition of a third metal which lowers the solidification temperature to an extent such that they remain liquid below the maximum temperature at which immiscibility can exist; thus the addition of copper leads to the phenomenon noted above. Similar reasoning explains why the addition of a fourth metal, nickel, which raises the solidification temperature again, results in the reappearance of homogeneous alloys.*

In general, the constitutional diagram proposed by Oesterheld was confirmed and amplified except in the following particulars:

(*a*) There is a definite solid solubility of beryllium in silver, which reaches a maximum of 3·5 atomic per cent. at the temperature of the freezing point of the eutectic alloy.

(*b*) The composition of the eutectic alloy is 10·49 atomic per cent. and not 15·3 atomic per cent. beryllium.

(*c*) The freezing point of the eutectic alloy is 881° C., and not 878° C.

The latter two differences may be accounted for by the use in the present work of purer materials and larger specimens.

The constitutional diagram has been completed except for the alloys containing more than 90 atomic per cent. beryllium, on which further work is desirable in order to determine the exact shape of the solidus curve and transformation in this region.

---

* A case analogous to the above is cited by Roozeboom: "Die heterogenen Gleichgewichte," Vol. 3, Part 2, pp. 6 and 12, in connection with the components, water–phenol–acetone. Below 68° C. water and phenol are only partly miscible. Above 68° C. they are miscible in all proportions. The systems acetone–phenol and acetone–water are completely miscible at all temperatures. In the ternary system, however, immiscibility occurs at temperatures well above 68° C.

PART 2.—*Tarnish-Resisting Silver–Beryllium Alloys.**

The tarnish-resisting properties of beryllium which are due to the formation of a very tenacious self-healing surface oxide film had already led some previous workers to consider the possibility of its application to silver and its alloys in order to render them stainless. The available data were, however, very contradictory. Jordan and his collaborators,[6] who investigated the effects of the additions of various metals to silver, stated that beryllium actually seems to decrease the tarnish resistance of silver. Ray and Baker [7] found that "beryllium made silver alloys containing more than 90 per cent. by weight of silver hard and brittle, and decreased the tarnish resistance." Cooper,[8] on the contrary, found that alloys containing more than 90 per cent. by weight of silver and from 3 to 5 per cent. by weight of beryllium were immune to the action of sulphur and its compounds. Such alloys were said to be brittle in the chill-cast state, but, by suitable heat-treatment, could be rendered almost as ductile as silver itself.

The chief application of tarnish-resisting silver alloys is to the silverware industry, in which at present the alloy chiefly in use is standard or "hall-marked" silver containing 92·5 per cent. by weight silver and 7·5 per cent. by weight copper. Investigation was accordingly confined to those alloys which contain 90–100 per cent. by weight silver, and particularly to those containing 92·5 per cent. by weight silver. The chief considerations which had to be borne in mind were that if tarnish-resisting alloys could be produced by the introduction of beryllium, such alloys should differ as little as possible in melting and casting temperatures, in working properties, and in appearance, from the materials already in use and for which a well-established technique has arisen.

Preliminary examination of the alloys advocated by Cooper confirmed his results, but the alloys were unsatisfactory owing to the comparatively high beryllium content. They were not only brittle, but were also very different from pure or "standard" silver in appearance. Reference to Fig. 3 will show that in these alloys the primary constituent is a hard beryllium solid solution. If the surface of such an alloy be polished, this hard primary stands in relief and gives the surface an almost macro-etched structure, which is very undesirable in most polished silver-ware. This is true not only in the binary silver–beryllium alloys, but also in ternary alloys containing more than 90 per cent. by weight silver, 3–5 per cent. by weight beryllium, the remainder being copper, in which the limit of solid solubility of the beryllium and

---

* The alloys described below form the subject of British Patent, No. 399,261, 1933.

the percentage above which beryllium or a beryllium-rich solid solution begins to separate as a primary constituent are not materially different from the values found in the binary system silver–beryllium. Moreover, these alloys have a very long solidification range, which leads to serious inhomogeneity and to a coarse structure.

These considerations imposed a further limitation to the useful range which could be investigated, and the beryllium content was accordingly kept below 1·2 per cent. by weight throughout. It soon became apparent that considerably less than the 3 per cent. by weight beryllium advocated by Cooper was required to produce immunity to the action of sulphur compounds.

The first alloy prepared had an approximate composition silver 92·5, copper 6·5, and beryllium 1·0 per cent. A comparison was made between the effect of sulphur compounds on this alloy and on "standard" silver. A very remarkable difference was found. Whereas the "standard" silver specimen became coated with a dark violet tarnish film, the new alloy was practically unchanged in colour.

The actual test used throughout this work was as follows: The specimens were rolled and cut to a standard size, 1 in. square and 0·02 in. thick. After being annealed, they were polished, weighed, and suspended, for periods up to 72 hrs., in an air thermostat maintained at 25° C., in an atmosphere of purified air containing a constant concentration of hydrogen sulphide and moisture. In different experiments the hydrogen sulphide content and humidity of the atmosphere could be varied within wide limits. The increases in weight of the specimens were noted together with the colours of the tarnish films.

A series of alloys ranging in composition from 90 to 100 per cent. silver, 0 to 1·2 per cent. beryllium, and 0 to 10 per cent. copper was then subjected to this test. Examination of the results revealed that two opposing factors were in operation. Increase in the beryllium content led to more complete immunity, whilst decreasing the silver or, rather, increasing the copper, led to less complete protection. In all cases the maximum immunity was obtained when the beryllium content had reached about 0·4 per cent. by weight. Further additions of beryllium seemed to have very little effect. It is to be noted that the solid solubility of beryllium in alloys of this type is approximately 0·4 per cent. by weight, and it appears that once the alloy is saturated with beryllium in the form of a solid solution, that is to say, once the beryllium is uniformly and finely dispersed throughout the whole mass, any excess, present either in the eutectic ground mass or as a primary constituent, has no further influence on the tarnish-resisting properties of the alloy.

Three alloys of the series were finally selected for more exhaustive tests. Their compositions are given in Table IV, and a comparison of their behaviours under the above test conditions, in Table V. Values for "standard" silver specimens are also included.

TABLE IV.

Number of Alloy.	Percentage, by Weight.		
	Silver.	Copper.	Beryllium.
SAB 1	94·41	5·05	0·52
" 2	92·52	6·56	0·90
" 3	92·46	7·10	0·41
"Standard" silver SS 1 . .	92·5	7·5	0·0
"Standard" silver SS 2 . .	92·5	7·5	0·0

It will be seen that under the conditions of the experiments these alloys are practically completely immune to the tarnishing effects of sulphur compounds.

A point of some interest is raised by a consideration of the increases in weight of the various specimens. It will be seen from the figures that the increase in weight is somewhat larger than might be expected to correspond with the very small colour changes associated with the films. It is suggested that the increases in weight are largely due to the formation of a colourless beryllium oxide film which protects the whole surface from sulphur tarnish.

The alloys were then subjected to the action of vinegar, fruit juices, and vegetable liquors. Whilst not completely resistant, the new alloys withstood these conditions more satisfactorily than did specimens of "standard" silver.

In appearance and colour, the new alloys are almost indistinguishable from pure or from "standard" silver. In melting temperature, casting, and general working properties they resemble "standard" silver very closely. Small age-hardening effects can be obtained by suitable heat-treatments. Moreover, control of composition, at any rate on the scale of the present experiments, presents no additional difficulties, whilst scrap metal can be readily remelted.

A suggested method of preparation is as follows. A beryllium–copper alloy containing the correct proportions as required in the final ternary alloy is prepared directly by electrolytic deposition of beryllium on to a molten copper cathode. This alloy is then melted with the correct weight of silver. It has been found that graphite crucibles and graphite protection for the surface of the melt are satisfactory for the production of sound castings. This method does not necessitate

TABLE V.

Atmosphere.	Period of Exposure, Hours.	Number of Alloy.	Weight Increments, Mg.		Appearance after Exposure.
			Expt. 1.	Expt. 2.	
0·005% Hydrogen sulphide. 40% Relative humidity temperature 25° C.	24	SAB 1	0·004	0·004	Practically unaltered.
		2	0·017	0·022	,, ,,
		3	0·022	0·018	,, ,,
		SS 1	0·101	0·109	Steel-blue film with purple edge about 2 mm. wide.
		2	0·095	0·123	,, ,, ,, ,,
	72	SAB 1	0·028	...	Practically unaltered—pale yellow edge about 3 mm. wide.
		2	0·039	...	Pale yellow film extending nearly halfway from edge to centre.
		3	0·046	...	Pale yellow film.
		SS 1	0·133	...	Purple film.
		2	0·143	...	,, ,,
0·005% Hydrogen sulphide. 75% Relative humidity temperature 25° C.	24	SAB 1	0·020	0·019	Practically unaltered—slight yellow edge about 1 mm. wide.
		2	0·022	0·026	,, ,, ,, ,,
		3	0·036	0·030	Pale yellow film extending nearly half-way from edge to centre.
		SS 1	0·112	0·111	Purple film with steel-blue centre.
		2	0·111	0·113	,, ,, ,, ,,

increasing the temperature of the silver very much above its own melting point, as the binary copper–beryllium alloys which are used have comparatively low melting points (between 950° and 1000° C.).[9] This greatly facilitates control of composition and prevents loss of silver by volatilization.

Very little trouble due to gassing is experienced, owing to the deoxidizing action of the beryllium. The beryllium oxide so formed rises to the surface. From the point of view of control of composition, it is desirable that as little oxygen as possible should come in contact with, or be contained in, the molten alloys, in order to avoid loss of a portion of the beryllium as oxide.

The question of inhomogeneity in different portions of a casting was examined, and it was found that, provided the melt was stirred just before pouring, segregation was negligible under the best conditions. The following analyses of the top and bottom of a small casting 1 in. square by 6 in. high are typical:

	Top, Per Cent.	Bottom, Per Cent.
Silver	92·25	92·27
Copper	6·82	6·80
Beryllium . . .	0·90	0·89

It is hoped that, at this stage of their development, these alloys may be investigated under production conditions, so as to bring to light difficulties which, so far, have not been found, but which may occur in their manipulation on a large scale.

ACKNOWLEDGMENTS.

The work described above was commenced under the direction of Dr. W. Rosenhain, F.Inst.Met., F.R.S., until 1931 Superintendent of the Metallurgy Department of the National Physical Laboratory, and completed under that of Dr. C. H. Desch, F.R.S., the present Superintendent of the Department.

The author wishes particularly to thank Dr. W. H. J. Vernon, of the Chemical Research Laboratory, who carried out the tarnish tests, and Mr. W. H. Withey, B.A., of the Metallurgy Department of the National Physical Laboratory, who carried out many of the chemical analyses. Thanks are also due to Mr. W. E. Carrington for his valuable help as assistant throughout.

REFERENCES.

[1] Masing and Dahl, *Wiss. Veröff. Siemens-Konzern*, 1929, **8**, 94.
[2] Oesterheld, *Z. anorg. Chem.*, 1916, **97**, 1.
[3] Sloman, *J. Inst. Metals*, 1932, **49**, 365.
[4] Sloman, *loc. cit.*
[5] Jaeger, *Proc. K. Akad. Wet. Amsterdam*, 1933, **36**, 636–644.
[6] Jordan, Grenell and Herschman, *Proc. Inst. Metals Div., Amer. Inst. Min. Met. Eng.*, 1927, 460.
[7] Ray and Baker, *Indust. and Eng. Chem.*, 1932, **24**, 778.
[8] Cooper, British Patent, No. 257,473, Sept., 1926. U.S. Patent, 1925.
[9] Masing and Dahl, *loc. cit.*

DISCUSSION.

PROFESSOR R. S. HUTTON,* D.Sc., M.A. (Member of Council): No doubt the first part of this paper is the more important, and we all trust that the splendid and sustained work carried out at the National Physical Laboratory on beryllium will finally be crowned with success. On the second part of the paper, however, I feel that I must be rather critical, and express a warning against too much optimism. The subject of the tarnish-resistance of silver is of immense importance to the world. Many attempts have been made to provide non-tarnishing silver alloys, and so far all have proved very costly and disappointing. I feel that these earlier proposals and the present one suffer from lack of a sufficiently thorough study of the properties of the alloys proposed.

The requirements for a tarnish-resisting silver destined to replace ordinary sterling silver are very many, and one has to remember that they have to be satisfied in a manner which will enable a branch of industry lamentably poorly equipped with scientific metallurgical knowledge to apply them. It is not simply a question of finding some alloy constituent which will confer a superior-

* Professor of Metallurgy, The University, Cambridge.

ity over existing materials so far as resistance to attack by sulphuretted hydrogen is concerned.

The first requirement which has to be met is the rather intangible æsthetic one of the appearance of the silver, on which anyone connected with silver and the silver trade or who is an amateur lover of silver will lay enormous stress. The exact tone and colour of the silver are of prime importance, and it seems to me that one of the first things that it is necessary to know about a new material of this sort is its reflectivity in relation to the whole range of the visible spectrum, in comparison with ordinary sterling silver and other tarnish-resisting silvers which have preceded it.

There are also many data on the workability of silver on which information is required before it can be recommended for use. The silversmith has to perform some difficult operations in shaping and in finishing his material. I refer, for instance, to the processes of raising, chasing and spinning metal, which are operations requiring a very special quality of workability in the metal which is not easy to satisfy. Many of the predecessors of this alloy have failed because of little difficulties of that sort. Again, the whole story of the subsequent behaviour of the work-hardened metal at different temperatures of annealing will play an important part in the possibility of its acceptance by the silversmith's trade.

Other properties which are almost equally important are those concerned with the finishing and polishing of the metal, the capability of readily producing at an economic cost a sufficiently fine surface finish to satisfy the severe critical assessment of the experts, and, of course, all the questions connected with the jointing of the metal, soldering and brazing, are again important—not simply whether the metal will take a brazing alloy, but the effect on the joint itself and on neighbouring parts.

I have still to come, in these critical remarks, to the supreme importance of this question of tarnish-resistance, and I think that there the silver trade might naturally demand a very complete investigation before they are asked to do what I take it they are asked to do here, to proceed to test the material under production conditions. A great deal has been done and a vast amount of money has been expended on previous alloys, right up to and past the stage of production, and then, on exposure to ordinary conditions of life, those materials have been rejected because of a slight but obvious inferiority to the ideal which the silver trade would like to see achieved. The silver trade, it must be remembered, is in rather a difficult position in regard to adopting new alloys, and although eagerly awaiting the advent of the ideal non-tarnishing silver, cannot afford to speculate on a series of half measures of achievement. There must be very high values of finished articles in the workshops and in the retail establishments of this country and other countries, made of the ordinary standard sterling silver, and the moment a new acceptable alloy arrives it renders the whole of that very valuable stock, if not absolutely obsolete, at any rate a back number. It is not merely a matter of the value of the metal, which is high, but of the still higher value of the workmanship put into those articles which makes this particular problem a very difficult one for the trade to face. That being so, I feel that we ought to have a very much more thorough study of this material in the laboratory from the point of view of tarnish-resistance. Silver is a particularly difficult metal to assess in this way, because it is quite possible to endow ordinary sterling silver with a sort of passivity which makes it behave in a superior way to the product in its normal condition, but this passivity is, of course, of rather a temporary value.

We have in Table V some comparative data of tarnishing no doubt thoroughly reliable, and obtained under the conditions specified, but we are only given weight increments, and in one single sentence the appearance after exposure. One misses any scientific measurement of the departure from the reflectivity of the original material as exposed. It is quite possible—Dr. Vernon did it in some of his own early work—to measure the progress of tarnishing by the loss of reflectivity of the metal, and here, if ever, is surely a case where that ought to be done. Perhaps I know a little more of the other side of the picture than the author does, because I have spent so much of my life among silver teapots; but I know that it is a very hard thing to get any material of this sort even tried out on a production scale until a really strong case, in comparison with other materials, has been put before the trade.

There is one question which I should like to ask the author. As I understand it, these new silver–beryllium alloys are covered by a British patent, and on the other hand there is a previous British patent by Cooper, who found that 3–5 per cent. by weight of beryllium rendered the silver immune to the action of sulphur and its compounds. I am sorry that I have not had an opportunity of seeing the claims of this new British patent, but I take it that the essential point is to achieve the object required with a much smaller addition of beryllium than is covered by Cooper's patent. If so, it is an advance which, from that point of view, will be highly welcome, considering that beryllium is by no means a cheap constituent.

I am sorry to have been so critical, but I feel that this is an immensely important subject to the scientific side of metallurgy, and particularly to our depressed silver industry, and that people are looking so eagerly for the solution of this problem that it is rather hard to put any new discovery before them with such tantalizingly limited data on which to base their further work.

Captain R. H. **Atkinson**[*] (Member): For some years I have been investigating the palladium and rhodium plating of silver, and I find, as Professor Hutton has already stated, that the silver manufacturers are very conservative. In the matter of the colour of silver, their attitude may be appreciated when I say that some of them describe platinum as " black " when it is put on silver. Very careful measurement of the whiteness of silver, therefore, is a matter of some importance. One of the difficulties which I have encountered is that the silver manufacturers feel that a non-tarnishing standard silver is due to be discovered. They have at the back of their minds, of course, the success of stainless steel, and they think that sooner or later somebody is going to develop a really non-tarnishing silver, so that there will be no need for them to consider the use of a plate of a platinum metal.

I congratulate the author on his valuable work, but I do not think the finish of the silver–beryllium alloys would satisfy the manufacturing silversmith. Of course, I realize that these are very early days in this research.

The hard constituent present in Mr. Sloman's specimens would, in my opinion, make it impossible to produce a finish which would satisfy the silversmith.

Dr. C. J. **Smithells**[†] (Member): We were asked recently to design a furnace for the bright-annealing of silver, and I was surprised to learn that silver tarnished when annealed in air. One is apt to think of pure silver, but standard silver contains so much copper that it goes quite black, and it is a very difficult matter to anneal silver so that it remains bright. I have wondered whether the beryllium–silver is better from that point of view and whether, for example, it can be annealed in air without tarnishing, and that the problem of bright-annealing is going to be simplified.

Professor Hutton made one remark on which I feel I must comment when he suggested that the existence of large stocks of any commodity might really prevent the introduction of an improvement. That is, of course, the attitude

---

[*] Assistant Works Manager, Acton Refinery, Mond Nickel Co., Ltd., London.
[†] Research Laboratories, General Electric Co., Ltd., Wembley.

of a few people in industry as a rule, but I do not think that it is a serious bar to the introduction of something which is positively an improvement, and in any case these new things are taken up so slowly—there are always people who prefer to see other manufacturers burn their fingers first!—that I think that existing stocks would be sold long before all the silversmiths had taken up Mr. Sloman's production.

I should like to congratulate Mr. Sloman not only of his paper, but on all the work that he has carried out on beryllium. Members may remember previous work of his, when the National Physical Laboratory tried to produce ductile beryllium, unfortunately without success. He has gone through all the spadework in that connection, and shown exactly how the problem can be solved, and he has been very generous in placing all that information at our disposal.

Professor HUTTON: I should like to give an explanation of one point to which Dr. Smithells has referred. I do not think that the attitude of the silver trade is necessarily so subject to criticism as might appear from his remarks. The position is that the silver trade is not so backward that it will not accept a new thing—I think that it is eagerly looking for the solution of this problem—but that it appreciates that it is very important that it should not put its money on the wrong horse. To vary the metaphor, it cannot afford to take two bites at the cherry; it must be quite sure that the material it adopts to replace the present silver, and which would, I think, very rapidly supplant sterling silver and add enormously to the output of the silver trade, is capable of doing all that is required of it, and is not itself going to be replaced in a brief period by something which will be very materially better. In other words, it wants this work of investigation to be very thorough before replacement commences. Anyone who knows the trade will be able to understand the real reason for the attitude that it adopts, namely the very high fashioning costs of the finished article in the silversmith's store.

Dr. W. H. J. VERNON * (Member): As both Mr. Sloman and Professor Hutton have spoken of the few tests which I was able to carry out at Mr. Sloman's request, perhaps I may refer briefly to several points arising therefrom.

With regard to surface condition, Mr. Sloman's specimens were, I believe, prepared by the usual metallographic methods; hence, whilst not possessing high polish, they were at all events quite smooth and represented a standard and reproducible surface. The size of the specimens precluded reflectivity measurements, with the apparatus available, but the description of their behaviour under tarnishing conditions appeared to meet the requirements of a preliminary investigation.

I should like to take the opportunity to emphasize the importance, in matters relating to comparison of tarnish-resistance, of taking into account the influence of surface condition. Perhaps I may illustrate this by referring to work published some years ago, in which we were comparing the tarnish-resistance of fine silver with that of standard silver and standard silver containing a small amount, 1·75 per cent., of cadmium. We were measuring loss of reflectivity, the tarnishing atmosphere being that of a domestic kitchen, chosen for the purpose, so to speak, of obtaining "local colour." If we took specimens which had been brightly polished in an industrial operation, giving the usual mirror finish by the ordinary mopping process, we had extraordinarily marked differences, represented by extremely divergent curves when loss of

---

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

reflectivity was plotted against time.* The fine silver was actually a deep purple colour whilst the special standard silver was scarcely affected. If, however, we used emeried surface, there was nothing to choose between the results; they fell on overlapping curves which, within the limits of experimental error, could be replaced by one common curve.

I mention this to emphasize the enormous importance of surface conditions. It means this, that two sets of workers on the same material might report in the one case no difference, whereas in the other they might report a tremendous difference, depending simply on the condition of the surface. This should be borne in mind by those who seek to reproduce the results of any work in the field of tarnish-resistance.

There is one further point which arises. The effects described must undoubtedly be connected with questions of surface flow. Now, cadmium, which we were using, has the effect of increasing tarnish-resistance, but it also has the effect of increasing the hardness. In Mr. Sloman's work, the beryllium has the effect of increasing tarnish-resistance to a much greater extent, apparently, than cadmium, and also of increasing the hardness to a much greater extent. This is significant, because both effects are probably acting in the same direction, and the argument that applies here almost certainly applies in the case of the author's specimens.

I hope that Mr. Sloman will be encouraged to go on with this very important work. It is doubtless a fact that beryllium does confer stainless properties, using the term in its conventional sense as meaning " less stain."

Dr. C. H. DESCH,† F.R.S. (Vice-President): I understand that the criticism we have heard was directed to the fact that comparatively little work had been done in the later stages of this research. The research was conducted under the auspices of a special committee of the Metallurgy Research Board. The work on beryllium has now been going on for a good many years, and the results have not given very great satisfaction from a technical point of view; they are interesting scientifically, but the technical results have been small. We know that in Germany vast sums of money have been spent on the development of beryllium with extremely small results; in fact, I believe that the work is now being abandoned there also. The Metallurgy Research Board did not feel justified in continuing further work on this metal, but this last development of stain-resisting silver seemed to have considerable interest, and my suggestion is that if the silver trade really takes sufficient interest in the production of stain-resisting material, it is for them to contribute towards the cost of the investigation. That is the view taken, I think, by the Research Board. The preliminary tests are, I submit, quite sufficiently satisfactory to indicate that work undertaken on behalf of the industry might repay itself, but it is not for the National Physical Laboratory, without support from industry, to pursue the matter further.

Dr. MARIE L. V. GAYLER ‡ (Member): There is one small point which I wish to criticize: I do so with diffidence, because I have not seen the actual alloys in question. At the bottom of p. 170 the author refers to Fig. 10, in which the crystal boundaries of the primary separation are straight-lined polyhedra, and then he says as shown in Figs. 11 and 12, at higher temperatures the surfaces begin to round off. By that I presume is meant that the separation

---

* First Report to Atmospheric Corrosion Research Committee (British Non-Ferrous Metals Research Association), *Trans. Faraday Soc.*, 1924, **19**, 884.

† Superintendent, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

‡ Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

from the liquid state takes place in polyhedral form which becomes rounded as the temperature of the melt decreases. In the case of the compound Mg_2Si, the crystalline form of which appears very similar to that shown in Fig. 10, as the temperature of primary crystallization was increased no indication of rounding was observed, and I would suggest that in the author's case two phases may possibly exist. I say that with diffidence, because I have not seen the specimens, and assume that these alloys have not been heat-treated. Fig. 3 shows that the liquidus surface tends to flatten from somewhere over 20 atomic per cent. of beryllium, which is approximately the composition of the alloy shown in Fig. 10, whilst the composition of the others are in the region of 60 per cent., and I suggest it is possible that an intermediate phase may exist. I have never seen primary crystals with a definite crystalline structure change their form as their temperature of crystallization is increased.

The AUTHOR (*in reply*): I anticipated Professor Hutton's remarks, and that the criticisms he raised would be levelled at this work. I feel, however, that Dr. Desch has explained the situation much better than I could have done. The work was definitely discontinued at a place where it was incomplete, and nothing further could be done but to publish the results already obtained.

With regard to the reflectivity of the specimens, we were not in a position to carry out tests at the time, because the specimens available were not large enough. Later, however, I produced some more specimens of rather larger size, and these are at present being examined. I do not yet know the results, but I hope that it may be possible to give them later in the written reply to the discussion.

Professor Hutton suggests that the patent was taken out in order to show that one could produce a much higher resistance to tarnish with a very much lower percentage of beryllium than was given in the previous patent of a few years before. As I said when introducing this paper, if the beryllium content is increased beyond 1 per cent. it is present as a primary, and one can never hope to get a mirror finish, which we all know is so desirable.

With regard to Dr. Smithells' questions, I cannot tell him offhand whether beryllium-silver can be annealed in air. All the heat-treatments in the binary system were carried out *in vacuo*. With regard to the ternary alloys, *i.e.* standard silvers containing beryllium, I do not think they can be annealed in air and remain completely untarnished.

Dr. Gayler's remarks bore on something on which I spent a long time, namely the question of the rounding of the primary crystals. She may be correct in suggesting that there is a second phase, but I do not think so, because as one crosses the diagram there is a gradual transition from polyhedra to completely rounded crystals.

CORRESPONDENCE.

THE AUTHOR (*in further reply*): I much regret that the reflectivity tests to which I referred in my reply to the discussion are not yet complete. It is not possible, therefore, to include them here as I had hoped. As was pointed out by several contributors to the discussion, the results of these tests are very important in assessing the probable value of the new alloys to the silver trade. I hope, therefore, to be given the opportunity of presenting them in the form of a short note at a subsequent meeting of the Institute.

THE DIFFUSION OF ZINC AND IRON AT TEMPERATURES BELOW THE MELTING POINT OF ZINC.*

By GILBERT RIGG,† MEMBER.

SYNOPSIS.

When clean rolled zinc sheet is heated in close contact with clean iron diffusion commences at below 300° C. and is fairly rapid at above 380° C.; it proceeds by the formation of cones of diffusion products which spread out from isolated points where the contact between the metals is most perfect, and gradually penetrate into the zinc and across its surface. The progress of the diffusion is governed to a large extent by the nature and smoothness of the iron surface, and does not seem to be dependent on the vapour pressure of the zinc. Two well-defined layers of diffusion products are formed, a thin layer of constant thickness (about 0·08 mm.) containing about 17 per cent. iron being next to the iron, and a thicker layer containing 0–11 per cent. iron outside this. On continued heating, the thin layer moves towards the zinc, being continuously converted into the zinc-rich layer; this would seem to indicate that the principal diffusing constituent is the iron. The rate of penetration depends on time and temperature, and is independent of the grade of zinc, but the thickness of the zinc-rich layer is less with electrolytic than with pure zinc. The mechanism of the diffusion process is discussed.

SOME preliminary experiments carried out about eighteen years ago showed that when pieces of zinc and low carbon steel with smooth surfaces were clamped together and heated to a temperature somewhat below the melting point of zinc for about 48 hrs., the two metals became strongly adherent to one another. During the last twelve months the present author has studied the matter in considerable detail in order to elucidate this action, the object of the present investigation being to study the diffusion of zinc and iron at such temperatures with special reference to the structure and composition of the product of diffusion.

In all these experiments the surfaces of the two metals, more or less polished, were brought together cold, and, with few exceptions, were kept in contact with a clamp. The heating was carried out in

---

* Manuscript received September 9, 1933. Presented at the Annual General Meeting, London, March 7, 1934.

† Metallurgical Engineer, Melbourne, Australia.

an electrically-heated oven, the temperature of which was controlled to ± 10° C. The temperatures used varied from 390° to 300° C. At the latter temperature, which is 119° C. below the melting point of zinc, the diffusion was small in amount and slow, but quite recognizable.

The zinc used was mostly in the form of rolled sheet. With cast zinc the action was usually, but not invariably, imperfect, and soon stopped, the same being true of electrolytic zinc cathode, although rolled electrolytic zinc worked well. The thickness of the zinc sheet varied from 0·01 to 0·1 in., and the area from 1 to 1·5 in.^{2}. The steel generally used had a carbon content of not more than 0·04 per cent.

Various degrees of polishing were tried on the steel, ranging from grinding wet with emery (0·01 in. diameter grains) to a metallographic polish. The degree of smoothness had a marked effect on the structure of the layer of diffusion product. In general, a surface obtained by grinding wet with fine emery (Wellington knife polish) gave good results. The zinc was cleaned by rubbing with whitening and water. The surface acquired during rolling was smooth enough for the purpose.

In order to obtain adhesion it is essential that the metals should be in perfect contact with one another, either over the entire surface or else at points sufficiently close together to start an action which can spread laterally and so become confluent.

When adhesion starts from a number of isolated points, cones of diffusion product begin to form at each centre from which growth continues from the steel into the zinc and radially along the surface of the steel. Fig. 1 (Plate X), taken from a specimen in which the action has just begun, shows a large number of small rough cones of diffusion product. The background is the surface of the steel plate which was ground with fine emery and water. The scratches due to grinding and general roughness of the surface are easily seen in the photograph. It will be noticed that the cones have a tendency to develop along scratches in the steel. As these scratches would be raised at the edges, the contact with the zinc would be good. The zinc surface showed pits corresponding with the cones on the steel.

Fig. 2 shows the result of an experiment in which the development of the cones has progressed considerably further. In this case a Belgian common spelter, rolled to 0·025 in., was used. The steel was of the same quality as used in the preceding experiment, and the surface of the metals was prepared in the same way. The zinc plate was sandwiched between two steel plates and the whole placed in a clamp and heated at an average temperature of 388° C. for 24 hrs. A corner was sawn off by two cuts at right angles and the sawn surface polished and etched with 5 per cent. concentrated nitric acid in water.

POLITECHNIKI

FIG. 1.—Steel Plate Heated for a Short Time at 380° C. in Contact with Zinc. Zinc Plate Removed. × 28, Oblique Illumination.

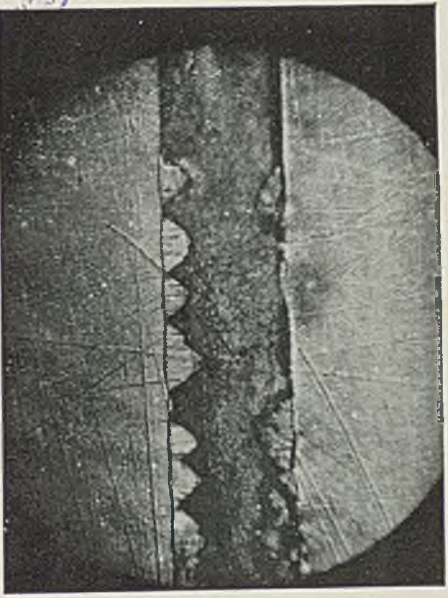


FIG. 2.—Rolled Zinc. Belgian Common Spelter, Heated for 24 hrs. at 388° C., between Steel Plates. × 30, Vertical Illumination. Etched with 5% HNO_3 in Water.

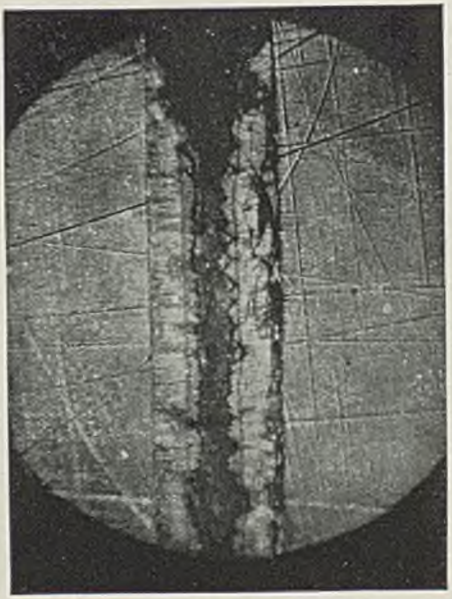


FIG. 3.—As Fig. 2. Another Part of the Same Specimen.

FIG. 4.—Zinc Sheet between Polished Steel Plates. Heated for 71 hrs. at 354° C. × 21

[To face p. 181.

This reagent was generally used with all polished specimens. The metals were strongly adherent and showed no signs of separating under the stress of sawing. The white areas at the sides of the photograph are the steel, and the dark area in the middle is the zinc. At the top of the photograph the zinc has not been attacked at all. On the left-hand side is a row of cones, sharply marked off from the steel on the one hand and from the zinc on the other. It will be noticed that the bases of the cones show a curve convex to the steel. On the right-hand side the action is less marked and more irregular, probably owing to the contact being less perfect than on the left.

Fig. 3 shows another part of the same specimen, where the action has progressed much further than that exhibited in Fig. 2. The contact between the diffusion product and the steel is a straight line, which is clearly seen on the left side and is somewhat broken on the right. The diffusion product now consists of two layers separated by a nearly straight line, the inner one, which is in contact with the zinc, showing a tendency to cone formation, particularly on the right-hand side of the specimen.

This formation of cones on the contact between the inner layer and the zinc is not by any means of general occurrence. Fig. 4 shows a specimen similar in most respects to that in Fig. 3, but the steel plates received a metallographic polish and the specimen was heated for 71 hrs. at a temperature of 354° C. This photograph shows a remarkable regularity in the development of the two layers. The parallelism of the layers of diffusion product and of the residual zinc is very marked.

In Fig. 5 (Plate XI) there is the absolute reverse of this condition. The same grades of steel and zinc were used and the heating was carried out at 388° C. for 91 hrs. The preparation of the steel surfaces, however, was done by grinding wet with coarse emery (0·01 in. diameter grains). The diffusion had taken place very irregularly, the rough irregular cones penetrating the zinc from opposite sides and leaving unattacked zinc between them. This result doubtless follows from the rough surface of the steel.

It has already been remarked that complete metal-to-metal contact is essential to the diffusion process. Apparently in these experiments this contact does not occur near the edges of the sheets. There is always a selvage of unattacked zinc surrounding the area of diffusion product. Inside this is a zone of more or less isolated cones, and inside this again a continuous layer of the product.

This reduced activity at the margin of the metal plates may be due to a slight bevelling of the steel plates during grinding and polishing, or to oxidation of the surfaces owing to penetration of air, or to both. In some cases, again, diffusion may take place almost entirely from one steel plate, the zinc being subsequently attacked from one side only. In these circumstances, individual marginal cones may grow to such a size as to pass almost through the zinc plate. This is shown in Figs. 6 and 7 (Plate XI).

A possible explanation of these structures is as follows:

Diffusion begins at a number of points of contact between zinc and steel which are more perfect than in the areas between. As the iron diffuses into the zinc a depression is formed in the steel surface, the diffusion product remaining adherent to it and drawing down with it the zinc to which it also adheres, so that as the process continues the surface of the zinc surrounding the original projecting point comes into contact with the steel, and the iron begins to diffuse into it. The depression, consequently, increases in area, but is always deeper at the centre, as the process of diffusion has been going on longer at the centre than at the periphery.

In Fig. 8 two cones are shown in vertical section, photographed from the same specimen as in Fig. 2 (Plate X). The magnification is 140 diameters. It will be noticed that at the base of the cone there is a curved depression in the steel, so that the cone is standing on the surface of the segment of a sphere. In all specimens examined this condition is present.

When two adjacent depressions have come into contact, the ridge between them will soon be eaten away, and the final result will be a flat depressed surface which gives the straight line of contact seen in the cross section (Figs. 3 and 4, Plate X).

Zinc vapour does not apparently play any part in this action between the metals. A thin piece of paper laid between the steel and the zinc plates completely inhibits it, although the paper is reduced to a charred condition by the heat.

The structure of the layers at higher magnifications is illustrated in Figs. 9 and 10 (Plate XII). In both of these photographs the different structures of the two layers is well shown, and in Fig. 9 the dark band of separation between the two layers is seen to have a granular structure. The outer layer shows a columnar structure oriented at right angles to the steel surface, and the inner layer a finer and less regularly oriented one. In Fig. 10, magnified 80 diameters, the columnar structure of the outer layer (here very thick relatively to the inner one) is well defined. In this specimen there is an additional thin layer present between the outer layer and the steel. This is not always shown, probably owing to imperfect preparation of the polished and etched surface (see Fig. 5).

The dark band between the outer and inner layer of diffusion product is probably due to the effect of difference in hardness of the two layers affecting the polishing and etching. These differences are accentuated by the etching, owing to the difference in solubility of the various layers in the etching reagent.

In the photographs of cross-sections the relative thickness of the two layers of diffusion product shows great variability. In Fig. 9, for example, the inner layer is slightly thicker than the outer, whilst in Fig. 10 the inner layer is only about one-fifth the thickness of the outer. If, however, the actual thickness of the inner layer in different specimens be compared, a considerable degree of uniformity is found, as is shown in Table I, which shows that in spite of large differences in the thickness of the outer layer, in the time and temperature of the heat-treatment, and in the quality of the zinc used, the thickness of the inner layer varies but little.

TABLE I.

Fig. No.	Thickness, mm.		Time, Hrs.	Temperature, ° C.	Grade of Zinc.
	Outer.	Inner.			
3	0·15	0·07	24	388	Common.
4	0·19	0·07	71	354	Common.
9	0·07	0·08	40	340	Pure electro.
10	0·31	0·06	316	382	Common.

In order to obtain some light on the cause of this double layer and the difference in structure between the outer and inner layers, it was decided to make a series of extractions with dilute hydrochloric acid and compare the iron : zinc ratio in the series of solutions so obtained.

For this purpose the specimen shown in Fig. 11 Plate XII (× 44 diameters) was chosen. In this experiment six sheets of common zinc foil were used, sandwiched between two low carbon steel plates. The aggregate thickness of the zinc sheets was 1·16 mm. The arrangement is shown in Fig. 12, where the action has not made much progress. The specimen was held in a clamp. Fig. 11 shows the condition of the specimen which was used in the extraction experiment. The aggregate thickness of the layers of diffusion product was 0·61 mm. The specimen was removed from the clamp and the plates were pulled apart at a surface of contact between two unattacked zinc foils. The unattacked zinc foils were peeled off the surface of the diffusion product, and the steel was painted with acid-proof enamel, the enamel covering the thin layer of diffusion product and isolated cones round the periphery of the area of diffusion product.

Five extractions were made, the acid used being cold dilute hydrochloric acid, 5 c.c. of concentrated acid in 50 c.c. of water. Both sides of the specimen were used, the first to work out a technique and the second for the final result. After the fifth extraction the layer had become so thin that there was a risk of iron being dissolved from the steel. The sixth extraction was made, therefore, by chipping, the chips being treated with a magnet to remove the steel. The thin bottom layer coating the steel was not removable.

The specimen was exposed to the cold acid for 10 minutes on the first extraction and for 15 minutes on the four succeeding ones. The results obtained are shown in Table II, from which it will be seen that there is a steady increase in the iron content of the diffusion product except in the last item. This variation is probably due to the dissolution of the enamel before the chipping was done, thus exposing some of the low iron product round the margin, some of which no doubt got into the final sample. There was no sign, under the microscope, of free zinc on the original surface of the diffusion product.

TABLE II.

Fraction.	Iron, mg.	Zinc, mg.	Iron, Per Cent.	Zinc, Per Cent.
1	2·1	44·5	4·5	95·5
2	10·5	118·0	8·2	91·8
3	10·5	102·5	9·3	90·7
4	9·8	82·5	10·6	89·4
5	17·8	83·0	17·7	82·3
6 (chips)	8·0	42·5	15·8	84·2
	58·7	473·0	11·0	89·0

In order to test the possibility of the fractions being contaminated by iron from the steel, a specimen of the latter, having a total surface area of 1 in.^{2}, was prepared and cleaned with a file free from grease. After exposure to the cold 5 per cent. hydrochloric acid for 15 minutes, only 3 mg. of iron were dissolved. As this area is vastly greater than any area of exposed steel which could have been present during the extractions (none was visible under the microscope), contamination from this source would appear to be negligible.

The surface exposed by the first extraction was of a different character from that shown in the later ones. It had a silvery-white appearance, and under the microscope the white material showed as an irregularly-corroded surface with here and there a smooth grey surface showing through from below. After the second extraction the white material was in very small amount. Its appearance, however, was quite distinct from the underlying layer, which maintained a uniform appearance throughout the subsequent extractions.

Bearing in mind the fact that the thickness of the inner layer was only one-fifth that of the outer, it would appear that the white material corresponded with the inner layer.

In order to obtain a figure for the composition of the layers as a whole, four specimens were chipped and their iron contents determined. The results were as follows :—

	Iron, Per Cent.
Specimen A	8·5
,, B	8·6
,, C	9·1
,, D	11·5

These figures are of the same order as those found in the fractions. The differences shown probably depend on the relative proportions of the outer and inner layers, which vary with different specimens, the inner layer being lower in iron than the outer, as shown by the extraction test.

So long as the iron content remains above a certain critical figure the structure is that of the outer layer; below it, of the inner layer. As long as the diffusion continues, the boundary line between the two continually advances towards the zinc, the inner being progressively converted into the outer.

It is possible that there is some diffusion of the zinc into the inner layer, but the constancy of the thickness of this layer suggests that the principal diffusing constituent is the iron.

For the grade of steel used, the rate of penetration depends on time and temperature. The grade of zinc, whether of high purity as the electrolytic, or impure as the common spelter, seems to have little if any effect.

Following Arnemann,[1] the alloys of iron and zinc fall into three groups :—

(*a*) 0·0–7·3 per cent. iron. Two structural elements: (1) Solid solutions of $FeZn_7$ and zinc, containing a maximum of 7·3 per cent. iron; (2) Pure zinc.

(*b*) 7·3–11·0 per cent. iron. Homogeneous alloys (one structural element) consisting entirely of the solid solution of $FeZn_7$ and zinc.

(*c*) 11–22 per cent. iron. Two structural elements: (1) $FeZn_3$, (2) $FeZn_7$.

In composition the inner layer of diffusion product corresponds with "*a*" in the above classification; the inner part of the outer layer up to 11 per cent. iron would correspond with "*b*," whilst the outer part (17 per cent. iron) would correspond with "*c*"; whether, however, $FeZn_3$ is actually present seems doubtful.

Tammann and Rocha [2] carried out experiments on the diffusion of electrolytic iron and zinc. In this case, however, the iron plates were dipped into molten zinc at temperatures up to 535° C., and after a fixed time the specimens were quickly cooled, cut through at right angles to the surface, and etched with alcoholic picric acid. They describe two examples prepared in this way. In the first the iron plate was kept in the molten zinc for 5 minutes at 450° C. Next to the zinc they found a layer of mixed crystals $FeZn_7$ and zinc, and next to that a further layer which they ascribe to the alloy $FeZn_3$. Between this latter and the iron there was a third layer much thinner than the other two and of unknown composition. In the second example the duration of the immersion was 10 minutes and the temperature 535° C. The sequence was similar to the first.

The experimental conditions here, however, are very different from those obtaining in the present author's experiments. In the latter the diffusion took place in the solid metals at temperatures never exceeding 400° C., and in some cases at 350° C. or less. From Arnemann's diagram it seems scarcely likely that $FeZn_3$ could form at such low temperatures, and there is no change in structure in the outer layer recognizable under the microscope from 8 per cent. iron to 17 per cent. iron. On the other hand, in the figures yielded by the fractional extractions there is a sudden break in the continuity of the percentages of iron between fractions 4 and 5, the figures being 10·6 and 17·7 per cent. This certainly suggests that two distinct compounds are present in the outer layer of diffusion product.

Further work on a larger scale is now being commenced in order to clear up this question.

It has been already stated that there is no evidence of the zinc diffusing into the iron under the conditions of the author's experiments. In this connection a recent paper by G. von Hevesy and W. Seith,[3] on the diffusion of metals in the solid state, may be mentioned. The authors compare, for example, the rate of diffusion of gold into lead and *vice versa*, the diffusion constant of gold into lead being given as 4×10^{-3} cm.^{2} per day at 150° C., and that of lead into gold as only 3×10^{-11} cm.^{2} per day at 141° C. They say further: "When we substitute in lead alloys other metals than gold, whose properties approximate more and more to those of lead, then these elements show a continuously diminishing diffusion rate. The interval between the rate of diffusion of these elements and that of lead becomes, therefore, less and less and the one-way diffusion becomes less and less marked." It would appear, therefore, that with solid iron and zinc one-way diffusion takes place at the iron–zinc and iron-diffusion product contact, but with the inner layer in contact with the zinc, and low in iron, zinc may diffuse into it.

In this connection the curved bases of the individual cones become of interest. If the explanation of cone formation which has been put forward earlier in this paper is correct, then the volume of the circular depression in the steel (see Fig. 8) is equal to the volume of the iron which has diffused into the zinc, and the volume of the cone above is that of the zinc into which it has diffused. By multiplying these volumes by the specific gravities of iron and zinc, respectively, the proportions by weight of the two metals can be obtained.

The results are, of course, only approximate, as neither cone nor segment is mathematically perfect, but they are nevertheless sufficiently close to be of interest. Three cones were taken at random and measured, with the following result :—

Per Cent.	Cone A.	Cone B.	Cone C.
Fe	10·6	13·1	13·5
Zn	89·4	86·9	86·5

These figures are well within the limits obtained in the various analyses already quoted. As the inner layer of diffusion product which is low in zinc is at the apex of the cone, and therefore small in amount, the percentage of iron in the cone would be expected to be on the high side.

In the conditions existing during these experiments the zinc plates show recrystallization, and where several are clamped together they become mutually adherent and show, when pulled apart, bright streaks where welding has taken place.

These experiments are now being extended to include high-carbon steels and alloy steels, and various classes of cast iron and also to zinc-bearing alloys.

REFERENCES.

[1] P. T. Arnemann, *Metallurgie*, 1910, 7, 204.

[2] G. Tammann and H. J. Rocha, *Z. anorg. Chem.*, 1931, **199**, 299–301.

[3] G. von Hevesy and W. Seith, *Z. Elektrochem.*, 1931, **37**, 528–531.

CORRESPONDENCE.

Dr. W. D. Jones,* B.Eng. : This work must have come as a surprise to many people. It was scarcely to be expected that reaction products of iron and zinc could be produced in such large quantities at temperatures below the melting point of zinc. The author is to be congratulated in bringing the matter to light.

There appears to be some doubt whether the phases produced are solid

---

* Sir John Cass Technical Institute, London.

solutions or intermetallic compounds. Undoubtedly the lack of an irreproachable iron–zinc equilibrium diagram is a handicap in the interpretation of the results, but even so there is little doubt that if the author had given rather more attention to the polishing and etching of his sections and had examined them under considerably higher magnifications, a more precise identification of the various phases would have been possible.

The work of Hume-Rothery * appears to indicate that intermetallic compounds of an invariable composition do not permit of diffusion. It is more than likely then that in this particular case we are dealing either with simple solid solutions or compound solid solutions. So far as can be distinguished from the photomicrographs, there are three such phases, each separated by a diffusion boundary. Now the author assumes that because the zinc-rich phase remains of a more or less constant thickness, whilst the intermediate and iron-rich phases increase in width, the iron must be the principal diffusing constituent: this deduction is by no means clear. Surely a little consideration will show that an exactly opposite explanation is also possible. We are dealing with reactions that are balanced. The thickness of each layer will depend not only on time and temperature, but also on the relative quantities of iron and zinc necessary to form each layer, on the rates of diffusion of both iron and zinc through the phases, and on the rate at which the diffusion of each of these metals diminishes with thickness in each phase. In view of the number of these variables, it is not possible to make such a simple deduction as that which the author has attempted. The fact that the pits in the zinc are much larger than those in the iron is merely an indication that the phases produced are in the main rich in zinc.

There are two minor points about which some explanation from the author would be welcome. Fig. 8 shows cones of reaction product at a magnification of 140 diameters. Why do these cones not exhibit two or possibly three phases as is so clearly revealed in Fig. 4 at a magnification of only 21 diameters? Finally, it is stated that with cast zinc the diffusion was imperfect and soon ceased. Is this due merely to the irregular surface of the casting, or is it intended to infer that some specific quality of the cast material is responsible for the effect?

* *J. Inst. Metals*, 1926, 35, 295; 1927, 38, 127.

A STUDY OF THE INFLUENCE OF THE INTERCRYSTALLINE BOUNDARY ON FATIGUE CHARACTERISTICS.*

By H. J. GOUGH,† M.B.E., D.Sc., Ph.D., F.R.S., Member, H. L. COX,‡ B.A., and D. G. SOPWITH,‡ B.Sc.Tech.

Synopsis.

With the object of studying the process of fatigue in relation to crystalline boundaries, tests under alternating torsional stresses have been made on three specimens of aluminium each consisting of two crystals. In one specimen the intercrystalline boundary was mainly transverse to the axis of torsion; in another it was mainly longitudinal through that axis, whilst in the third the boundary had no special form, but the two constituent crystals were in mutual twin orientation.

The deformation occurring during test has been studied by observation of the slip bands produced, and particular attention has been paid to the markings in the immediate neighbourhood of the intercrystalline boundaries. The distribution of slip bands showed that the effect of the boundaries on the distribution of stress was extremely slight, each crystal of each specimen behaving as if it alone composed the whole specimen; whilst the close approach of the general systems of slip to the boundary and the very small amount of anomalous slip in that region showed that even locally the boundary had a very limited field of influence. Although major differences of behaviour of the three specimens were not observed, the deformation of the specimen with the longitudinal boundary and of the twin specimen, in which the boundary was irregular, did appear to occur with rather less ease than in the case of the specimen with the transverse boundary; and although the present tests were not sufficient to establish definite differences of fatigue strength, they showed that the orientation of the boundary had a considerable effect at least on the endurance at any given range of stress. The presence of the boundaries appeared scarcely to affect the formation and propagation of cracks. In each specimen cracks were formed in a normal manner in regions of previous heavy slip, and in their development showed no tendency either to avoid the boundary or, on the other hand, to seek it out. In one or two cases, cracks commenced to propagate along the boundary, but proceeded thus for only a short distance before deviating entirely into one or other of the crystals.

It appears that the presence of intercrystalline boundaries may considerably strengthen the constituent crystals against fatigue; but that the effect of the boundaries on the distribution or even on the amount of slip is very small. It is probable that the major effect of the boundary may lie in some restriction of strain that it imposes. Further investigation of this aspect of the problem will be undertaken.

---

* Manuscript received June 9, 1933. Presented at the Annual General Meeting, March 7, 1934.

† Superintendent, Department of Engineering, National Physical Laboratory, Teddington.

‡ Assistant, Department of Engineering, National Physical Laboratory, Teddington.

I. INTRODUCTION.

THE research in progress at the National Physical Laboratory on the fundamental aspects of fatigue failure has been conducted up to the present mainly by tests on specimens consisting of only one crystal. This method of attack was adopted because experience of the fatigue failure of crystalline aggregates had shown that failure normally commenced within one or more of the constituent grains, the cracks formed within the crystals being afterwards propagated across the intercrystalline boundaries into the adjacent grains. Tests on specimens consisting of a single crystal appeared, therefore, to afford opportunities for studying in a fundamental manner the primary formation of fatigue cracks under known conditions of stress and strain. Having determined these characteristics, the effect of the intercrystalline boundary could then be approached by a study of specimens containing various numbers of large crystals.

The first tests on single crystal specimens were made on specimens of aluminium, and the results of tests under a wide range of stress conditions soon rendered possible the formulation for this material of one general law of deformation and the development of a descriptive theory of the process of fatigue. Attention was next devoted to other materials, experiments being made to determine whether the same general law of deformation and the same process of fatigue were applicable to all metals. With this object, tests were carried out on single crystals of iron, zinc, antimony, silver, and bismuth.

Meanwhile, the problem of the effect of the boundary was not entirely neglected. At an early stage, a test * under alternating torsional stresses on a specimen of aluminium consisting of three crystals was carried out, and the general characteristics of deformation were compared with those of single crystals of the same material.

The present paper describes the results of tests under alternating torsional stresses on three specimens of aluminium, each consisting of two crystals. In one specimen the boundary between the constituent crystals was mainly transverse to the axis of torsion; in another the boundary was mainly longitudinal through that axis, whilst in the third the boundary was irregular but the two constituent crystals were in mutual twin orientation. The orientation of the constituent crystals in each specimen was determined before test by X-ray analysis, and the processes of deformation and failure were studied in relation to the structure of the crystals and to the distribution of resolved stresses on the slip planes.

* *Aeronaut. Res. Cttee. R. and M.* No. 1025, 1926.

II. CHOICE AND PREPARATION OF SPECIMENS: STRESSING SYSTEM.

The specimens used in the present tests were machined from bars of aluminium that had been subjected to the same process (Carpenter and Elam) of strain and heat-treatment used for the production of single crystals; these bars, in fact, represented a partial failure of the normal procedure to achieve its object. Partial failures of this type are a not uncommon result of attempts to grow single crystals, and from the available stock of such bars, two were chosen from which cylindrical specimens having boundaries approximately transverse and parallel, respectively, to their axes could be machined. This choice was made in the expectation that, under alternating torsional stresses these orientations would represent an approach to the two extreme cases of the influence of a single boundary. It was not possible to make any particular selection of the orientations of the constituent crystals in either of these specimens, but from the results of tests on a number of single crystal specimens of aluminium of widely different orientations and from the general law of deformation under fatigue to which these results conformed, the independent behaviour of each constituent crystal (apart from any effect due to the boundary) could be regarded as generally predicable. The third specimen was chosen in view of the special type of the relative orientation of the constituent crystals, the structures of the two crystals being mirror images of one another in an octahedral plane that was thus common to both crystals.* Particular interest was attached to the behaviour at the boundary in regions where this common plane was the operative slip plane in one crystal but not in the other. In general also, it was thought that the boundary between two crystals in twin relationship might represent a special case of the general problem.

Details of all three specimens in their final machined forms are given in Table I. In each case the test portion, of which the dimen-

TABLE I.

Specimen Reference Mark.	Description.	Test Portion.	
		Diameter (Inch).	Length (Inch).
AL5A	Transverse Boundary.	0·335	0·7
CHJ4G2	Longitudinal Boundary.	0·338	0·5
AL1B	Twin Specimen.	0·497	0·6

---

* Twins of this "spinel" type have been only rarely observed in aluminium (see Elam, *Proc. Roy. Soc.*, 1928, [A], 121, 237). The present specimen is probably the largest twin that has ever been observed in aluminium.

sions are given, was joined to the enlarged ends, by which the specimen was gripped in the testing machine, by fillets of large radius. For the purpose of measurement of twist, reference marks were scribed on the enlarged ends of each specimen.

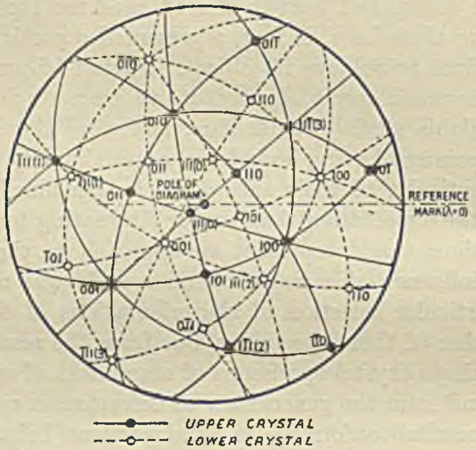


Fig. 1.—Specimen AL5A. Stereographic Projection of Principal Planes.

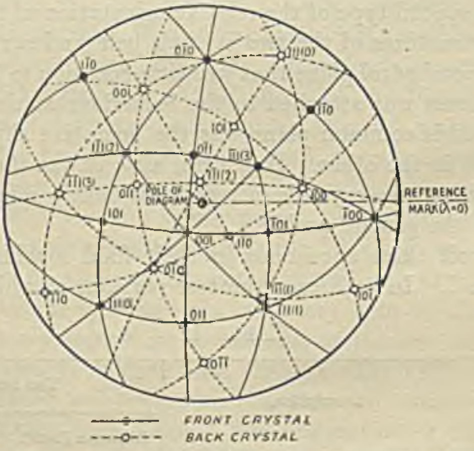
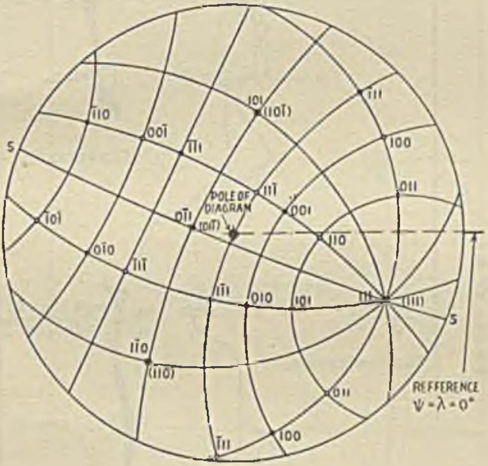


Fig. 2.—Specimen CHJ4G2. Stereographic Projection of Principal Planes.

The orientations, relative to the axis and to one of the reference marks on the enlarged ends, of the principal planes and directions of the two crystals of each specimen are shown in Figs. 1, 2, and 3; whilst the dispositions of the boundaries on the developed surfaces of the specimens are shown in Figs. 4, 5, and 6. In these diagrams, as elsewhere, the two crystals of the specimen AL5A are distinguished by the terms "top" and "bottom"; of the specimen CHJ4G2 by the terms "front" and "back"; and of the specimen AL1B by the letters A and B. In order to ensure that the effect of the transverse boundary would not be influenced by the proximity of the enlarged ends, the specimen AL5A was so machined that the boundary between the two crystals lay approximately midway between the enlarged ends (Fig. 4); for the same reason, the test portion of this specimen was made rather longer than normal. It will be seen (Fig. 5) that in the specimen CHJ4G2, the two intersections of the intercrystalline boundary with the cylindrical surface of the specimen were approximately parallel to the axis and almost diametrically opposite one another. In the specimen AL1B, practically the whole of the trace of the boundary on the surface was included in the parallel length (Fig. 6).



● AND ○ REFER RESPECTIVELY TO PLANES OF CRYSTAL A AND CRYSTAL B

■ REPRESENT PLANES OF THE SAME TYPE WHICH ARE COMMON TO BOTH CRYSTALS. THE NOTATION ENCLOSED IN BRACKETS REFERS TO CRYSTAL B

THE OCTAHEDRAL PLANE, 111, IS THE TWINNING PLANE

Fig. 3.—Specimen AL1B. Stereographic Diagram Showing Principal Planes of Both Crystals.

All three specimens were tested under alternating torsional stresses, because normally under this type of stress very little overall deformation occurs, and thus the study of the gradual process of fatigue in relation to the structure is facilitated.

III. Stress Analyses.

Up to the present time, no method has been developed for the theoretical determination of the distribution of stress set up by any applied loading system in a specimen consisting of more than one crystal. If the material (in the single crystal form) is elastically isotropic, and so long as the elastic range is not exceeded in any of the constituent crystals, the distribution of stress is entirely independent of the boundaries; but even in the case of an isotropic material, this distribution must be altered as soon as plastic deformation occurs in any crystal.

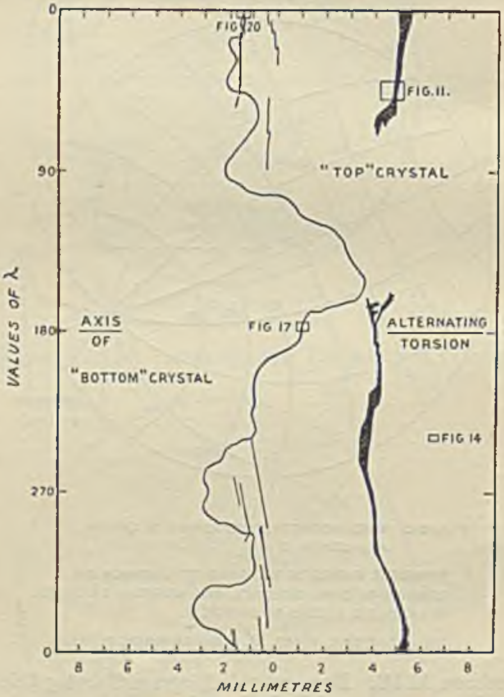


Fig. 4.—Developed Surface of Specimen AL5A.

For the purpose of the present experiments, the stresses set up in each individual crystal of each specimen have been calculated on the assumption that the boundary has no effect, *i.e.* that each crystal behaves as if it alone composed the whole specimen. Whilst this assumption is certainly not justified, comparison of the actual distribution of slip bands with the distribution predicted by this analysis of stress was expected to indicate the extent of the influence of the boundary and to yield information as to its nature. The constants in the equations to the shear stresses (as thus defined) on the slip planes in the slip directions were evaluated for both crystals of each specimen, using the consistent co-ordinates (corrected from the X-ray readings) shown in the stereographic diagrams Figs. 1, 2, and 3. The ratio of the "resolved shear stress" S_r at any point to the nominal maximum shear stress ($S = 2T/\pi r^3$, where T is the applied torque and r is the radius of the specimen) is given by the formula $S_r/S = A \cos(\lambda - \alpha)$,* where A and α depend only on the orientations of the slip plane and direction 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. The

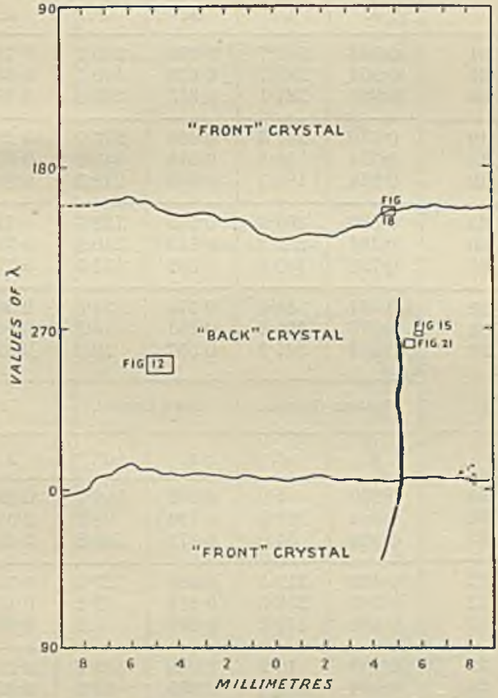


Fig. 5.—Developed Surface of Specimen CHJ4G2.

---

* *J. Inst. Metals*, 1926, 36, 185.

values of these constants together with the nomenclature of the principal crystallographic planes and directions are recorded in Table II.

TABLE II.—*Constants in Resolved Shear Stress Equations.*

Octahedral Plane.	Contained Direction.	Specimen AL5A.		Specimen CHJ4G2.		Specimen AL1B.	
		Top Crystal.		Front Crystal.		Crystal A.	
		A.	α°.	A.	α°.	A.	α°.
0(111)	01	0·963	162·7	0·764	305·2	0·784	62·9
	02	0·952	280·7	0·678	149·5	0·531	95·1
	03	0·985	221·1	0·315	242·9	0·439	22·6
$1(1\bar{1}\bar{1})$	12	0·830	247·5	0·468	275·0	0·292	0·1
	13	0·724	84·8	0·516	348·9	0·680	126·8
	10	0·256	190·3	0·593	218·3	0·885	142·1
$2(1\bar{1}1)$	23	0·680	353·9	0·525	133·7	0·713	90·2
	20	0·304	252·3	0·188	210·8	0·389	173·7
	21	0·799	195·8	0·596	151·5	0·773	60·2
$3(11\bar{1})$	30	0·481	44·3	0·778	36·5	0·590	121·9
	31	0·526	106·7	0·351	76·3	0·039	135·5
	32	0·523	341·2	0·557	12·7	0·628	122·7
		Bottom Crystal.		Back Crystal.		Crystal B.	
		A.	α°.	A.	α°.	A.	α°.
0(111)	01	0·620	1·0	0·762	158·2	0·784	62·9
	02	0·804	107·5	0·199	98·2	0·531	95·1
	03	0·864	64·0	0·877	146·8	0·439	22·6
$1(1\bar{1}\bar{1})$	12	0·499	219·1	0·509	127·2	0·765	176·4
	13	0·748	256·5	0·491	69·2	0·177	169·4
	10	0·469	119·3	0·486	6·3	0·940	175·2
$2(1\bar{1}1)$	23	0·234	10·2	0·908	178·7	0·596	13·3
	20	0·594	314·4	0·955	61·0	0·470	41·2
	21	0·709	291·2	0·965	117·5	0·283	142·6
$3(11\bar{1})$	30	0·185	176·7	0·781	91·5	0·701	146·2
	31	0·925	150·5	0·629	65·4	0·882	81·4
	32	0·761	324·6	0·351	143·7	0·863	33·9

In Figs. 7, 8, and 9 the values of S_r/S have been plotted against λ for the twelve possible slip systems of both crystals of each specimen. In order to avoid complication in the case of the specimen CHJ4G2, each set of curves has been drawn only over that region in which it is operative at the surface of the specimen (cf. Fig. 5); whilst in the case of the specimens AL5A and AL1B separate diagrams have been drawn.

The normal stresses on the slip planes were also evaluated, but since it did not prove necessary to take these normal stresses into account, their consideration has been omitted from the present paper.

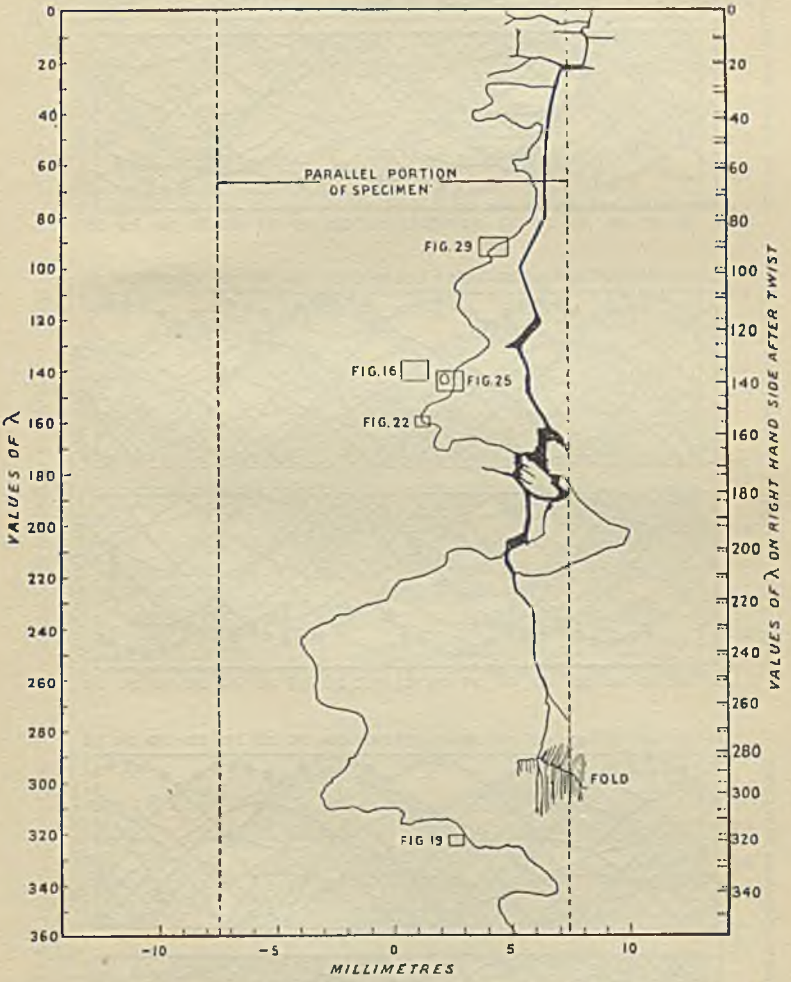


Fig. 6.—Developed Surface of Specimen AL1B.

IV.—Traces of Planes.

The slopes of the traces of the slip planes of both crystals of each specimen were calculated and the slopes of the slip bands observed were correlated with the calculated values.

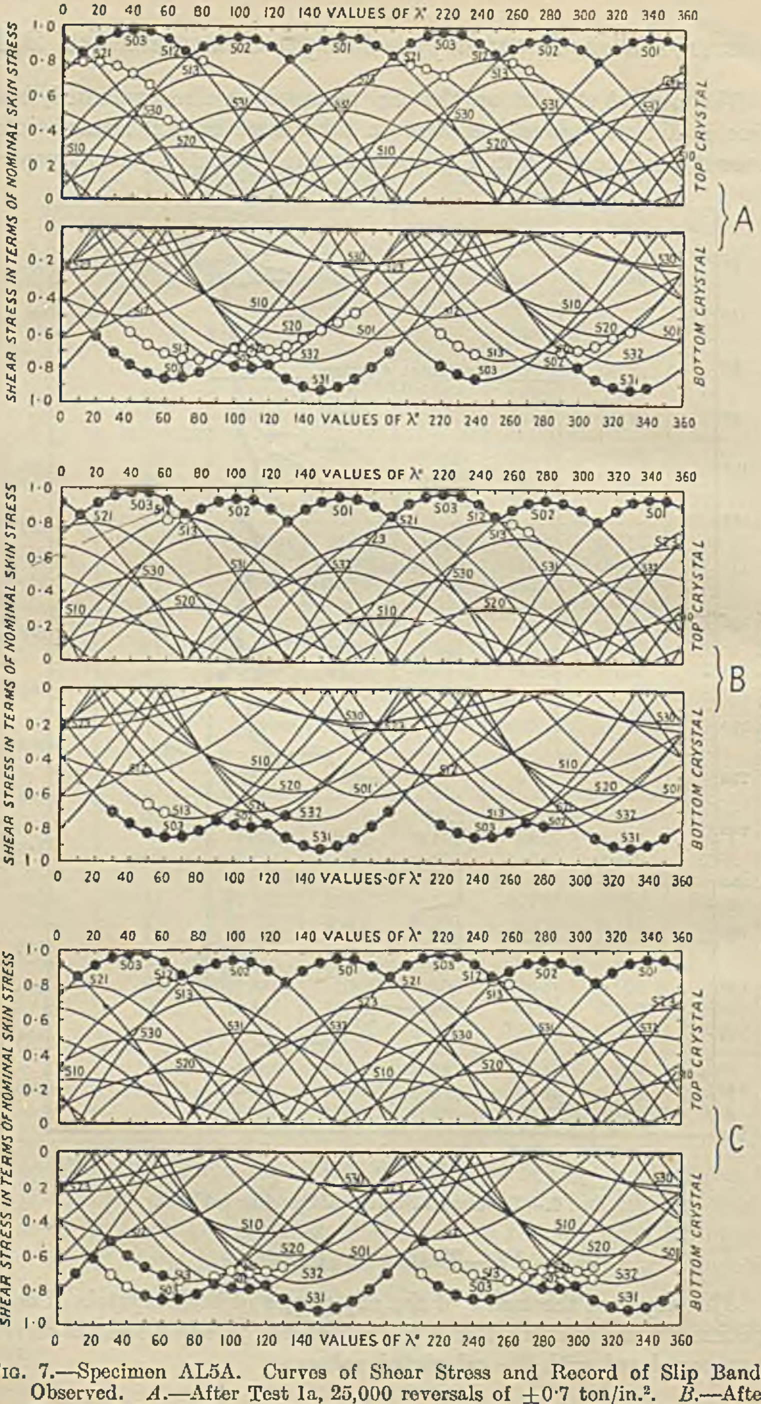


Fig. 7.—Specimen AL5A. Curves of Shear Stress and Record of Slip Bands Observed. *A.*—After Test 1a, 25,000 reversals of ±0·7 ton/in.². *B.*—After Test 1e, 0·25 × 10^6 reversals of ±0·7 ton/in.². *C.*—After Test 2b, 3·50 × 10^6 reversals of ±0·9 ton/in.². Full Circles Indicate General Systems of Slip, Open Circles Indicate Occasional Bands.

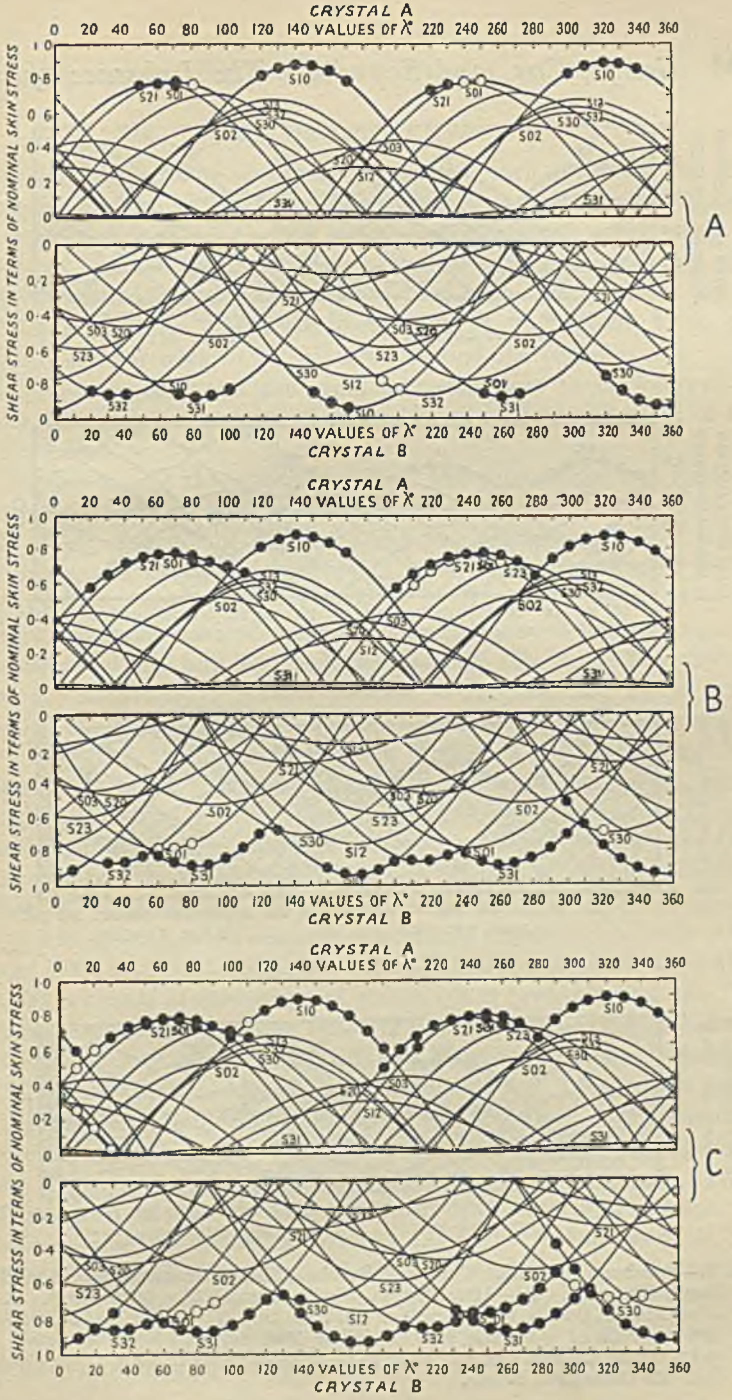


Fig. 8.—Specimen AL1B. Curves of Resolved Shear Stress and Record of Slip Bands Observed. *A*.—After Test 1a, $0{\cdot}12 \times 10^6$ reversals of $\pm 0{\cdot}95$ ton/in.^{2} *B*.—After Test 3a, 6000 reversals of $\pm 1{\cdot}6$ ton/in.^{2}. *C*.—After Test 3b and fracture, $0{\cdot}64 \times 10^6$ reversals of $\pm 1{\cdot}6$ ton/in.^{2}. Full Circles Indicate General Systems of Slip. Open Circles Indicate Occasional Bands.

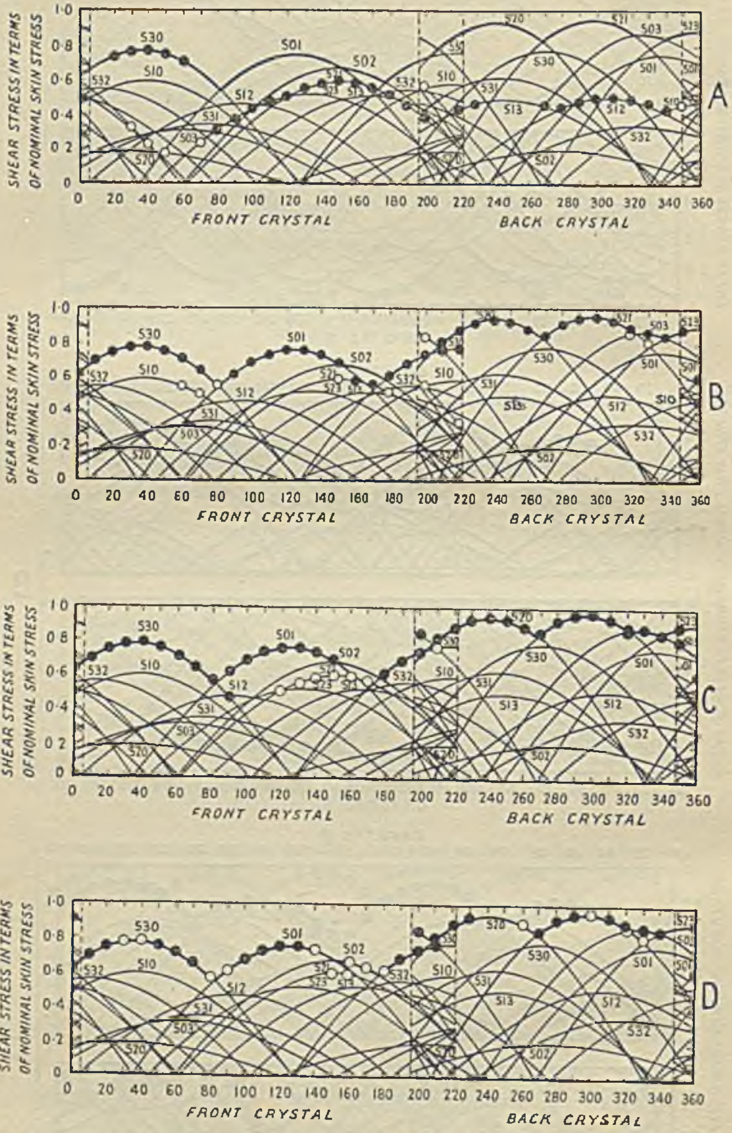


Fig. 9.—Specimen CHJ4G2. Curves of Resolved Shear Stress and Record of Slip Bands Observed. *A*.—After Test 1a, 25,000 reversals of ±0·7 ton/in.². *B*.—After Test 1b, 0·29 × 10^6 reversals of ±0·7 ton/in.². *C*.—After Test 3a, 0·26 × 10^6 reversals of ±1·1 ton/in.². D. After Test 4a, 0·27 × 10^6 reversals of ±1·3 ton/in.². Full Circles Indicate General Systems of Slip, Open Circles Indicate Occasional Bands.

V.—Details of Tests.

A complete list of all the tests to which each specimen was subjected is given in Tables III, IV, and V. It was originally intended to subject each specimen to a series of short runs at a safe range of stress ($\pm$ 0·7 ton/in.^{2}), and after each run to examine the slip produced, particularly in relation to the boundary. This process was to be continued until slip under this range was exhausted, when the applied stresses were to be increased beyond the probable safe range (to $\pm$ 0·9 ton/in.^{2}) and the same procedure was to be followed in order to watch the process of failure in relation to the effect of the boundaries.

In the case of the specimen AL5A, this programme was followed throughout, and failure of the specimen occurred after a total of $5{\cdot}27 \times 10^6$ reversals of $\pm$ 0·9 ton/in.^{2} nominal resolved shear stress. In the case of the specimen CHJ4G2, however, the programme had to be amended, because, after a total of $12{\cdot}15 \times 10^6$ reversals of $\pm$ 0·9 ton/in.^{2} nominal resolved shear stress, not only were there no signs of imminent failure, but the production of new slip bands had entirely ceased. Accordingly, it was decided to increase the stress range applied to the specimen CHJ4G2. After $6{\cdot}20 \times 10^6$ reversals of $\pm$ 1·1 ton/in.^{2}, the production of new slip bands had again practically ceased, and it was therefore decided still further to increase the stress range. After $2{\cdot}24 \times 10^6$ reversals of $\pm$ 1·3 ton/in.^{2}, the rate of production of slip bands had again become very slow; whilst even after $1{\cdot}26 \times 10^6$ reversals of $\pm$ 1·5 ton/in.^{2} practically no slip could be observed. Accordingly, the applied range was still further increased to $\pm$ 1·75 ton/in.^{2}, when cracking commenced almost immediately (after about 2000 reversals); complete failure of the specimen occurred after 63,500 reversals of this range of stress. It is probable that the true fatigue range of the specimen CHJ4G2 (*i.e.*, the fatigue range developed after the understressing described) was actually about $\pm$ 1·5 ton/in.^{2}. It is possible that this true range was less than $\pm$ 1·5 ton/in.^{2}, but it is regarded as unlikely that it was below $\pm$ 1·3 ton/in.^{2}. Some caution, however, is necessary in this surmise, in view of the results obtained from a previous specimen.* This specimen consisted of three crystals (of unknown orientation) subjected to reversed torsional stresses. It fractured after the following history: (*a*) $5{\cdot}07 \times 10^6$ cycles of $\pm$ 0·64 ton/in.^{2} (nominal shear); (*b*) $13{\cdot}27 \times 10^6$ cycles of $\pm$ 0·75 ton/in.^{2}, and (*c*) $30{\cdot}79 \times 10^6$ cycles of $\pm$ 1·0 ton/in.^{2}. Thus the fatigue limit of this specimen, which contained two longitudinal boundaries, was certainly less than $\pm$ 1·0 ton/in.^{2} resolved shear stress.

---

* *Loc. cit.*

TABLE III.—*Details of Tests of Specimen AL5A.*

No. of Test.	Range of Nominal Shear Stress, Ton/in.^{2}.	Reversals.	Total Reversals at Same Range of Stress.	Remarks.	Treatment Prior to Next Test.
1a	± 0·7	25,000	25,000	Fairly general slip.	Repolished.
1b	± 0·7	0·25 × 10^6	0·27 × 10^6	,, ,,	Etched and repolished.
1c	± 0·7	0·25 × 10^6	0·52 × 10^6	,, ,,	Repolished.
1d	± 0·7	1·00 × 10^6	1·52 × 10^6	Very little slip.	Repolished.
2a	± 0·9	1·00 × 10^6	1·00 × 10^6	General slip; heavy in places.	Repolished.
2b	± 0·9	3·50 × 10^6	4·50 × 10^6	Same as 2a, with number of cracks.	Repolished.
2c	± 0·9	0·77 × 10^6	5·27 × 10^6	Large crack developed.	...

TABLE IV.—*Details of Tests of Specimen CHJ4G2.*

No. of Test.	Range of Nominal Shear Stress, Ton/in.^{2}.	Reversals.	Total Reversals at Same Range of Stress.	Remarks.	Treatment Prior to Next Test.
1a	± 0·7	25,000	25,000	Very little slip.	Etched and polished.
1b	± 0·7	0·29 × 10^6	0·31 × 10^6	Fairly general slip.	,,
1c	± 0·7	0·27 × 10^6	0·58 × 10^6	No slip.	None.
1d	± 0·7	0·96 × 10^6	1·54 × 10^6	,,	Repolished
2a	± 0·9	1·00 × 10^6	1·00 × 10^6	General slip: fairly heavy.	,,
2b	± 0·9	3·05 × 10^6	4·05 × 10^6	Heavier slip; but not general.	,,
2c	± 0·9	2·30 × 10^6	6·35 × 10^6	Fairly general slip.	None.
2d	± 0·9	5·80 × 10^6	12·15 × 10^6	No slip.	,,
3a	± 1·1	0·26 × 10^6	0·26 × 10^6	Fairly general light slip.	Repolished
3b	± 1·1	2·78 × 10^6	3·04 × 10^6	Very little slip.	None.
3c	± 1·1	3·16 × 10^6	6·20 × 10^6	Practically no further slip.	Repolished.
4a	± 1·3	0·27 × 10^6	0·27 × 10^6	Fairly general light slip.	None.
4b	± 1·3	1·97 × 10^6	2·24 × 10^6	Very little slip but fairly heavy.	Repolished.
5	± 1·5	1·26 × 10^6	1·26 × 10^6	Practically no slip.	,,
6a	± 1·75	2000 approx.	2000 approx.	Number of cracks.	,,
6b	± 1·75	63,500	65,500	Large crack developed.	...

TABLE V.—*Details of Tests of Specimen AL1B.*

No. of Test.	Range of Nominal Shear Stress, Ton/in.^{2}.	Reversals.	Total Reversals at Same Range of Stress.	Remarks.	Treatment Prior to Next Test.
1	± 0·75	$0{\cdot}25 \times 10^6$	$0{\cdot}25 \times 10^6$	No slip visible.	Repolished.
2a	± 0·95	$0{\cdot}12 \times 10^6$	$0{\cdot}12 \times 10^6$	General slip.	„
2b	± 0·95	$0{\cdot}25 \times 10^6$	$0{\cdot}37 \times 10^6$	Fresh slip.	None.
2c	± 0·95	$0{\cdot}63 \times 10^6$	$1{\cdot}00 \times 10^6$	„ „	„
2d	± 0·95	$1{\cdot}78 \times 10^6$	$2{\cdot}78 \times 10^6$	No fresh slip.	Repolished.
3a	± 1·60	6000	6000	Heavy slip; 2·7° twist.	None.
3b	± 1·60	$0{\cdot}64 \times 10^6$	$0{\cdot}64 \times 10^6$	Large crack; 6·2° twist.	...

In the case of the specimen AL1B, no slip occurred under a stress range of ± 0·75 ton/in.^{2} nominal shear stress, whilst under a range of ± 0·95 ton/in.^{2}, slip was exhausted after about one million reversals. The stress was accordingly increased to ± 1·6 ton/in.^{2}, when fracture resulted after $0{\cdot}64 \times 10^6$ reversals of this range of stress. For this specimen also, it is unsafe to attempt a close estimate of the actual fatigue strength. The fatigue limit was probably greater than ± 0·95 ton/in.^{2} and certainly less than ± 1·6 ton/in.^{2} nominal shear stress. At the present stage, careful study of the characteristics of deformation appears to be of greater value than the accurate determination of fatigue limits. At a later stage it is hoped to obtain quantitative data by a series of tests in which each specimen is tested throughout at one range of stress.

VI.—EXPERIMENTAL OBSERVATIONS.

(a) *Method of Presentation.*

The measurements and records made of the deformation of the three specimens tested were very extensive, and adequate presentation of the results constitutes a problem of some difficulty. It appears advantageous to divide the discussion of the changes of microstructure occurring during the tests into two parts, describing in the first part the general behaviour in regions remote from the boundary, and in the second the special features observed close to the boundary.

(b) *Microstructure in Regions Remote from the Boundary.*

In all three specimens, the general appearance of the slip bands in regions remote from the boundary was, throughout the tests, entirely similar to that of slip bands produced by similar tests on single crystals; moreover, apart from some anomalous slip occurring in the early stages of test (and this again is characteristic of the single crystal), the distribution of the bands was in every case in good agreement with the distribution anticipated on the basis of calculated shear stresses. This result is a clear indication of the very small effect of the boundary on the general stress distribution and, coupled with the facts that the regular systems normally approached very close to and often intersected the boundary, and that very little anomalous slip near the boundary was observed, it suggests that the major effect of the boundary is limited to a very small region in its vicinity. Typical diagrams illustrating the general distribution of slip bands at various stages of the tests are shown in Figs. 7, 8, and 9, in which full circles indicate general slip on the plane indicated by the stress curve on which the circle is placed at the value of λ given by the abscissa, whilst open circles indicate localized slip which in most cases was confined to the neighbourhood of the boundary. Photomicrographs illustrating the appearance of slip bands in regions remote from the boundary are shown in Figs. 11–16 (Plates XIII and XIV).

The general manner in which slip bands were formed at each range of load is shown in Tables III, IV, and V, but for effective comparison of the behaviour of the specimens some further remarks are necessary.

The behaviour of the specimen AL5A was throughout entirely similar to that of the single crystal. The range of nominal shear stress of $\pm$ 0·7 ton/in.^{2} at first produced fairly general slip in good agreement with the distribution of resolved shear stress (Figs. 7 *A*, *B*), and this slip was exhausted after about one million cycles. The increased range of $\pm$ 0·9 ton/in.^{2} then again produced general slip, which finally culminated in heavy slip (Fig. 7 *C*) and failure.

Although the first test of the specimen CHJ4G2 at a stress range of $\pm$ 0·7 ton/in.^{2} produced a system of slip not in accordance with the resolved shear stress distribution (Fig. 9 *A*), the normal slip distribution resulted from a further test at the same range (Fig. 9 *B*), but slip at this range was always light and was exhausted after about 250,000 reversals. Thereafter a stress range of $\pm$ 0·9 ton/in.^{2} produced general slip that continued for at least five million reversals and then ceased completely, no further slip being produced during a further run of six million reversals. Stress ranges of $\pm$ 1·1 ton/in.^{2} (Fig. 9 *C*) and 1·3 ton/in.^{2} (Fig. 9 *D*) both in turn produced slip that was at first fairly general but which showed no tendency to develop into heavy bands, but rather to grow lighter and less general, and finally to cease altogether, whilst a stress range of $\pm$ 1·5 ton/in.^{2} produced no discernible slip whatsoever. The rapidity of failure at $\pm$ 1·75 ton/in.^{2} suggests that slip would have occurred at $\pm$ 1·5 ton/in.^{2} if sufficient reversals

BIBLIOT OLITECHN ASKIEJ

PLATE XIII.

FIG. 11.—Specimen AL5A. $\lambda = 45^\circ$.
After test 1c. × 100.

FIG. 12.—Specimen CHJ4G2. $\lambda = 291^\circ$.
After test 1b. × 100.

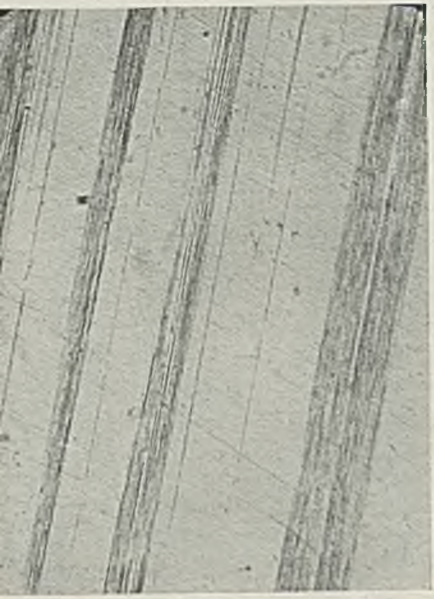


FIG. 13.—Specimen AL1B. $\lambda = 140^\circ$.
After test 2a. × 100.

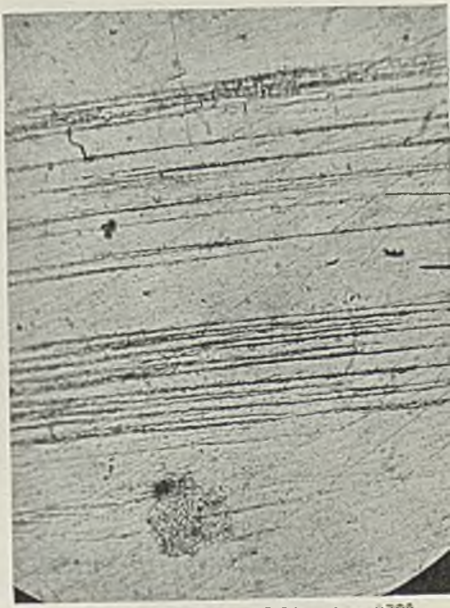


FIG. 14.—Specimen AL5A. $\lambda = 239^\circ$.
After test 2b. × 330.

All figures reduced by ½ in reproduction.

FIG. 23.—Specimen Al.1B. λ = 88°.
d = 4·2. After test 3b. × 100.

Reduced by ½ in reproduction.

had been imposed, but throughout the tests slip appeared to occur only with difficulty and to be very quickly exhausted at any one range of stress.

The first test of the specimen AL1B at a stress range of ± 0·75 ton/in.^{2} produced no slip at all, whilst slip under a stress range of ± 0·95 ton/in.^{2} was fairly general (Fig. 8 *A*) but grew lighter as the test proceeded, and finally, after about one million reversals, ceased altogether. A small amount of anomalous slip occurred, but the calculated range of stress on the plane concerned was only very slightly less than the actual maximum, so that this anomaly is probably unimportant. Thereafter the stress range of ± 1·6 ton/in.^{2} resulted in general slip (Figs. 8 *B* and *C*) and fairly rapid failure; but the number of cycles of this range that the specimen endured suggests that the behaviour at intermediate ranges might have been very similar to that of the specimen CHJ4G2.

Reviewing the general behaviour of the specimens in relation to their structure, it is inevitably concluded that the differences of behaviour must be related chiefly to strain restrictions imposed by the boundaries, for no correlation can be exhibited between these differences and the orientations of the individual crystals, whilst purely stress effects due to the boundaries are excluded by the excellent agreement of the slip band system with the distribution of resolved shear stress. The essential nature of the differences of behaviour and the manner in which they may be ascribed to the boundaries will be discussed in detail later.

Two further features of the general distribution of slip bands are perhaps worthy of comment. In certain regions (remote from the boundary) the slip bands formed on the surface of the front crystal of the specimen CHJ4G2 showed a tendency to group along fairly definite lines approximately at right angles, these directions being nearly, but not exactly, parallel and perpendicular to the direction of the constituent slip bands themselves. Such grouping has previously been observed in tests on single crystals, although the effect has not been so pronounced. It probably represents differences of hardness; the cause of these is not known.

In the last two tests on the specimen AL1B a system of double slip in "herring-bone" formation was produced (Fig. 16, Plate XIV). The double slip system corresponds with deformation on two octahedral planes, one of which is that subjected to the maximum resolved shear stress at the point, whilst the second is subjected to the next greatest stress value; moreover, the stress difference is small. It is easy to understand that in a position near the boundary, where strain conditions are probably complex, this process of slip on the two planes of highest stress intensity affords a suitable means of adjustment of total strain. Slip on two planes was also observed after fracture in crystal A in the region $\lambda = 60°–90°$, the systems being S_{01} and S_{21} on which the stresses are almost equal. This " herring-bone " type of slip was also observed on some occasions in previous tests on single crystals; in all cases the two planes concerned were those subjected to the two highest values of shear stress.

(c) *Microstructure in Regions Adjacent to the Boundary.*

It is not possible to give any concise and detailed description, either diagrammatically or otherwise, of the distribution of slip bands in the immediate neighbourhood of the boundary. From the recorded observations it would have been possible to show the complete distribution of slip after each test on diagrams of the developed surface (Figs. 4, 5, and 6), but it would have been impracticable in such diagrammatic representations to record the actual appearance of the slip bands, for which purpose only complete photographic panoramas would have been satisfactory.

Photographic methods, including the preparation of panoramic diagrams, were used freely during the course of the tests, but in this paper the presentation must be restricted to a general description supplemented by a few representative photomicrographs.

In all the tests (except those that culminated in fracture) the structural differences between areas close to and remote from the boundary lay almost entirely in the size, number, spacing, and general appearance of the slip bands. Only in one or two isolated spots was a system of slip bands observed different from or additional to that observed at the same value of λ in regions remote from the boundary, and in every case these anomalous bands were faint and few in number. In the majority of cases these bands were produced in regions where the intersection of the boundary with the surface of the specimen was rapidly changing direction, and it was obvious that they owed their origin to the restrictions imposed by this cause.

Apart from these small areas of anomalous slip, the general system of slip produced in regions remote from the boundary continued right into the region adjacent to the boundary without any marked change. In some cases slip continued right up to the boundary * on both sides (Fig. 17, Plate XIV), in some it appeared to stop short on one side (Fig. 18,

---

* The expression " right up to the boundary " must not be interpreted too literally without reference to the experimental technique. Although the resolving power of the 4 mm. apochromat objective used for the examinations was very high, yet in terms of atom spacing the smallest distance that could be resolved was very large, and in all cases it is possible that slip may not have approached to within one thousand or so atoms of the true boundary.

Plate XIV), whilst in others the slip did not intersect the boundary on either side. There seemed to be no correlation between the behaviour of the specimens in this respect and the stress and strain conditions. Thus in Fig. 17 (Plate XIV), where close and fairly heavy systems of slip are shown approaching the boundary closely on both sides, it might have been anticipated that the very considerable curvature of the boundary would have produced a marked shielding effect, whilst in other places there appeared to be no adequate reason why the slip bands should stop short. In general, it may perhaps be said that systems of heavy slip tended to continue right up to the boundary, whilst sparser systems tended to stop short, but this statement is true only in a general sense, and several exceptions were noted. Although in many cases the intersection of a slip band in one crystal with the boundary appeared to be the point of origin of a band in the other crystal, this was in general not the case, the two sets of slip normally appearing disconnected (Fig. 17).

Although so much of the evidence regarding the effect of the boundary on the process of slip is inconclusive, one definite phenomenon was observed. In regions of heavy slip, where the shear movement close to the boundary had clearly been considerable, the slip band spacing decreased as the boundary was approached. This effect was most noticeable in the case of slip bands nearly perpendicular to the boundary, when a number of short subsidiary slip lines were formed in between the main bands (Fig. 17), but the effect was also observed in cases where the slip bands were nearly parallel to the boundary (also Fig. 17). In general, however, the amount of the decrease in the spacing of the bands was greater with greater angle between the boundary and the direction of the slip bands.

In the specimen AL1B the intercrystalline boundary was very irregular in form and, owing to the twin relationship of the component crystals, there were regions on the surface of the specimen where its course could not be determined with certainty.* The true course of the boundary in cases of doubt was revealed, however, by the slip distribution in its neighbourhood, and, in particular, the occurrence of slip revealed several small outcrops of one crystal in the other. The distribution of slip in and around such islands proved of special interest, for slip continued right up to the boundary in every case, both internally and externally, and in both areas occurred on the plane predicted by shear stress analysis; in other words, both the island and the matrix

---

* The boundaries of all three specimens were of course recorded from observations of the etched surfaces; but in the case of the specimen AL1B the symmetry of the twin precluded differential etching effects at certain orientations of the surface relative to the crystal structure.

in which the island was imbedded behaved as if they each severally composed the whole crystal. Whilst it must not be forgotten that these outcrops were joined presumably to the parent crystal below the surface of the specimen, and cannot be regarded therefore as completely independent crystals, it should also be remarked that the more strongly the island was connected to the parent crystal the more the part of the other crystal lying between the island and the true boundary would be relieved of the dominating influence of its own parent crystal. *It appears, therefore, that the effect of the boundary on the stress distribution is extremely slight.*

In the case of the specimen AL1B, particular interest was attached to the occurrence of slip on the common (twinning) plane. This plane was not an "operative" slip plane—by reasons of resolved stress—at any point in crystal B, but at about $\lambda = 54°$ and 234° the resolved stress intensity on the plane was only about 3 per cent. below the calculated maximum at this point. At corresponding positions in crystal A, plane 0 was the operative slip plane, and it would appear probable that slip on this plane in crystal A would have continued into crystal B. This was not the case after test No. 2a, however, when the slip occurring on the common plane in crystal A ceased at the boundary. After tests Nos. 2b and 2c no slip occurred on the twinning plane, although after test No. 2c it occurred on A_{21}* at $\lambda = 75°$, at which point the stress on this plane is slightly lower than that on A_{01}. This was not a boundary effect, and was probably due to the restricting effect of the enlarged end on slip nearly parallel to the axis; that on A_{21} was nearly perpendicular to the axis, and so less restricted.

After test No. 3a, at the higher stress, slip on the O plane in crystal A continued for some distance into crystal B, as shown in Fig. 23 (Plate XVI), although in B the stress on B_{01} was considerably less than that on B_{31}. It should be noted, however, that very heavy distortion occurred during this test, and that the occurrence of slip on B_{01} may have been largely affected by the presence of the crack which would be expected entirely to alter the local stress distribution. In general, it may be said therefore that at stress ranges which produced slip but not marked "mass distortion" or cracks, the slip occurring on the common octahedral plane was controlled by resolved shear stress considerations only.

(d) *Fracture.*

(i) *Specimen AL5A.*

It has been recorded already that the distribution and appearance of the slip bands produced on the surface of the specimen AL5A at

---

* A_{21} indicates slip in crystal A, on plane 2, in direction 21.

points remote from the boundary were entirely characteristic of a single crystal. The development of these bands in the latter stages of test was also exactly similar to the process as it occurs in the single crystal. The effect of the unsafe range of stress was (i) to produce heavy slip of the type shown in Fig. 14 (Plate XIII); (ii) to cause the formation of a number of fine cracks on the site of previous heavy slip; and (iii) to result in fracture by the development of one or more of the fine cracks. The stage of actual failure was reached only in the upper crystal, almost complete fracture of this crystal occurring before any independent cracks of appreciable size had been formed in the lower crystal. Although the actual maximum resolved shear stresses for the two crystals were not very different (Fig. 7), this difference in behaviour can be attributed to the greater uniformity of resolved shear stress in the upper crystal, and to the fact that the deformation of this crystal occurred entirely by slip on the one slip plane * that was almost perpendicular to the axis of torsion (Fig. 1) and parallel to the boundary.

In addition to the main crack, which could be said to constitute the primary cause of failure, a number of smaller cracks was also formed in the upper crystal. The positions of all the cracks observed have been recorded on the diagram of the developed surface (Fig. 4). It will be seen that the main crack approached the boundary closely, but that it did not intersect nor run along the boundary. The portion of the boundary close to the end of this main crack had obviously suffered very considerable distortion, but there was no sign of any cleavage along the boundary, nor did any of the numerous heavy slip bands in this region show any sign of development into cracks.

Several of the subsidiary cracks did, however, intersect the boundary in several places. One of these cracks originated in the upper crystal, probably on the site of previous heavy slip in the region $\lambda = 20^\circ$; it then extended upwards to the boundary where its development was temporarily arrested, passed through a portion of the lower crystal back into the upper crystal, intersected the boundary again in several places, and finally continued into the upper crystal. At the lower end the crack appeared to have continued through the upper crystal until it met the boundary, when it passed into the lower crystal. Although the process of cracking in this case almost certainly started along the site of previous slip bands, it should be noticed that the crack was propagated into the lower crystal along a plane parallel to which very little slip had previously occurred. Development along this plane rather than along the slip plane actually operative at this point (in

---

* The particular and interesting orientation of this crystal is unique among those hitherto tested at the National Physical Laboratory.

the lower crystal, Fig. 7) was clearly decided by the preference of the crack to develop without serious deviation from the circumferential direction rather than to extend axially into the lower crystal. The portion of the crack that tends to run along the boundary (Fig. 4 and Fig. 20, Plate XV) is also of interest in this connection. At several points the crack has started to develop axially into the lower crystal, but has penetrated only a short distance before returning to the circumferential direction. In view of the fact that the axial slip bands previously formed in the lower crystal themselves showed definite signs at this stage of developing into cracks, this behaviour is an excellent illustration of the strong tendency (often previously observed) for a crack formed in a crystal subjected to torsional fatigue to propagate in the circumferential direction.

(ii) *Specimen CHJ4G2.*

At no stage of the tests on the specimen CHJ4G2 were there observed any heavy bands of the type that usually presage failure and in the test immediately prior to that in which cracking commenced no slip at all occurred. Fracture eventually commenced under a stress range of ± 1·75 ton/in.^{2}, one or two fine cracks being produced after a few thousand reversals of this range. These small cracks were formed in the region $\lambda = 300°$ parallel to plane 2 of the back crystal. Subsequently, after about 60,000 further reversals of ± 1·75 ton/in.^{2}, one of these cracks developed to such an extent as to constitute complete failure. This main crack finally extended from $\lambda = 238°$ to $\lambda = 40°$, intersecting one edge of the intercrystalline boundary at about $\lambda = 355°$. Although this main crack stopped well short of the other edge of the boundary (at about $\lambda = 208°$), considerable disturbance of the surface was observed in this region, and it is probable that the failure of the crack to cross the boundary was due only to the cut-out of the machine operating before the crack was propagated so far. The positions of all the cracks observed on the surface of the specimen after failure are shown in Fig. 5.

The curves shown in Fig. 9 show that in the region $\lambda = 300°$, the plane 2 of the back crystal was very highly stressed. In addition, although in test No. 5 (immediately preceding the test in which failure commenced) practically no slip occurred in this or in any other region, in all the preceding tests, in which any slip at all occurred, well-marked bands parallel to the plane 2 of the back crystal were always observed in this region. The initiation of a fatigue crack in this area was therefore to be anticipated.

Fig. 21 (Plate XV) shows the appearance of slip bands in the neighbourhood of the fracture after test No. 6a. It will be seen that many of the bands show signs of developing into cracks.

(iii) *Specimen AL1B.*

Failure of the specimen was presaged by the appearance in test No. 3a (6000 reversals at ± 1·5 ton/sq. in.) of considerable permanent twist, with the formation of a " corrugated " surface and of alternating slip systems occurring on different planes (Fig. 16, Plate XIV).

Failure occurred after a further 635,700 reversals at the same range of stress by the formation of a roughly circumferential crack, confined almost entirely to crystal B. The course of the crack, together with that of the boundary, on the surface of the specimen is shown in Fig. 6. The specimen was found to have suffered a permanent twist of about 6·2°, about 1° of this being distributed over the length of the specimen, and the remainder being due to the two parts of the specimen (separated by the crack) having rotated relatively to each other about the remaining comparatively small sound area.

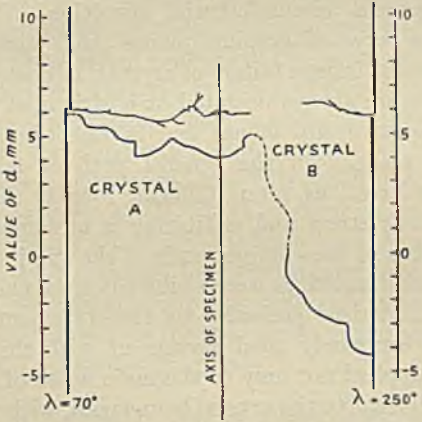


Fig. 10.—Specimen AL1B. Map of Cross-Section of Specimen after Fracture (Showing Crack and Boundary).

The specimen after fracture was cross-sectioned longitudinally along the plane containing the axis and λ = 70° and 250°. The section was polished and etched, and the crack and boundary mapped (see Fig. 10).

The crack followed in general the trace of the 3 plane (crystal B) for a large portion of its length. The plane of maximum resolved stress in the whole specimen was the 1 plane, but as this plane very nearly contained the axis of the specimen, the constraint imposed by the enlarged end and the boundary probably prevented the crack from developing along this plane. It is at least possible, however, that the crack started at $\lambda = 165°$, for the following reasons :—

(1) This is near the point of maximum stress in the whole specimen;
(2) The crack is here parallel to the plane (1) of maximum stress;
(3) The crack is here open to the widest extent, and this is also about the middle of the crack.

Plane 3 was the next most highly stressed and was also the most favourably placed plane for crack propagation, *i.e.*, that most nearly perpendicular to the axis. The crack has consequently propagated along this plane, with occasional deviations, probably required to maintain the general circumferential direction. These deviations sometimes follow crystallographic planes and sometimes do not. General experience of fatigue failure of crystals indicates that, although the fatigue cracks are always initiated at positions of maximum shear stress of the operative slip planes and in directions parallel to the traces of these planes, yet the general path of failure frequently proceeds in other directions, often following roughly the plane of maximum *nominal* shear stress and exhibiting a preference to avoid the restraining influence of the enlarged ends of the specimen.

Profuse slip band markings were visible after the final test (Fig. 8 *C*). These can be summarized generally by the statement that their distribution was in extremely good agreement with the resolved shear stress law; this applied not only to the main areas of the crystal, but also to regions adjacent to the crystal boundaries, with the exception of small areas where a few signs of slip on other planes were observed (see Fig. 23, Plate XVI). The only other regions where more than one system of slip was observed were in fairly close proximity to large cracks and were those where the two planes concerned were subjected to ranges of stress which did not differ greatly in intensity.

It was difficult to trace the exact course of the fracture relative to the boundary at points where it crossed the boundary, but there appears to be only a very slight tendency for the crack to proceed *along* the boundary; in general, the crack was approximately perpendicular to the boundary.

VII.—SUMMARY OF RESULTS AND CONCLUSION.

(a) *Distribution of Shear Stress.*

The first general conclusion, particularly from the earlier stages of the tests, is that the effect of the presence of the boundary on the slip deformation, as estimated by applying the resolved shear stress law to each individual crystal, is extremely small. In this connection, it may be mentioned that, in many cases, a greater amount of slip, which does not conform to the shear stress law, has been observed during the first loading of *single* crystals than in the two-crystal specimens investigated in the present tests. This general conclusion needs modification neither for the special case of the octahedral plane common to both crystals at positions where the plane is " operative " in one crystal but not in its neighbour, nor for that of the small " out-crops " of one crystal through the other. These out-crops were small, and situated at distances from their parent crystals which were large in terms of the surface diameters of the out-crops, and they may be regarded therefore as analogous, to some extent, to individual crystals in a fully-divided aggregate. The slip distribution observed on these out-crop crystals agreed exactly with the resolved shear stress analysis of the parent crystal.

It appears, therefore, that the presence of boundaries has but little effect on the stress distribution, which in each individual crystal is that corresponding with the distribution that would be set up if that crystal composed the whole specimen, and that this conclusion may apply even if the crystal size is fairly small. If the deformations concerned were purely elastic, this result would indicate little more than that aluminium crystals are probably isotropic, but, considering that it applies with equal force after considerable slip has occurred, it suggests that slip itself does not result in serious internal stress nor in any other manner effectively alter the stress distribution.

(b) *General Process of Deformation.*

In reviewing the general process of fatigue, it is important to remember that all three specimens were prepared in the same manner, and subjected to tests that differed only in the number of reversals imposed at the various ranges of stress. The position of the boundaries as such has already been sufficiently remarked; it remains to consider the effect of the position of the boundary in relation to the enlarged ends and to the orientation of the constituent crystals. The number of effectively different orientations (relative to given axes) of a single crystal of aluminium is strictly limited by the symmetry of the lattice, so that the orientation of the constituent crystals should not be of major importance. It was, however, unfortunate that the top crystal in the specimen with the transverse boundary should have had an octahedral plane nearly perpendicular to the axis of torsion and hence nearly parallel to the boundary, for under these conditions the process of slip in this crystal would be expected to be almost independent of any effect due to the boundary, and the result, that this crystal behaved exactly as a single crystal, was almost a foregone conclusion. If this crystal had not had this particular orientation, it is possible that the effect of the boundary might have been greater or at least more marked, but the behaviour of the lower crystal in the same specimen (see Fig. 20, Plate XV) suggests that the difference would probably not have been very great, as, before final failure of the specimen, the lower crystal had developed markings, which appeared to be cracks in an early stage of development, on an octahedral plane (3) approximately perpendicular to the boundary.

The position of the boundary in relation to the enlarged ends of the specimen is likely to have been of greater moment. The enlarged ends presumably act as fairly rigid boundaries transverse to the axis of torsion. The effect of an intercrystalline boundary also transverse to the axis is, therefore, apart from local effects, only equivalent to reducing the test length of each constituent crystal, whereas if the boundary is longitudinal a different *type* of restriction is imposed. It might have been anticipated that this difference would have been reflected in the amounts of permanent twist occurring during the tests. No real difference between the two specimens with nearly plane boundaries in this respect was, however, observed; the amount of twist occurring in each individual test was small (usually less than 2°) and the values recorded appeared to be quite irregular.

From the results of the tests, it can be concluded that the behaviour of the specimen with the transverse boundary was not appreciably affected by the presence of the boundary, each crystal deforming and fracturing as if it alone composed the whole specimen. The behaviour of the specimen with the longitudinal boundary differed from that of a single crystal in three main particulars: (i) under each range of stress, deformation by slip appeared to be slightly delayed, whilst hardening was slightly accelerated; (ii) the heaviest slip bands that were produced were not definitely of the "massed" type, that usually presages the commencement of failure, so that the process of slip afforded but little clue to the probable value of the fatigue limit; (iii) although the actual process of failure was similar to that of the specimen with the transverse boundary, and hence similar also to that of a single crystal, the initiation of this failure (by the production of small intercrystalline cracks) did not occur until a stress range much greater than that sufficient to cause failure of the specimen with the transverse boundary was imposed. The behaviour of the twin specimen, the boundary of which was irregular in form, was mainly similar to that of the specimen with the longitudinal boundary. No slip at all occurred at the lowest stress range ($\pm$ 0·75 ton/in.^{2}), whilst at a stress range of $\pm$ 0·95 ton/in.^{2} slip was exhausted before any sign of imminent failure was observed. Fracture of this specimen was generally similar to that of the other two specimens, but the relatively slow failure at the high stress range imposed (± 1·6 ton/in.^{2}) indicates that this specimen was more nearly comparable to the specimen with the longitudinal boundary than to that in which the boundary was transverse.

(c) *Deformation Near the Boundary.*

Particular features of the microstructure observed only in the neighbourhood of the boundary were very few. Slip occasionally occurred on planes on which the resolved shear stress was not a maximum; slip bands occasionally appeared to be continuous, across the boundary, changing slope as they crossed; but, except in one case of slip on the twinning plane of the twin specimen, there was no trace either of slip in one crystal penetrating into the other or of bending of the slip bands as the slip plane changed at the boundary. In some cases slip approached the boundary closely on both sides, in some it stopped short on both sides, but its behaviour in this respect could not be correlated to the stress system, to configuration of the boundary, or to any other possible cause. In many cases additional slip bands were formed at the boundary in between the main bands. These additional bands presumably served to distribute the strain to which the boundary was subjected.

(d) *Failure.*

No essential difference was observed between the three specimens in the cracking stages, except, of course, in the magnitude of the applied stress range at which failure commenced. In all cases, cracks were formed in one crystal on, or at any rate close to, the site of previous heavy slip, and in the subsequent propagation the cracks showed preference for the circumferential direction in a manner entirely in accordance with previous work on single crystals. In this propagation, also, the boundaries appeared to offer but little resistance to the *passage* of the cracks, the paths of which were apparently not influenced by any tendency to avoid crossing the boundary. Although in certain instances cracks did commence to occur along or in the near neighbourhood of the boundary, in general, the propagation of the crack across the boundary into the other crystal appeared to occur much more readily than along the boundary.

(e) *Strength.*

The main difference between the three specimens was in their apparent strengths, for, although it cannot be stated definitely that the fatigue strength of either of the specimens CHJ4G2 or AL1B was greater * than that of the specimen AL5A, it is at least certain that the form of the stress-endurance curve was altered.

Since the effect of the boundary on the primary stress distribution appears to be so very slight, it can only be concluded that the values of the stresses also are but little affected and the influence of the boundary must be in some other direction. It is possible that the boundary causes some restriction of strain and that this restriction may result in (*a*) limitation of slip (in amount); (*b*) partial prevention of slip damage; (*c*) delay in the propagation of cracks. The results of the present tests, in particular the behaviour of the specimen with the longitudinal boundary, are in favour of (*a*), and (*b*) might well follow therefrom, but until further tests to much greater endurances have been carried out (*c*) cannot be overlooked.

ACKNOWLEDGMENTS.

The authors desire to acknowledge their indebtedness to the Department of Scientific and Industrial Research and to the Executive Committee of the National Physical Laboratory for the opportunity to carry out these experiments and for permission to publish the results; to the Physics and Metallurgy Departments of the National Physical Laboratory, in which the X-ray analyses and some of the polishing of the specimens, respectively, were carried out; also to Messrs. W. J. Clenshaw, B.Sc., and G. Forrest, B.Sc., of the Engineering Department, National Physical Laboratory, for very considerable help afforded in the experimental work.

DISCUSSION.

Professor D. Hanson,† D.Sc. (Vice-President): This paper seems to me so conclusive that one has simply to accept the evidence which the authors present. All that I can do is to offer some comments on the general problem.

The authors are quite right, I think, when they say that the doubts which were expressed as to whether results of experiments on single crystals had any bearing on the behaviour of aggregates are being removed by this work. Particularly striking is the verification of the law of resolved shear stress shown in the case of the specimen with the two crystals in twin relationship and the other specimen in which a small outcrop is surrounded by a large portion of single crystal. There the correlation between the original theory and what takes place is notable, and I am particularly glad because I have been teaching the resolved shear stress law to my students for the last six years, but only as being true in the case of single crystals. I think, however, that there is little doubt that it applies in the case of aggregates, and, if it

---

* To make this claim with confidence many more reversals at the lower ranges would have had to be imposed (cf. *Aeronaut. Res. Cttee. R. and M.* No. 1025, 1926).

† Professor of Metallurgy, The University, Birmingham.

applies to that little outcrop, it will certainly apply when we study masses which consist of a large number of minute crystals.

The other point which emerges is the importance of slip as leading up to fracture. In single crystals that is well established, but some doubt has been expressed whether that result could be extended to aggregates. All the work which has been carried out so far has tended to confirm the belief that the cracks start along the seats of initial slip, and there is evidence in other directions of the importance of slip-bands as leading to fracture, both in the work on corrosion-fatigue, with which Dr. Gough and his colleagues have been associated, where the fatigue cracks certainly started along seats of heavy previous slip, and in the work which Mr. Wheeler and I carried out on the flow of aluminium crystals under creep stresses, where cracking again began on the lines of the initial heavy slip-bands formed during the first stages of deformation. I have come to regard it as very nearly proved that during this slipping action the metal may be strengthened, but at the same time severe damage is done to the internal structure which does ultimately lead to breakdown at those points, either when the stresses are repeated sufficiently often, as in the case of fatigue, or when the load is applied sufficiently long, as in the case of creep stresses, or when the stress is increased considerably, as in the case of failure by normal tension.

Having adopted that view, I find especially interesting Dr. Gough's suggestion as to the influence of the boundary on strength, or it may be on endurance, because it is fairly clear that the boundary has some effect; it seems to limit the amount of slip and that might also limit the amount of damage done to the crystal structure, because I suppose that the slipping, in that case, would be likely to be distributed over a greater number of slip-bands. That is rather consistent with what sometimes happens in testing aggregates of aluminium under creep conditions, where in certain circumstances the amount of slip can be distributed in aggregates over a very large number of slip-bands, and, by carefully regulating the conditions of stressing, those bands can be made so slight that it is very difficult to see them at all, whereas in single crystals, where there are no boundaries, it is extraordinarily difficult to obtain slip except on widely spaced and rather heavy slip-bands. I believe that the damage done to the metal by heavy slip is considerable, and that it is on those heavy slip-bands that fracture begins, so that I find it quite reasonable to picture the action of the boundary as affecting the amount of slip and consequently the damage to the crystal structure, rather than to attribute it to some alteration in the mechanism of deformation.

From this point of view, it might be interesting if the authors could carry out some similar tests on specimens at elevated temperatures, where under creep conditions, this closely spaced type of slip can be made to take place more readily. If they could avoid the production of heavy slip-bands, and get the slip distributed more uniformly throughout the crystal, they might obtain information which would have a bearing on this problem.

I should also like to direct attention to the ingenious type of stressing system which has been used in these tests; that is, the subjecting of the specimen to alternating torsions, whereby a very considerable amount of deformation can be imposed on the material without altering the orientation of the crystals in relation to the direction of the stresses. Much of the success of the work has been due to the use of this particular type of stressing action. I mention this as it was the use of that particular type of action which brought home to Dr. Gough in the first place the reality of the resolved shear stress law, because the use of that kind of stressing system on single crystals showed that even on the same crystallographic plane slipping could take place in one direction in one part of the crystal and in another direction in another part, controlled entirely by resolved shear stress considerations.

Finally, I think that this work, associated with other work in allied directions which is mainly being carried out by Dr. Gough and his colleagues, but to which some others are also contributing, shows us that fatigue failure is not, as was at one time supposed, a special kind of failure of metals, but that the mechanism is very similar to that of other types of failure, and that the differences can be accounted for entirely by the differences in the stressing systems involved, and not by a difference of mechanism in the metal itself.

I would direct the attention of members to the work on this general problem that is being undertaken in other directions by Dr. Gough, and I would refer in particular to the magnificent review of the subject which he has given recently in the Edgar Marburg Lecture delivered to a joint meeting of certain American societies.

Mr. H. Sutton,* M.Sc. (Member): Those of us who deal more particularly with practical problems before us appreciate the persistent endeavours of the authors in search of fundamental data on fatigue failure. Their method of observing and studying the characteristics of deformation before attempting an accurate determination of fatigue limits on their specimens has been fruitful, and their choice of this method of attack seems to be fully justified by the results obtained.

I should like to ask whether the authors have seen a preponderance of intercrystalline cracking in any fatigue failure of aluminium-rich alloys or in aluminium. I have not seen any such case; the few I have examined seem to have been cases of simple transcrystalline cracking. I should also like to ask whether they foresee any need to study dimensions of fatigue test-pieces in ordinary materials in order to make our research results capable of interpretation in the future.

Dr. U. R. Evans,† M.A. (Member): The authors' researches are leading to an understanding of an important and complicated subject. I am in general agreement with their conclusions. The question could perhaps be raised as to whether conclusions which are valid as regards the secondary crystals present in annealed metal would necessarily be valid for the primary crystals present in cast metal, but I do not propose to discuss that, because I understand that it is being studied in other researches. In any case I believe that an ounce of agreement is worth a ton of controversy, and the metallurgical public are not interested in points where different investigators, having approached the subject from different directions, for the moment disagree, but would welcome emphasis on the considerable number of points where, notwithstanding the different direction of approach, different investigators have reached similar conclusions. The public want a view of corrosion which they can adopt with reasonable confidence that they will not have to change it frequently, and I think that we should try to provide this.

Dr. Gough's various researches have afforded evidence that the weakening produced by corrosion-fatigue is not due to the rounded pits which are so prominent a feature of many types of corrosion, but rather to very narrow cracks with sharp ends. Dr. A. J. Gould, of Rangoon University, approaching the matter in a different way, has reached almost the same conclusions. He examined the corrosion of wires, measuring the damage produced (*a*) by corrosion alone, and (*b*) by the same corrosion with alternating stresses superimposed, and assessed the damage in four different ways, namely by loss of (1) weight, (2) electrical conductivity, (3) tensile strength, and (4) fatigue

---

* Senior Scientific Officer and Head of the Metallurgical Department, Royal Aircraft Establishment, South Farnborough.

† Cambridge.

strength. When the loss of weight or of electrical conductivity was the criterion of damage adopted, alternating stress did not increase the rate of damage which was produced by corrosion operating alone; but when the damage was assessed by loss of fatigue strength, alternating stresses were found greatly to increase the rate of damage over and above the rate produced by corrosion alone. We are evidently dealing with a form of cavity which produces practically no increase of loss of weight or of electrical conductivity, but a considerable extra loss of fatigue strength; the only type of cavity which fulfils those conditions is the narrow, sharp cavity. Such a cavity will produce very little loss of weight, owing to the small amount of metal destroyed, and in a long wire very little loss of conductivity (except at the last moment when the cavity has extended almost through the specimen); but there will be a very great loss of alternating stress strength, provided the cavity is sharply pointed. Dr. Gould, therefore, has reached conclusions similar to those reached, by different methods, by the authors.

Professor B. P. HAIGH,* M.B.E., D.Sc. (Member): In spite of the importance of this paper, it represents only one step in many which the authors have taken to elucidate this problem. That makes it somewhat difficult, however, to criticize, because it is not easy to concentrate on the one point now brought before us.

When we look for the influence of the boundary on the slip and the crystal round about it, it seems to me that there are two directions in which evidence can be sought. In the first place, the authors have looked to see whether the boundary stopped or tended to prevent slip in the matter round about it, and secondly, they have looked to see if it altered the directions of slip. I think that they tell us clearly that it has tended to delay slip; at any rate the piece with the longitudinal boundary has stood out against much higher stresses than the other, and the authors have told us that it has altered the directions of slip in the early stages. That is important, as I believe that it would indicate that the boundary is producing an initial stress in the matter round about it which has altered the selection of the planes on which slip has occurred; but on the whole it is certainly remarkable that the boundary has had so little effect. Only in one of the three pieces do we see it very plainly, and there is not a great deal of effect there.

Much of the interest of the paper, however, extends into the more general field, and the shear stress theory has been demonstrated afresh to be true for the directions selected by the slip-bands, a wonderfully clear and convincing demonstration that the directions selected are those of the planes of maximum resolved shear stress, but I wonder whether the authors are prepared to say the same for the direction of the crack. They have pointed out that the crack shows again this time the same preferential selection of the circumferential direction. Some of the figures in the paper show the crack following the slip planes for part of their way and then jumping across. It would be very helpful if the authors would say something about those directions in which the cracks jump across. They must have analyzed those directions, and they will be able to say whether they are directions in which slip, if it could not be expected definitely to occur, because the shear stress was less, are at any rate directions in which the shear stress reached a fairly high value. It seems possible that they are, but it also seems possible that they are not, and that on the contrary they may be planes of maximum normal stress. We are accustomed to see fracture occur in more brittle substances through normal stress; for example, in glass, one does not find slip, but one does find cracking under normal stress. In this aluminium crystal, which

---

* Professor of Applied Mechanics, Royal Naval College, Greenwich.

is probably as plastic a material as one could find, it would be interesting to know if there is any evidence of normal stress coming into operation at all.

Dr. C. H. Desch,* F.R.S. (Vice-President): It has been shown here that the influence of the boundary in these particular cases is small, and perhaps rather unexpectedly small, although we know that when the ratio of boundary surface to volume increases very much, as with fine-grained metals, the influence of the boundary is very clearly seen. I think that Professor Hanson's suggestion that the spacing of the bands may depend very much on the grain-size is a point which needs to be followed up, but I would suggest that probably the boundary effect comes in mainly in those properties of metals into which the time factor enters. We know how important it is in creep, and if we were to carry out high-temperature experiments I imagine the boundary effect would be greatly increased. It might also have some effect on fatigue properties if it were possible to vary the frequency within very wide limits. Within all practicable limits the effect of frequency on fatigue is comparatively small. If experiments could be carried out with extremely high, and extremely low, rates of alternation, I believe that the influence of the boundary would be found to be considerably greater.

Dr. C. F. Elam,† M.A. (Member): The effect of the crystal boundaries has been dealt with already. The amount of plastic distortion is so small in this form of testing that there is no change of orientation occurring in the neighbourhood of the boundary such as is obtained in other forms of testing where the distortion is very much greater. Dr. Gough and his co-workers will probably remember the work that W. L. Aston carried out on tensile tests of aluminium test-pieces consisting of two or three crystals. He found that the changes which occurred at the actual boundary were practically nil, but its influence was felt perhaps 2 mm. or 3 mm. at least away. This effect is less marked where the orientation does not change during the test and the gradually changing influence of one crystal orientation on another is not obtained.

When discussing boundaries between twin crystals it must be clearly borne in mind that these may be of two kinds. If the plane of composition is actually the twin plane, rather different results may be expected from those which are obtained where the plane of composition resembles in every way a normal crystal boundary. My experience is that twin boundaries are exactly like any other kind of boundary, and affect the orientation and the change of orientation and the type of slip in exactly the same way as ordinary crystal boundaries.

One of the most interesting cases would be that in which the actual twin (octahedral) plane was the plane of maximum resolved shear stress in both parts of the twin.

Is it true that cracks always follow planes of slip? I think on the whole that they do not, although in some cases it is so. I have lately examined some β brass crystals where the planes of slip are also the planes of fracture, and in certain brittle substances that is also the case, but it is a little doubtful whether one can assume that changes that take place on the slip plane are the same as those causing fracture.

The authors may be interested to know that I have quite definite proof of the type of structure to which they refer as their "herring-bone" structure, which is caused by slip in one region on one plane and in the neighbouring

---

* Superintendent, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

† Cambridge.

region on another. In some β brass crystals which I have examined these bands form pseudo-twins where bands of material slipping on one plane alternating with bands of material slipping on another plane which may be at 60° or even 90° to the first are obtained. If sections are cut through these and polished they look like twins. If the orientation were not determined it would be said that they were twin crystals. This, I believe, is what Dr. Gough himself thinks happens with aluminium crystals. It is also noticeable that this type of deformation takes place at or near crystal boundaries, and I have always believed that the boundary, in some way which it is rather difficult to explain at the moment, just turns the scale, as it were, between slip on one particular plane or another, thus causing the banded structure to which I have referred.

Another point which I should like to mention is that the absence of visible slip-bands does not necessarily mean that slip-bands do not exist. It has always been stated that β brass crystals never show slip-bands, but they do show slip-bands if they are polished carefully and if they are looked for properly. The point is, that if the actual amount of movement on each slip-band is less than a certain definite amount no evidence of them is seen even under high magnification, but this does not mean to say that they are not there.

Mr. F. HARGREAVES,* A.R.S.M., D.I.C. (Member): I believe that the authors have definitely established the resolved shear stress law in the case of single crystals, and also when two are present. I suppose that it may now be assumed that the law is operating when they work on a microcrystalline test-piece and see slip, but this in itself does not seem to get us very far, and I wonder how the knowledge is going to be applied in that case. It has been pointed out more than once that a test-piece consisting of more than two crystals is not comparable in some ways with a microcrystalline test-piece, because there can be no adjustment of orientation of individual crystals by movement of one over the other; but the work the authors are carrying out should decide that point.

In a paper on the corrosion-fatigue of a test-piece consisting of two crystals,† the first cracks observed were associated with the crystal boundary. They were ½ in. long and ¼ in. long, respectively, when first seen. In a case like that I think that I am right in saying that it is not possible to determine where they started. They are there, and whether they started at one end or the other or in the middle cannot be stated. It seems that in order to decide that question, great patience as well as good fortune will be required in order to note the cracking at its birth, so that it can be known exactly where it starts, and not where it has finished.

Lead fails by intercrystalline cracking under fatigue action, whilst iron does not. Aluminium is in some ways intermediate between these two metals, and I think that it is possible that under different conditions both the intercrystalline type and the other type of fatigue-cracking might be observed. In this work there is a certain hint that it may have occurred, because it has not been possible to say exactly where the cracking started.

I should like to raise another point. One gathers from this work that a disturbance in metals by fatigue stresses is very much the same as that produced by ordinary cold-working or straining, the effect of which is well known; so long as it is not over-worked, heat-treatment will restore the original properties of the metal. It might be of assistance in the work the authors are undertaking if they carried out some such test so as to determine once

---

* Chemist, Southern Railway, Eastleigh.

† *J. Inst. Metals*, 1933, 52, 57.

for all whether the effect of fatigue stresses is the same as that of other methods of cold-working. Laute and Sachs[*] carried out tests on these lines on nickel–steel, and the results indicated that recovery did not take place. They found the endurance of test-pieces, and then subjected other similar ones to a number of reversals of stress below that which would cause failure. They then annealed them, tested them again, and found that the annealing had not restored them. Machine parts can be removed and annealed at different times during their life, and the question arises whether by so doing we may not be actually reducing their life. In certain parts of locomotives that particular question faces us now, and the authors might help themselves and help us by considering this point.

Mr. Sopwith (*in reply*): Professor Hanson mentioned that the restricting effect of the boundary was such that in single crystals one obtained only very heavy and well-marked slip-bands, but I think that a later remark by Dr. Elam showed that there might be slip-bands present even on single crystals which were very similar in type to those which occurred on aggregates. We are indebted to Professor Hanson for his suggestions as to tests at high temperature.

Mr. Sutton remarked that the size of fatigue specimens might have some effect, but it seems to us that that effect is likely to occur only if the size of the individual crystals and specimens is such that they extend over a relatively large portion of the diameter; it is generally accepted that in small crystal aggregates no fatigue scale effect occurs, at any rate in the range covered by specimens of from ¼ in. up to 2 or 3 in. in diameter.

The account of Dr. Gould's work given by Dr. Evans is of great interest, and we are glad to hear that work on other lines has confirmed our opinions as to the operative causes in corrosion-fatigue.

The direction of the cracks was mentioned by Professor Haigh, who stated that although a considerable proportion of the length of the crack followed the most highly stressed directions, there were "jumps." In practically all cases these followed planes on which the stress was almost, if not quite, as high as that on the operative plane, the amounts of the cracking on the two or more planes being such that the direction of the crack as a whole was roughly circumferential, as for instance in Fig. 6, in which there are several quite clearly discernible slip directions.

Dr. Elam mentioned that the effect of the boundaries might be different in the case of the twin specimen if the plane dividing the two crystals had been the plane of composition, the twinning plane. Some evidence on that point is given by the work carried out by Dr. Gough and Mr. Cox on the behaviour of zinc in alternating torsion, in which case a considerable amount of the distortion takes place actually by twinning, and the boundary between the original structure and the twinned structure is straight. Exactly the same thing occurs in these cases as has occurred in the present crystals; that is to say, the slipping in the neighbourhood of the boundary is entirely unaffected by the presence of the boundary. The herringbone structure, we have found, normally occurs only after a considerable amount of distortion has taken place, and it occurs, as Dr. Elam mentioned, usually on the two most highly stressed planes. The reason for this seems to be similar to that which I have just referred in connection with the different directions taken by the cracks, to accommodate the distortion by shear in the two most highly stressed directions.

It is intended to go on from these tests on specimens consisting of two crystals to specimens consisting of four crystals. We have no intention of making any assumptions, but intend finally to build up to microcrystalline aggregates, as mentioned by Mr. Hargreaves.

[*] *Z.V.d.I.*, 1928, 72, 1188; and (summary) *The Metallurgist* (Suppt. to *Engineer*), 1928, 4, 173.

CORRESPONDENCE.

THE AUTHORS (*in further reply to the discussion at the meeting*): We would express our thanks to Dr. Hanson for his very interesting and congratulatory remarks, and note that he is in agreement with our general deductions regarding the influence of the intercrystalline boundary on fatigue. He refers to the very interesting work on slip-bands carried out by himself and Mr. Wheeler and, with respect to his suggestion, it would appear interesting to carry out fatigue tests on single crystals at elevated temperatures and to find out whether a different type of slip-band was produced and the method of failure; we may do this if opportunity permits. As Professor Hanson remarks, the behaviour of a single crystal under alternating torsional stresses is probably the most convincing demonstration of the application of the maximum resolved shear stress law. In reply to Mr. Sutton, we have not yet made any tests on the fatigue properties of aluminium-rich alloys and, therefore, have no information. Our experience with regard to aluminium is contained in the paper.

Dr. Evans' remarks on the results obtained by Dr. Gould at Rangoon are extremely interesting. We shall look forward with great interest to the publication containing the detailed results of these researches.

Professor Haigh raises a very interesting point as to the direction of propagation of fatigue cracks in single crystals and asks whether these follow in general the planes of maximum resolved shear stress or are influenced by normal stress considerations. I think that our general experience could probably be summed up by the statement that, in general, the direction of propagation of fatigue cracks is *not* necessarily associated with slip direction. In some crystals in which the slip planes happened to coincide with the easiest direction of fracture (with respect to the applied external forces) the cracks followed the same general direction as the slip plane but, in many other cases, this was not so; it appears that the point of initiation of a fatigue crack is determined by the maximum resolved shear stress but we have considerable reason to believe that the propagation of the crack is greatly influenced by normal stress considerations. Particularly is this the case in an experiment, the results of which are not yet published, in which two crystals were subjected to similar ranges of alternating shear stress, but, whereas in the one case an axial tensile stress was superimposed, in the other an axial compressive stress was applied; conditions during the fracture stage were very greatly influenced by the superimposed normal stress.

Dr. Desch made a very interesting suggestion that the boundary would be found to exert a greatly increased effect at very high rates of alternation. We also believe that this is probably the case especially in view of the work of Professor C. F. Jenkin.

Dr. Elam remarks that, in the cases described, the total amount of plastic distortion occurring during the test is very small compared with, for example, static tensile tests. This is, of course, quite true and it is for this particular reason that torsional straining is mainly employed in our work. We would also remind her that in the normal fatigue failure occurring in practice, very little "mass" distortion occurs. Her experiences regarding the effect of boundaries on the deformation of twin crystals are extremely interesting. Dr. Elam also refers to the relation between fatigue cracks and slip planes, and we would refer her to our reply to Professor Haigh. We are glad to have Dr. Elam's confirmation that the herring-bone structure is caused by slip in one region on a series of planes and in an adjacent region on another set. We have checked up this conclusion in several cases. When one considers that in some parts of the specimen, competing slip planes are subjected to very nearly the same amount of shear stress, it is not at all surprising that the herring-bone structure is sometimes observed. It is also quite possible, as Dr. Elam suggests, that when this structure occurs in the neighbourhood of a boundary, the boundary may have had some influence in determining the operative slip planes.

Mr. Hargreaves raises a very interesting point when he asks whether the process of fatigue can be removed by heat-treatment. This is an aspect of fatigue phenomena which is definitely in our programme to investigate at some time but on which, for the moment, I regret that we have no experimental evidence of our own.

THE CONSTITUTION OF COPPER–IRON–SILICON ALLOYS.*

By Professor D. HANSON,† D.Sc., Vice-President, and E. G. WEST,‡ Ph.D.

Synopsis.

The constitution has been examined of alloys containing up to 8 per cent. of iron and 8 per cent. of silicon. The solubility of iron in copper is decreased by the presence of silicon. Over the greater portion of the range of compositions examined, iron exists in the alloys as such, containing only a small amount of silicon and copper in solution; its solubility in the solid state decreases rapidly with fall of temperature and becomes very small below 700° C. Within certain ranges of composition, iron and silicon combine to form another constituent, probably FeSi, which forms a series of alloys with the α solid solution. FeSi also appears to form systems of alloys with the α, β, γ, δ, and ϵ constituents of the copper–silicon series. The shape of the liquidus and solidus curves has been determined and the changes occurring in the system during the process of cooling from the liquid state, have been indicated.

The constitution of the alloys suggests the possibility of modifying their mechanical properties by heat-treatment.

Introduction.

Copper-rich alloys containing metallic silicides have attracted attention recently on account of their capacity for heat-treatment, but very little has been published on the subject of the constitution of these alloys. The present paper deals with alloys of the system copper–iron–silicon.

Corson's [1] paper on the precipitation of silicides in copper-rich alloys gave only a few examples of copper–iron–silicon alloys, and the results tabulated are for physical properties only. It is evident from his photomicrographs that his alloys were not nearly in a state of equilibrium, but uniform solid solutions were said to be obtained at 930° C. in all alloys containing less than 1·0 per cent. of iron. He suggested that Fe_2Si was the effective silicide of the system with a solid solubility between 1·3 per cent. and 2·5 per cent. Ellinghaus [2] gave

---

* Manuscript received November 2, 1933. Presented at the Annual General Meeting, March 8, 1934.

† Professor of Metallurgy, The University, Birmingham.

‡ Research Student, Metallurgical Department, The University, Birmingham.

results for nine alloys of this system, principally mechanical and electrical properties. Annealing temperatures above 800° C. were not employed, but the softening temperatures after cold-working were obtained. The effective silicide was stated to be FeSi, and an alloy containing 2·38 per cent. of iron and 2·54 per cent. of silicon was stated to be a homogeneous solid solution when cast. His contention that the solubility limit of iron in copper is raised by addition of silicon does not seem to be in accordance with his photographs.

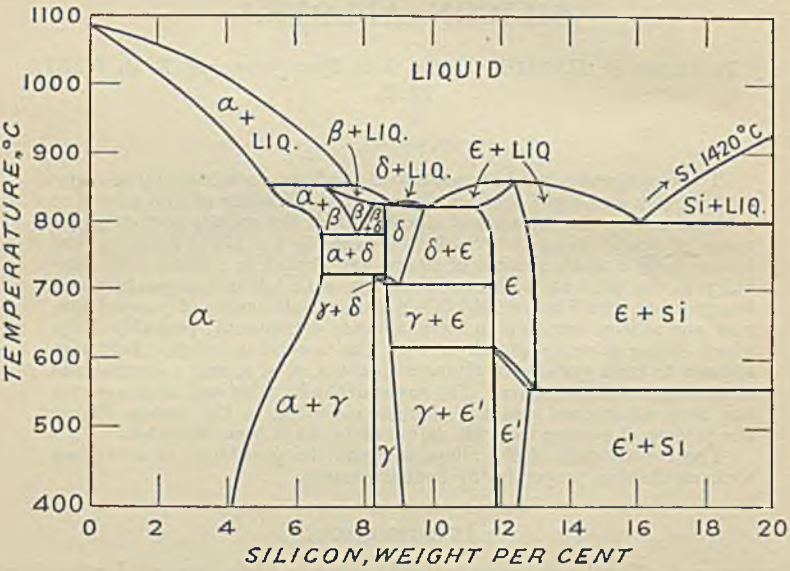


FIG. 1.—Copper-Silicon Alloys. (Smith.)

THE BINARY SYSTEMS.

These have all been investigated recently, and the equilibrium diagrams may be summarized as follows:

(i) *Copper–Silicon.* The reactions according to Smith[3] are given in Fig. 1, the chief points being the configuration of the α-phase boundary and the complexity of the reactions beyond this. The solid solubility of silicon in copper increases from 5·25 per cent. at 852° C. to 6·7 per cent. at 785° C., and remains at this figure until a temperature of 725° C. is reached; below this temperature, the solubility falls to 4·1 per cent. at 400° C. The photomicrographs given in this paper enabled the phases under review in the present research to be readily identified. Later work by Matuyama,[4] Iokibe,[5] and others, has not altered this part of the diagram.

(ii) *Copper–Iron.* The diagram of Ruer and Goerens,[6] taken in conjunction with the work of Hanson and Ford,[7] gives a complete survey of the system, which is shown in Fig. 2. The solubility of pure iron in solid copper decreases from 3·9 per cent. at 1100° C. to less than 0·2 per cent. at 750° C.

(iii) *Iron–Silicon.* Published diagrams vary in a number of details; that due to Haughton and Becker [8] is given in Fig. 3, this having been used in preference to others published. They state that two compounds are definitely present, and possibly a third. These are FeSi at approximately 33 per cent. of silicon, Fe_2Si_5 at 55 per cent., with Fe_3Si_2 at 26 per cent. of silicon as a possible solid solution of FeSi in the α phase.

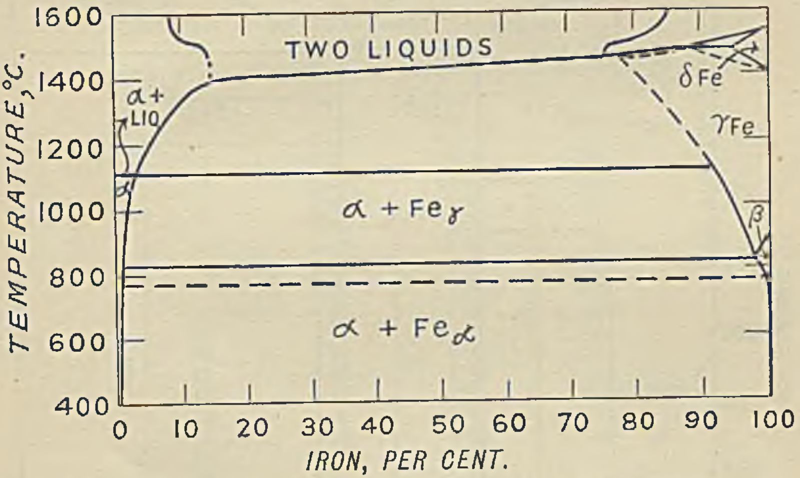


Fig. 2.—Iron–Copper Alloys. (Ruer and Goerens; Hanson and Ford.)

The present paper deals mainly with the α (copper-rich) solid solution range, but other parts of the ternary system have to be considered in the survey of the copper corner.

Experimental Details.

The experimental methods are given in some detail, as the slight variations in procedure sometimes cause corresponding variations in the results obtained by different workers in researches of this nature.

(i) *Casting and Working.*

To facilitate alloying, which is rather difficult when the pure components are used, temper alloys were employed, and their compositions,

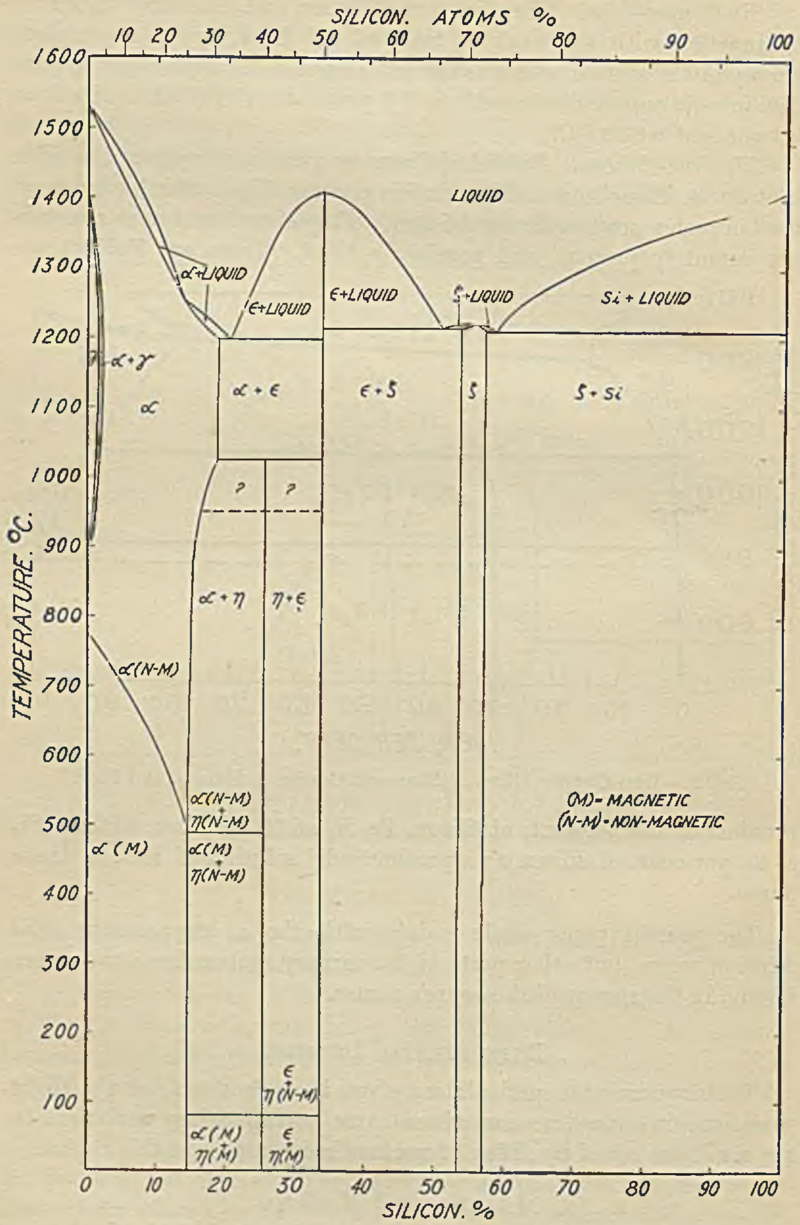


FIG. 3.—Iron-Silicon Alloys. (Haughton and Becker.)

together with the analyses of the original materials, are given in Table I.

TABLE I.

Material.	Copper, %.	Silicon, %.	Iron, %.	Carbon, %.	Other Elements, %.
American washed iron	...	...	96·1	3·8	0·10, max. impurity
Silicon . . .	...	97·0	1·8	trace	1·0 Al, 0·2 Ca, trace Zn
Temper alloy 1 . .	19·3	13·2	67·2	trace	...
Temper alloy 2 . .	75·1	24·6	trace	...	trace Al
Temper alloy 40 .	48	18	34	trace	...

TABLE II.—*Compositions (by Analysis) of the Alloys.*

No.	Iron, %.	Silicon, %.	Copper, %.
1	67·2	13·2	19·3
2	trace	24·6	75·1
3	0·10	0·54	...
4	0·10	4·4	...
5	0·25	2·54	...
6	0·25	7·0	...
7	0·31	1·34	98·31
8	0·50	8·9	...
9	1·1	4·8	...
10	1·3	0·7	...
11	1·45	1·45	...
12	1·85	1·3	96·82
13	1·0	7·0	...
15	2·94	1·36	...
16	2·95	1·8	...
17	3·3	2·65	...
18	2·7	3·98	...
20	4·7	1·7	...
21	4·2	1·75	94·01
22	4·1	2·2	...
23	3·6	5·5	...
24	4·15	5·4	...
27	5·0	1·0	93·8
28	5·5	1·8	...
29	6·3	2·1	...
31	4·95	5·5	...
33	0·62	0·26	99·04
34	0·47	0·74	...
35	0·10	2·14	97·76
36	0·5	2·1	97·2
37	1·27	1·8	...
38	1·8	1·6	...
39	1·05	0·25	98·5
40	34·0	18·0	48·0
41	2·0	0·85	...
42	2·54	1·28	...
43	2·95	1·45	96·4
47	2·5	2·05	...
48	3·45	1·0	...

Traces of carbon and aluminium were found in the temper alloys, but these were eliminated in the making of the final alloys, in which neither carbon, aluminium, nor calcium could be detected.

The final alloys were made as follows: copper was melted under charcoal in a closed Salamander crucible in a gas-fired furnace and the required amount of temper alloy No. 1 added. The metal was well stirred and allowed to stand for a few minutes before alloy No. 2 was added. The melt was again well stirred and cast from 1200° C. into split chill moulds 1 in. in diameter. The bars were about 4 in. long and 12 oz. in weight.

The compositions of the alloys are given in Table II.

(ii) *Thermal Analysis.*

Cooling and heating curves of all alloys were obtained, a gradient furnace being used. The cooling curve was taken first, and the heating curve then obtained immediately, and the specimen allowed to cool in the air. The lid was kept on the crucible throughout, to prevent oxidation of the melt, and chemical analysis showed that the changes in composition were negligible, the maximum silicon loss being 0·05 per cent. Segregation had occurred in some cases, however. The rate of heating and cooling was about 20° C. per minute, readings being taken every 5° C. The couple was calibrated at intervals, the melting points of copper, silver, silver/copper eutectic, aluminium, zinc, and tin being used, and considering all possible errors due to calibration, e.m.f. measurement, and plotting, the maximum inaccuracy is approximately 10° C.

The results of the thermal analysis are given in Table III.

(iii) *Heat-Treatment.*

According to Smith * the rate of diffusion of silicon to the surface of copper–silicon alloys is extremely high, and preliminary experiments confirm this; to avoid oxidation losses, the alloys were annealed *in vacuo*. It was also apparent that the alloys were likely to require very long annealing periods to attain equilibrium, and the apparatus was devised with each of these points in view. Specimens approximately $\frac{1}{2} \times \frac{1}{4} \times \frac{1}{4}$ in. were cut from the chill-castings and were cold-worked by hammering before treatment. They were cut longitudinally for examination in every case. Specimens were annealed in thick silica tubes, 18 in. long by $\frac{3}{8}$ in. internal diameter, sealed at one end, six specimens being placed in this end. Four tubes were heated in a Nichrome wound furnace, giving a uniformly heated zone 4 to 6 in. long in the centre.

* *Loc. cit.*

Table III.—*Data for the Liquidus and Solidus Surfaces.*

Alloy No.	Liquidus, °C.	Second Stage, °C.	Solidus, °C.		
			Liquid.	No Liquid.	Solidus.
3	1077	...	...	...	...
4	987	...	905	895	900
5	1038	...	990	985	985
6	877	...	855	850	850
7	1064	...	1040	1035	1040
8	830	...	817	810	813
9	*	968	885	870	875
10	1075	...	1045	1030	1040
11	1060	...	1010	1000	1005
12	1062	...	1010	1000	1005
13	891	...	865	855	860
15	*	1067	1025	1015	1020
16	*	1055	1010	1000	1005
17	*	1037	970	965	965
18	*	1007	940	925	930
20	*	1067	1025	1015	1020
21	*	1058	1020	1000	1010
22	*	1045	1005	995	1000
23	*	985	920	910	915
24	*	973	920	910	915
27	*	1080	1045	1035	1040
28	*	1078	1040	1025	1032
29	*	1060	1030	1010	1020
31	*	980	935	925	930
33	1080	...	...	...	...
34	1072	...	1060	1040	1050
35	1052	...	...	...	...
36	1057	...	998	995	995
37	1050	...	1005	995	1000
38	1054	...	1005	995	1000
39	1083	...	...	...	...
41	1075	...	1040	1030	1035
42	1067	...	1010	1005	1010
43	*	1064	...	...	...
47	*	1045	990	990	990
48	*	1070	...	...	...

* The arrests at the liquidus were too small to be recorded with any certainty. The liquidus corresponding with the separation of iron crystals was determined roughly by observing the temperature at which crystals appeared at the clean surface of alloys melted in nitrogen and cooled slowly from above the liquidus temperature. The low density of the iron crystals facilitated their detection in this manner, and the method could probably be made very accurate. The following observations were obtained :

Iron, %.	Silicon, %.	Liquidus, ° C.
3·0	2·0	1126
4·0	2·0	1210
3·0	3·0	1235
2·0	4·0	1135
2·0	7·0	1158

The projecting ends of the tubes were stopped with air-tight bungs and connected to a pump through air-tight cocks. The pump was run daily for short intervals, and specimens were quite bright when removed. The temperature was controlled by a Haughton–Hanson thermostat and was measured by a Chromel–Alumel couple placed among the annealing tubes, and connected to a thread recorder. The annealing temperatures employed were 1025°, 970°, 925°, 870°, 800°, 750°, 675°, and 550° C., and the corresponding variations in the annealing period are given in the tabulated results. The annealing temperature never rose above the required figure, and the maximum fall did not exceed 10° C., even this being only momentary. Quenching was carried out as follows: all the cocks were closed, and one tube at a time was opened, withdrawn from the furnace, and inverted over a large bath of water at 15° C. The time taken to quench the specimens was about one second, and no appreciable cooling took place before they entered the water.

The results of the heat-treatments are given in Tables IV and V.

(iv) *Determination of the Solidus.*

The annealing temperatures were too far apart to give the solidus, and the gradient furnace was modified to allow specimens to be quenched rapidly from a known temperature. A metal quenching bath, 8 in. deep and 6 in. in diameter, was fitted round the pillar, *P* (Fig. 4), wax being used to ensure a water-tight joint. The couple was placed inside the pillar, and the hot junction was bent at 90° at the top of the pillar.

TABLE IV.—*Microstructure of Annealed and Quenched Specimens.*

Temp., ° C.	870	830	800	750	675	550
Time, Hrs.	170	100	200	240	270	300
Alloy No.	Constituents present.					
4	α	...	α	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe + \gamma$
6	$\alpha + L$	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \delta + FeSi$	$\alpha + FeSi + \gamma$	$\alpha + FeSi + \gamma$
9	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe + \gamma$
12	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
13	Liq.	$\alpha + \beta + FeSi$	$\alpha + \delta + FeSi$	$\alpha + FeSi + \gamma$	$\alpha + FeSi + \gamma$	$\alpha + FeSi + \gamma$
15	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
16	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
17	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
18	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
20	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
21	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
22	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
27	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
28	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
38	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$
43	$\alpha + Fe$	...	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$	$\alpha + Fe$

TABLE V.—*Microstructure of Annealed and Quenched Specimens in the α Range.*

Temperature, ° C.			1025	970	925	870	800	750	675	650
Time, Hrs.			48	100	100	170	200	240	270	300
Alloy No.	Iron, %.	Silicon. %.			Constituents present (see note below).					
3	0·1	0·54	A	A	A	A	A	A *	B	B
4	0·1	4·4	L	C	C	A	A *	B	B	D
5	0·25	2·5	C	A	A	A *	B	B	B	B
7	0·31	1·34	A	A	A	A	B	B	B	B
9	1·1	4·8	L	L	C	B	B	B	B	D
10	1·3	0·7	A	A ?	B	B	B	B	B	B
11	1·45	1·45	C	B	B	B	B	B	B	B
12	1·85	1·3	C	B	B	B	B	B	B	B
33	0·62	0·26	A	A	A	A	B	B	B	B
34	0·47	0·74	A	A	A	A	B	B	B	B
35	0·10	2·14	C	A	A	A	A	B	B	B
36	0·5	2·1	C	A	A *	B	B	B	B	B
37	1·27	1·8	C	B	B	B	B	B	B	B
38	1·8	1·6	C	B	B	B	B	B	B	B
39	1·05	0·25	A	A	A	B	B	B	B	B
41	2·0	0·85	A	B	B	B	B	B	B	B

Note.—* indicates that the alloy was on the limit at this temperature.

A . . . . homogeneous α.
B . . . . α + iron.
C . . . . α + liquid.
D . . . . α + iron and traces of γ.
L . . . . all liquid.

A small piece of Nichrome foil rested over the hot junction, and a silica tube was placed inside the pillar, projecting from the lower end. The details are given diagrammatically in Fig. 4.

The hot zone of the furnace was maintained at 1050° C. and the furnace calibrated, so that, by means of a scale fitted to the side, any required temperature was obtained by moving the furnace over the specimen. Small specimens about ½ × ¼ × ¼ in., were coated with a wash of Alundum to prevent excessive oxidation and placed on the foil. The furnace was lowered and the temperature maintained for 15 minutes. The temperature was checked and the specimen dislodged by an upward thrust of the silica tube, so that a rapid quench was obtained. The bath was maintained at 15° C. Identical specimens were quenched at temperature intervals of 10° C.

(v) *Polishing and Etching.*

Specimens (other than silicon-rich alloys) polished in the usual manner on emery paper and finished on moist chamois leather with magnesia powder, exhibited large holes when viewed under the microscope. These were due to the removal of particles of an iron-rich constituent, and all specimens were therefore polished in the absence of water. Paraffin was used on the emery papers and alcohol on the chamois leather, when good surfaces free from holes were obtained. Alcoholic solutions were used for etching whenever possible. Ferric chloride solution in alcohol, chromic acid (Vilella's reagent), 10 per cent. hydrochloric acid in alcohol, and Smith's bichromate-chloride reagent were found satisfactory for etching the copper matrix and copper-silicon phases: hydrofluoric acid, preferably applied on a pad of cotton wool, darkened the iron constituents. Both types of reagent were usually applied to develop the structure of the same specimen.

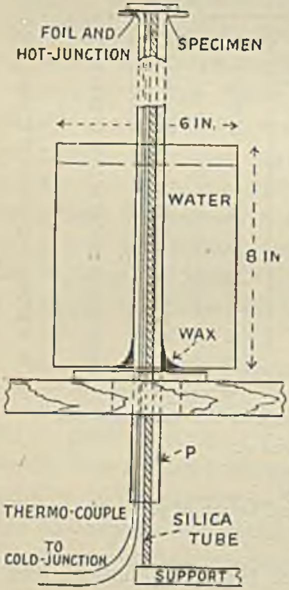


Fig. 4.

Identification of the Phases.

No new phases are introduced, within the range of alloys examined, beyond those belonging to the two binary systems. Near the copper-silicon side of the system, the α, β, γ, δ, and ε phases defined by Smith were readily detected, and could be identified by the etching methods which he used and the general characteristics of the phases which he has recorded. In addition to these phases, two other constituents were observed. One was identified with the iron constituent of the copper-iron series, and is essentially iron containing some dissolved copper and silicon. This constituent occurs in particles approximately globular in form, and is distributed fairly evenly throughout the alloys. The other constituent was hard and angular; it was distributed unequally in the matrix of the alloys, and showed a marked tendency to segregate at the top of the ingot, and it occurred in alloys containing more than about 5 per cent. of silicon and rather low iron contents.

Several methods were used to identify these constituents, the most fruitful being microscopical examination, chemical analysis, and hardness. The first constituent had all the micrographic characteristics of the α iron constituent of the copper-iron series, and a photograph is shown in Fig. 5 (Plate XVII), referring to an alloy containing 5·5 per cent. of iron and 1·8 per cent. of silicon. The second constituent is illustrated in Fig. 6 in an alloy containing 4·34 per cent. of iron and 8·9 per cent. of silicon. The particles are similar in form to the primary FeSi crystals shown in Phragmén's paper[9] on the FeSi alloys. The low density (6·05) given by Phragmén would also account for their segregation.

In some of the alloys containing high iron with low silicon (particularly in certain samples outside the range of composition reported herein), some of the iron appeared to separate while the alloy was still wholly molten. The iron-rich portion had all the metallographic characteristics of the one micro-constituent. A small portion of this constituent was extracted from one of the alloys and was magnetic and brittle. It was crushed, and the adhering copper-rich matrix removed by solution in dilute nitric acid. An analysis of the residue gave the following result: iron 90·5; silicon 7·5; copper 2·0 per cent. This confirms that these particles are essentially a solid solution of silicon and copper in α iron. A similar method could not be used to identify the other constituents, since no particles sufficiently large to be extracted could be found. By comparing the analyses of the upper

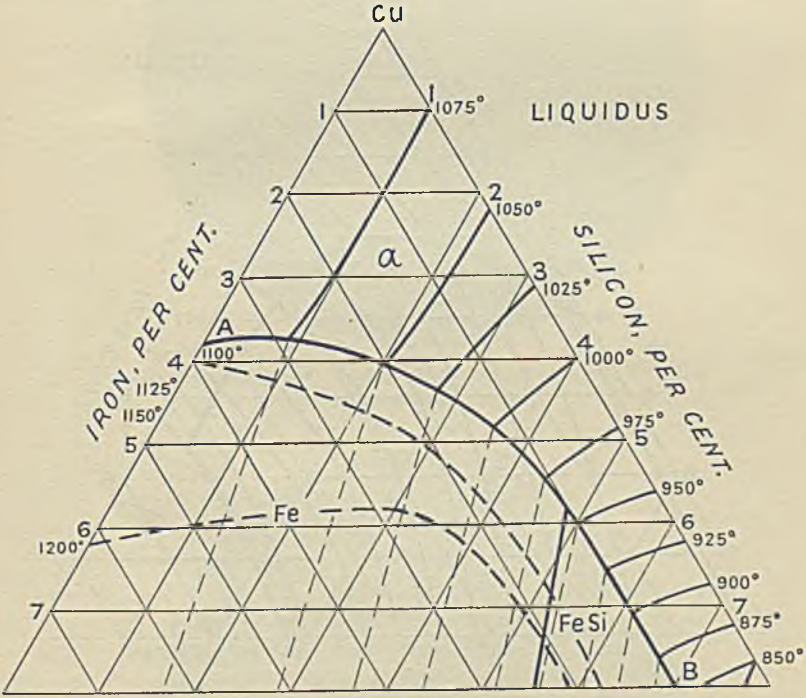


Fig. 7.

and lower halves of a slowly-cooled ingot in which this constituent was segregated to the top of the ingot, it was established that the iron and silicon in this constituent were present in proportions corresponding with the formula FeSi.

A series of hardness measurements was made by means of a sclerometer on specimens containing large particles of each of the two iron-rich constituents; a conical diamond under a load of 150 grm. was used. The results of the measurements are shown in Table VI. The large difference in hardness between the two constituents is definitely established, and the measurement of the scratch-hardness was found useful in identifying constituents during the microscopical examination of some of the alloys. For purposes of comparison, the corresponding constituents in pure iron–silicon alloys were also tested.

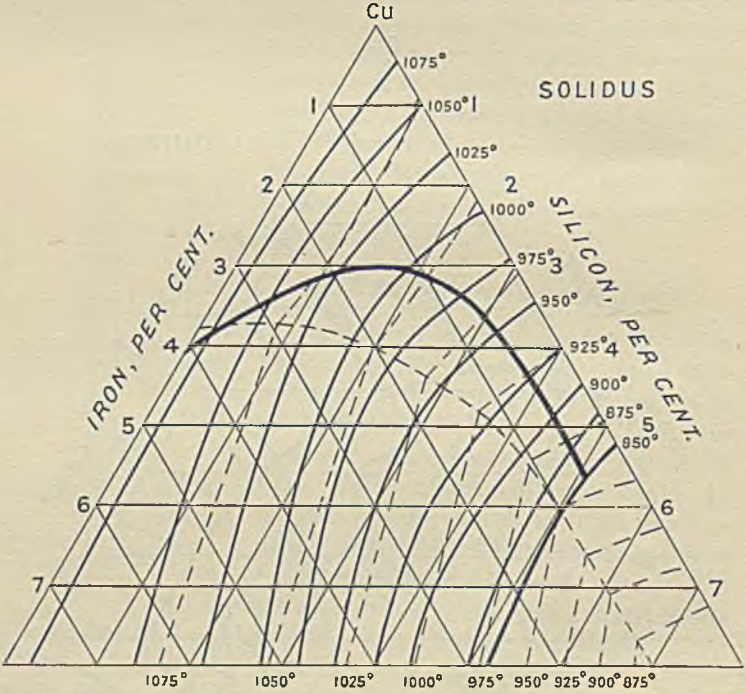


Fig. 8.

The Equilibrium Model.

The results of the thermal analysis and microscopical examination of the heat-treated specimens are given in detail in the Tables. From

FIG. 5.—Iron 5·5%, Silicon 1·8%. Iron Crystals in a Matrix of a Solution. × 150.

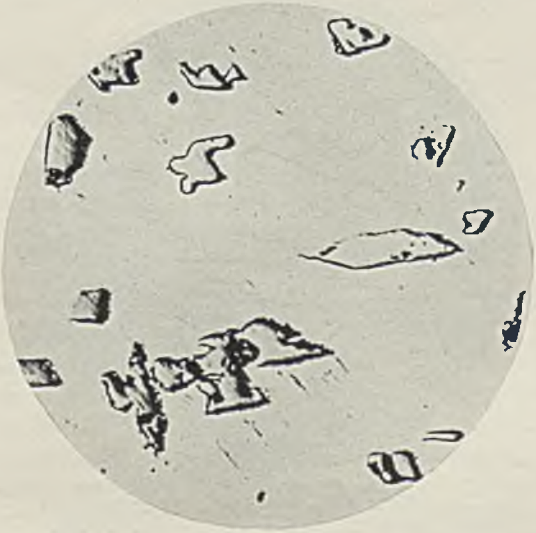


FIG. 6.—Iron 4·34%, Silicon 8·9%. FeSi Crystals. × 500.

[*To face p.* 240.

FIG. 17.—Silicon 5·0%, Iron 1%. a + Fe. × 500.

FIG. 18.—Silicon 0·7%, Iron 1·3%. Quenched from 970° C. Re-heated to 675° C. a + Fe. × 500.

these data, an equilibrium model was constructed, the form of which is shown by Figs. 7–16.

The process of solidification is indicated in Figs. 7 and 8; in the former, the true shape of the liquidus surface is indicated by the heavy isothermal lines on which the temperatures are marked. The thin, dotted isothermal lines refer to the second stage in the solidification. The liquidus surface consists of three main sections, corresponding with the separation of primary crystals of α solid solution, iron crystals, and FeSi crystals; in the extreme right-hand corner, a small portion of the surface representing the separation of the β phase is also shown. The α liquidus shown in the diagram is practically complete, but the surfaces representing the separation of iron and FeSi extend very much further into the whole system, probably to the opposite face representing alloys of iron and silicon. The isothermal lines on the α liquidus are substantially correct, since the data from the cooling curves are sufficient to indicate this surface with fair accuracy. The form of the liquidus corresponding with the separation of iron and FeSi is shown by the

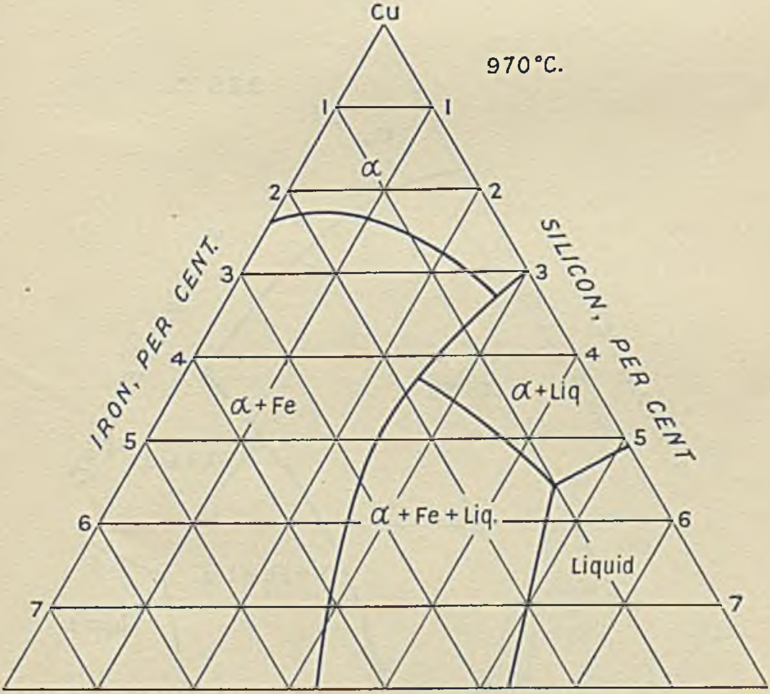


Fig. 9.

dotted, heavy lines, and is only approximate, since the arrests corresponding with this transformation were very small, on account of the small amount of iron-rich constituent involved. The general form of the curves is, however, probably correct.

Alloys the compositions of which fall within the limit of the α field do not separate a second phase except along a zone near the junction with the iron and FeSi fields, whilst those which fall within the iron and FeSi fields complete their solidification by depositing copper-rich α solution, which deposition commences at the surface of secondary separation shown by the thin, dotted isothermal lines in Fig. 7.

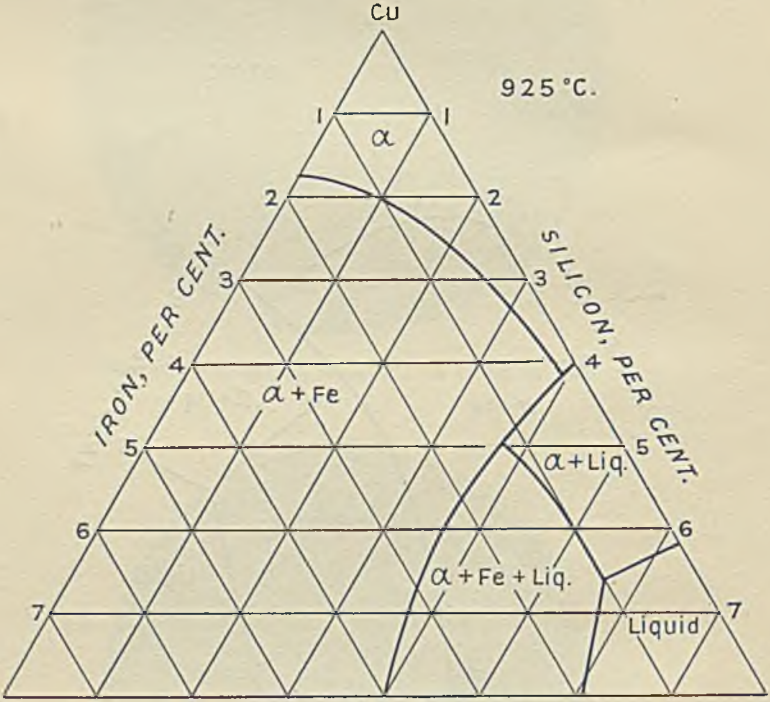


Fig. 10.

The completion of the solidification process can be pictured by means of Fig. 8. In this diagram, the full lines represent the solidus of the system, whilst the dotted lines represent, over the α region, the liquidus surface, and over the iron and FeSi regions, the upper surface of secondary separation. The temperatures of the isothermal lines on the solidus surface are indicated on the copper–silicon face, and those on the other surfaces, on the base of the diagram.

The constitution at lower temperatures is indicated by the series of horizontal sections through the model shown in Figs. 9–15. The data from which these have been constructed are shown in the Tables. The phase fields are indicated on the diagrams, and require no further amplification. The boundaries of the α and α + Fe fields are probably fairly accurately indicated. In the extreme right-hand corner of the model the phase boundaries have not been closely determined, partly because insufficient alloys were prepared for the purpose, and partly because equilibrium was difficult to attain in this region of the diagram; they should be regarded as only tentative, and as being qualitative rather than quantitative.

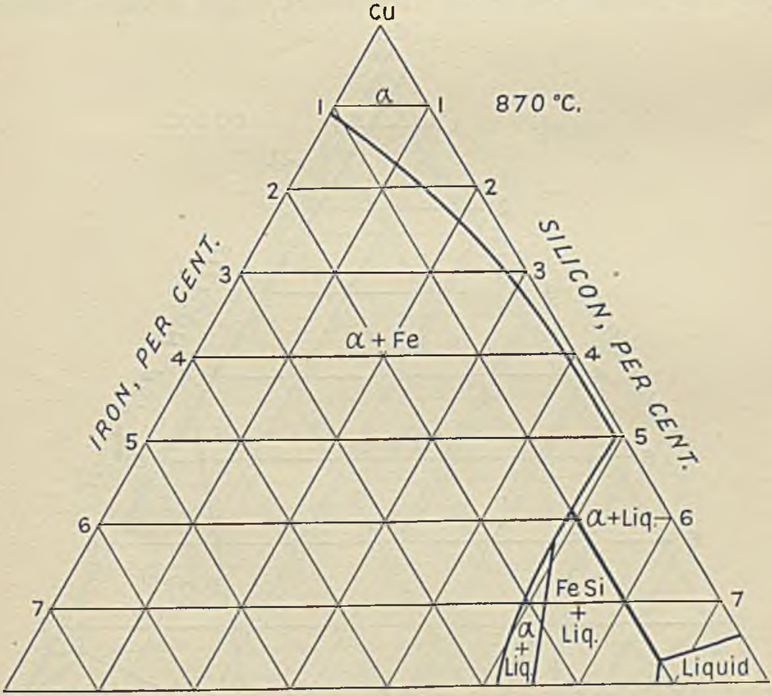


Fig. 11.

Fig. 16 shows the shape of the boundary of the phase field below the solidus line. The solubility of iron decreases rapidly below the solidus as the temperature falls, and becomes very low below about 700° C.; in addition, the solubility of iron, even at high temperatures, is decreased by the presence of silicon. These effects give rise to a somewhat complicated solubility surface, and the complication is increased by the fact that, close to the copper–silicon surface, the solubility of the γ-phase actually increases with fall of temperature between about 850° C. and 750° C.

GENERAL NATURE OF THE ALLOYS.

The constitution of alloys of this ternary system appears to be one in which the constituents of the iron–silicon system combine with those of the copper–silicon system, as is indeed to be anticipated, since copper and iron themselves form no intermediate phases. The α solid solution (copper-rich) forms a series of alloys with iron (the α solution of Haughton and Becker's diagram) and with FeSi. The β, γ, δ, and ε constituents also form a series of alloys with FeSi, but not with iron; examples of alloys of this type were met with in the right-hand corner of the present system, and in the alloys outside the range of the present diagram, but this investigation is not more than enough to detect their existence.

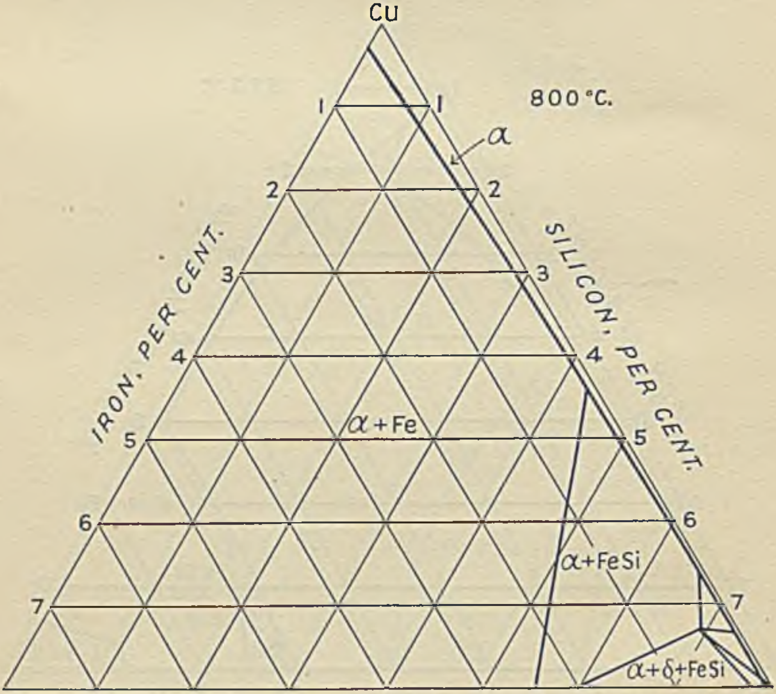


FIG. 12.

The diagrams enable one to picture fairly closely the nature of the reactions which occur during the cooling of alloys of this system. Copper-rich alloys within the α range solidify by depositing a copper-rich solid solution, whilst iron and silicon become concentrated in the residual liquid; except near the limits of the field, such alloys consist, when they are just solid, of a single phase. As cooling proceeds still further, iron is precipitated from solid-solution as indicated by the sloping surface in Fig. 16, from which it can be seen that only in a very narrow zone close to the copper–silicon face does iron remain in solid solution, the amount in this case being very small. Alloys the compositions of which fall outside the α range commence to solidify by depositing iron or FeSi. In that case, the liquid becomes rapidly impoverished in iron, until its composition reaches that indicated by the boundary between the α and the Fe or FeSi fields (*AB* in Fig. 7). When this point is reached, the stage of secondary separation commences, the liquid composition changing with temperature, as indicated by this boundary line, in such a manner that it becomes enriched

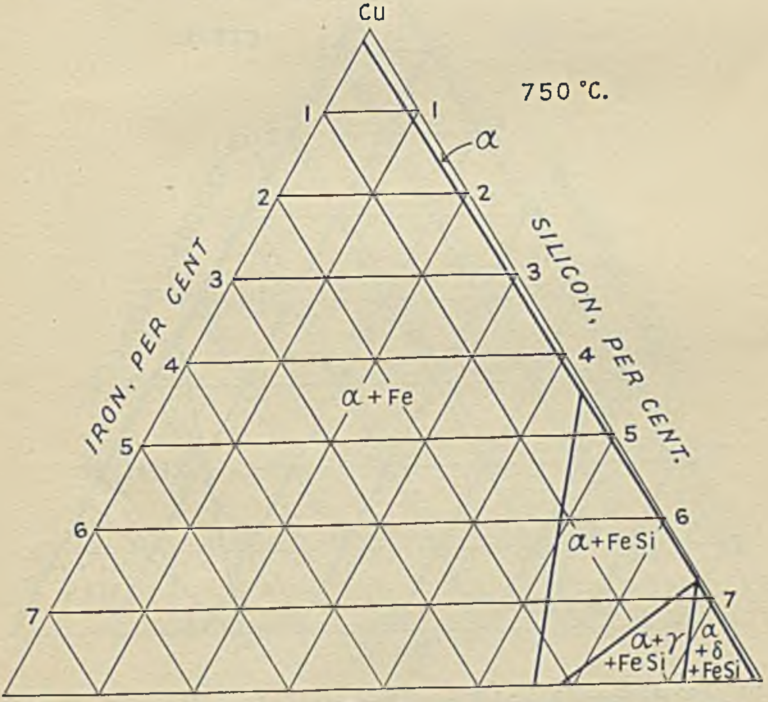


Fig. 13.

with silicon, but still further impoverished in iron. Thus we see that in such alloys the liquid phase loses iron in the first portion of the solidification process, without much change in the silicon content, and loses copper during the second portion of the solidification process while the silicon content of the residue mounts rapidly. The iron-rich constituents are deposited first, then the α solid solution together with a little more iron-rich constituent are formed, and finally, the silicon-rich phases during the final stage in the solidification. In all alloys, precipitation of iron from the α solid solution occurs with fall of temperature, and in alloys close to the copper–silicon face some precipitation of the γ-phase was also observed below 600° C.

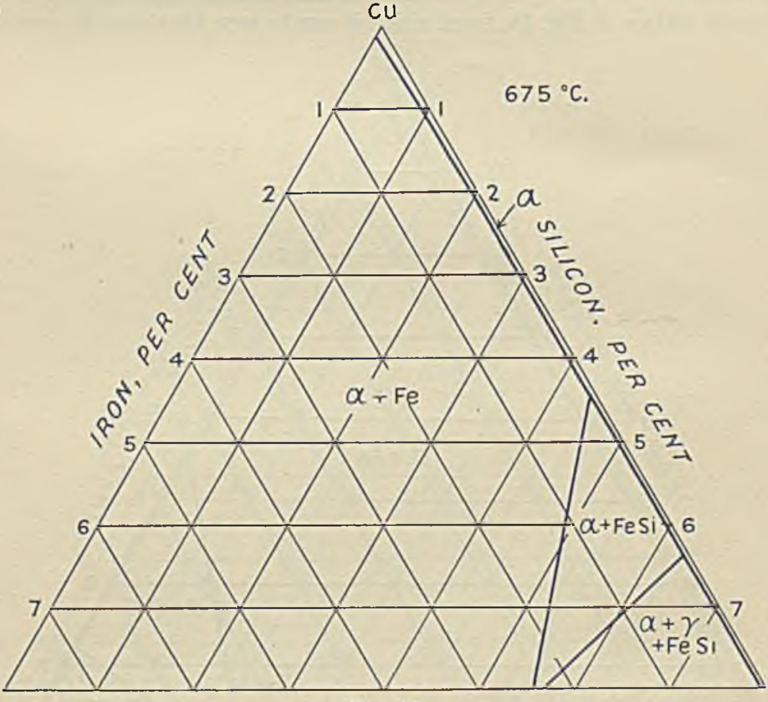


Fig. 14.

Two typical photomicrographs are shown in Figs. 17 and 18 (Plate XVIII).

PRECIPITATION-HARDENING.

The wide range of composition over which precipitation of the iron constituents occurs on cooling suggests that the alloys of this system should be amenable to heat-treatment. Corson has already reported increases in hardness in copper alloys containing iron and silicon as a result of quenching followed by re-heating, but the improvement in strength which he obtained was not very great. A further examination of the possibilities in this direction appears to be justified in the light of the results now obtained, since alloys of this system possess the type

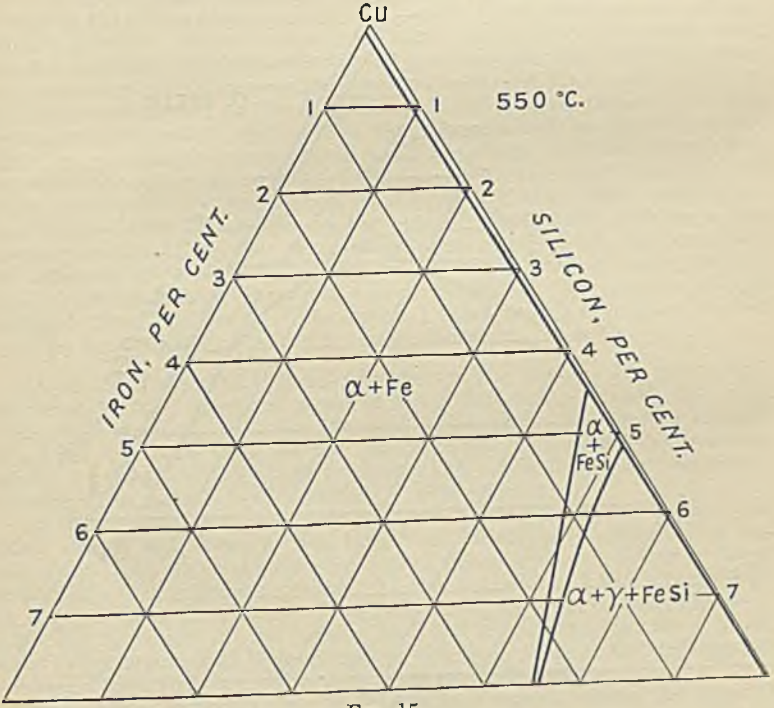


Fig. 15.

Table VI.—*Scratch Hardness Results for the Iron-Rich Phases.*

Description.	Mean Scratch, Widths, Inch.			Mean.
	1st Scratch.	2nd Scratch.	3rd Scratch.	
FeSi in alloy 26	0·051	0·060	0·056	0·056
FeSi in iron–silicon alloy	0·049	0·056	0·051	0·052
Globule in alloy 28	0·087	0·092	0·085	0·088
Globule in alloy 20	0·085	0·087	0·085	0·086
Globule in alloy 23	0·076	0·080	0·083	0·079
Globule in alloy 24	0·076	0·080	0·069	0·075
6·5% iron–silicon alloy	0·086	0·085	0·085	0·085

of constitution associated with hardening by heat-treatment. The authors have made a few preliminary experiments, the results of which were disappointing since the increases in hardness obtained were not very great, and this is in keeping with the experience of Hanson and Ford on copper–iron alloys. Nevertheless, the possibilities have not yet been fully explored.

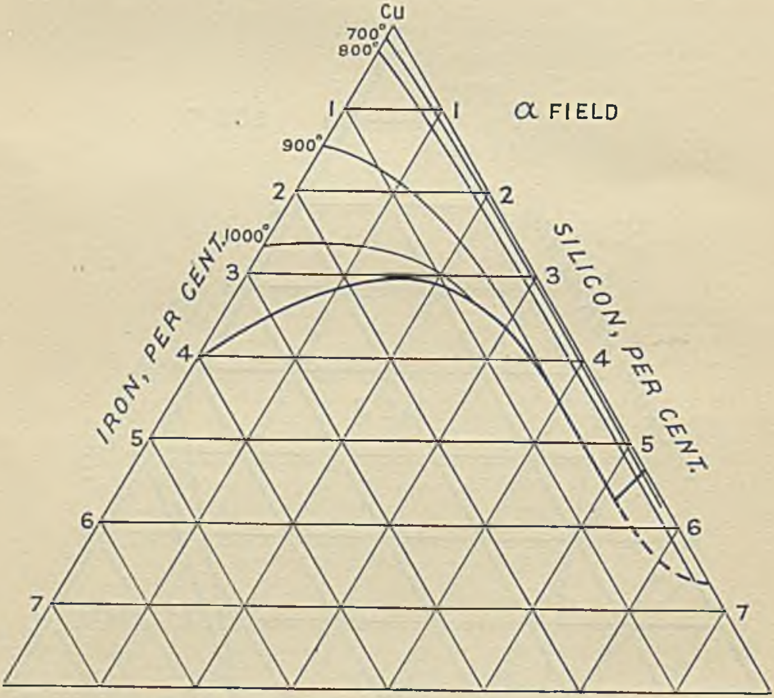


Fig. 16.

BIBLIOGRAPHY.

[1] Corson, *Proc. Inst. Metals Div., Amer. Inst. Min. Met. Eng.*, 1927, 435–450: *Iron Age*, 1927, 353–356; *Rev. Mét.*, 1930, 27, Feb.–May (especially pp. 202–205).
[2] Ellinghaus, *Abhandl. Inst. Metallhütt. u. Elektromet. K. Tech. Hochschule, Aachen, B.I.*, 1921, 5–23.
[3] C. S. Smith, *J. Inst. Metals*, 1928, 40, 359–373; *Amer. Inst. Min. Met. Eng., Tech. Paper* No. 142, 1928; *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1930, 164–193.
[4] Matuyama, *Sci. Rep. Tohôku Imp. Univ.*, 1928, [i], 17, 665.
[5] Iokibe, *Kinzoku no Kenkyu*, 1931, 8, 433–456.
[6] Ruer and Goerens, *Ferrum*, 1917, 14, 49.
[7] Hanson and Ford, *J. Inst. Metals*, 1924, 32, 335–360.
[8] Haughton and Becker, *J. Iron Steel Inst.*, 1930, 121, 315–332.
[9] Phragmén, *J. Iron Steel Inst.*, 1926, 114, 397–403.

DISCUSSION.

DR. J. L. HAUGHTON * (Member of Council): With regard to the equilibrium model to which the authors refer, they have reproduced a number of isothermal sections, by the careful study of which one can reconstruct the model, but it is a difficult business. I wish that the authors had given either a drawing of the model or perhaps some vertical sections through it, as these would have rendered it easier to visualize the constitution of the system.

On p. 238 segregation troubles are referred to, and in Table III it will be noticed that there are a number of blanks in the liquidus determinations, which, it is stated, are due to the arrests at the liquidus being too small to be recorded with any certainty. Do the authors associate that with the results of segregation? In this connection I would like to refer them to the paper by Mr. Payne and myself on the magnesium–nickel system, presented at this meeting. We found in that system that we obtained no liquidus points over a certain range of composition when the alloys were not stirred, but that when the alloys were stirred while the curve was being taken we did obtain the points. Do the authors consider that if they could have stirred these alloys—it would have been a very much more difficult problem in the present case than in the case of the magnesium–nickel alloys, because of the big difference in temperature—they might have obtained more definite liquidus determinations or perhaps even a different temperature of the liquidus? From the shape of the curves I think that it is unlikely that it would be very different, but it is a matter of interest.

MR. E. H. BUCKNALL,† M.Sc. (Member): The authors are to be congratulated on their successful study of the constitution of these copper-rich alloys, more especially as in the course of that work an entirely new method has, I believe, been used for the determination of solidus temperatures, namely, by the use of a gradient furnace, which seems to be a method which will offer advantages in investigations on other systems.

On the constitutional side there seems to be little to discuss beyond the points already mentioned by Dr. Haughton, although an extension of the field of study to alloys of somewhat higher silicon content appears to be of considerable theoretical importance. In this connection, I was surprised at the appearance of the ε phase of the FeSi system in these copper-rich alloys before the appearance of the η phase, as I had anticipated that the η phase of the FeSi system would be isomorphous with the γ phase of the CuSi system and would form with it a continuous range of solid solutions.

On p. 247 it is stated that "alloys of this system possess the type of constitution associated with hardening by heat-treatment." At the risk of correction, I would suggest that that remark, whilst possibly true, is a little in advance of our present knowledge of hardening by phasial changes. It is certainly well known that in a great number of alloy systems in which a sloping solubility line separates homogeneous from duplex fields, ageing phenomena occur; on the other hand, there is very frequently, in metallic alloys, a close approach to the "ideal solution" of the physical chemist, and in that ideal solution there is no evolution or absorption of heat when a solute atom passes into or out of solution in the solvent. Should the α field of this system be a solid solution which approaches the ideal type, no age-hardening would be anticipated, although there might be a decrease in solid solubility with reduction in temperature.

---

* Principal Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

† Junior Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

Again, there is, I think, no case known of a ternary alloy which age-hardens by the separation of a pure metal or the α solid solution of that metal, although that state of affairs does occur in binary systems. In the case of ternary alloys a more complex separation phase is probably necessary before the ageing occurs.

The constitution of these alloys seems to differ very markedly from that of the ternary alloys of copper with nickel and silicon, cobalt and silicon, &c.—with which Corson dealt—where the precipitated phase, described by him as a definite silicide, probably includes in each case at least two and probably all three of the components.

Mr. A. J. Murphy * (Member): As one who has always to bear in mind the possibility of commercial exploitation of cuprous alloys, I wish to express my gratitude to the authors for providing such a sound basis on which to consider questions of that nature in reference to the copper–iron–silicon alloys. A number of points which arise in one way or another from the attitude of mind to which I refer may possibly be worth mentioning.

The first is a question of general significance, I think, on the possibility of securing useful improvement of mechanical properties in cast alloys, and particularly cast copper alloys. We see in many cases the success with which heat-treatment is applied to forged materials showing diminution of solid solubility in the α phase with decrease of temperature, but we are rarely given equally complete information as to the sequence of events in the cast material when the same treatment is applied. I know that there are other grounds for doubting the possibility of that heat-treatment being usefully applicable to these alloys, but, in case that position changes, it would be useful to know whether these alloys are especially sluggish in the rate at which homogenization is obtained by annealing at what may be termed the solution temperature, or whether they are rather speedy in that respect. I have some difficulty in deducing from the paper which, if either, of those two represents the position, because there is a reference to the fact that the alloys were likely to require very long annealing periods to obtain equilibrium, and that the apparatus was devised with this point in view. Smith, however, records that the rate of diffusion of silicon to the surface of copper–silicon alloys is extremely high, and experiments confirm that. I realize that there is another factor there, namely the removal of silicon by oxidation from the surface increasing the concentration gradient; but on the face of it those two observations would appear to lead to opposite conclusions.

Arising from that point, may I comment on the procedure in determining the solidus. On p. 237 the authors mention that they took small specimens—I presume previously annealed at a lower temperature to secure uniformity—and then increased their temperature to somewhere in the region of the anticipated solidus and maintained the temperature there for 15 minutes. That would appear to be rather a short time, unless there is some other explanation, because, of course, the solidus will be different if sufficient time has not been given for equilibrium to be established at the higher temperature.

Regarding the more detailed ternary diagrams, Mr. Bucknall has referred to the material precipitated being pure iron, and not an iron compound. I should welcome any remarks which the authors might make on the significance of that in relation to the physical properties. It is also worthy of note that the maximum rate of change of concentration of the α solid solution with temperature occurs in the region where iron would be the material precipitated and not FeSi. From 800° C. downwards there is very little change in con-

---

* Chief Metallurgist, J. Stone and Co., Ltd., Deptford.

centration of the saturated α solid solution where the neighbouring second phase is FeSi, so that it is unlikely that any improvement of properties can be obtained due to precipitating a compound instead of a pure metal here. Another unfortunate feature, if one has a practical application in view, is that the rate of change in the limit of the α solid solution in the alloys containing less than 4 per cent. of silicon is a maximum at a rather high temperature, a temperature so high that the neighbouring phase is liquid. In other words, at 870° C. the solubility of iron in copper is 1 per cent. (Fig. 11), and there is a reduction in this limit as the silicon increases, but at the temperature which it would be desirable to use for securing solution the alloys containing 5 to 7 per cent. of silicon and up to 1 per cent. of iron are liquid, so that in applying the solution heat-treatment in practice one would probably be compelled to use a temperature which was lower than that which would give the maximum amount of solution.

I realize that all these points are perhaps labouring something which the authors more or less firmly refuse to take up, but I would, if I might, invite them to tread a little further on the dangerous ground to which Dr. West referred in introducing the paper and give us some indication of the amount of hardening which is obtained by solution and tempering.

Dr. MARIE L. V. GAYLER * (Member): I can find no reference to the transformation of γ iron to α iron, which must play a part. In none of the sections shown is there any evidence of the γ field or the α field; it is all called "iron." That change, however, must take place, and a two-phase field, α and γ iron, must exist. It may be very narrow and may not have much effect, but theoretically it is important and should be added. This emphasizes Dr. Haughton's suggestion that vertical sections would have been of great value in this paper. The authors have investigated an extremely complicated diagram; in their own words, the constitution of these alloys tends to be a change from the copper-silicon to the copper–iron, and from the copper–silicon diagram (Fig. 1) it will be seen that it is extremely complicated. I suggest that it would be of very great assistance to those who are going to use this from the practical point of view, as well as from the theoretical, if vertical sections were added, with the appropriate phase fields.

Dr. CYRIL S. SMITH,† B.Sc. (Member): My experience leads me to believe that the two-liquid field shown in Ruer and Goerens' or in Müller's copper–iron diagrams is actually not present in moderately pure melts of any composition or at any temperature up to 1700° C. On the other hand, if a small amount of silicon is added—I forget the exact amount, but believe that it is of the order of 1 per cent.—an alloy containing about 50 per cent. iron separates into two distinct layers at all temperatures above the liquidus, even when the melt is made in a high-frequency induction furnace. Much smaller additions of carbon produce the same effect.

I would like the authors to explain the purpose of the "lines of secondary separation" in Figs. 7 and 8. These seem to confuse the diagrams, and are really unnecessary, for the temperatures referred to can easily be determined from a liquidus surface of the ordinary kind.

Dr. E. VOCE,‡ M.Sc. (Member): In support of Dr. Smith's remarks I would say that quite recently I have had to make up a few alloys of roughly

---

* Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

† Research Laboratory, The American Brass Company, Waterbury, Conn., U.S.A.

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

50 : 50 copper–iron, with certain minor additions, and I found no clear evidence of the presence of two liquid phases. A high-frequency induction furnace was used.

Professor HANSON (*in reply*): I will begin by replying to the point mentioned by Dr. Haughton and Dr. Gayler, that we have given the sections through this model horizontally instead of vertically. This is because horizontal (isothermal) sections have a quantitative value and show exactly the nature of the system at the temperature concerned, whereas vertical sections are qualitative only, and frequently misleading, since they offer no guide to the course of the internal transformations.

Dr. Haughton referred to the small arrest at the liquidus point. The alloys were stirred before the curves were taken and the heat arrest was still found to be very small, no doubt due to the very small amount of the constituent which separated from solution. In actual fact, we used the segregation which is due to the difference in density of the solid crystals which separate from the liquid to indicate the position of the liquidus by melting in an inert gas and watching for the first appearance of the crystals to float up to the surface; and, whilst the experiments were carried out with apparatus rather hastily put together, I think that where there is a big difference in density that method could be made very sensitive for determining the liquidus point. It was the only method with which we could obtain any evidence at all.

The question of the two-liquid layer has been referred to. That is interesting, because there is in the literature a good deal of conflicting evidence on that point, some investigators maintaining that the two-liquid phase field comes right down to the next horizontal line in the system, and others maintaining that there is a region of homogeneity extending right across the diagram. I think that the contributions of Dr. Smith and Dr. Voce on that point are interesting, and particularly Dr. Smith's reference to the effects of small amounts of silicon and of carbon, because in making these alloys a carbon steel is usually used as the form of iron and a certain amount of carbon is generally present.

Mr. Murphy really referred to the principal importance of this paper. We knew that changes in the solubility of iron or some iron constituent did occur during the annealing of alloys of this type, and we set out primarily to determine what those changes were. I think that we have succeeded in showing the way in which the solubility changes, and we do not propose to carry it any further; we consider that those in industry should now be able to make use of this basic information. As to what is the degree of improvement that can be obtained, I do not know. Our preliminary experiments showed the increases in strength to be rather small. Miss Ford and I found the same thing in dealing with iron–copper alloys. But the system seems to be worth exploring much more fully than we have been able to explore it; I suggest that, now that the basic information is available, it is the function of industry to pursue the matter in these directions.

The alloys are rather sluggish at high temperatures. Annealing times must be prolonged and segregation must if possible be prevented during casting, because there is a very marked tendency for primary crystals of iron or FeSi to segregate during casting; in determining the solidus we found that, once homogeneity had been obtained, diffusion was fairly rapid, provided that it did not involve the diffusion of iron and silicon together for considerable distances through the alloy. The first appearance of melting in that homogeneous solution is quite quick, and, although we used periods of 15 minutes in our experiments, longer heat-treatments were previously tried; we came to the conclusion, however, that 15 minutes was long enough.

I refuse to follow Mr. Bucknall into the field of speculation as to the general nature of age-hardening, particularly in ternary and more complex systems, since the evidence to enable us to form an opinion is not yet available. The iron–silicon phases involved in this system are certainly the α and the FeSi phase, but there is evidence that with higher iron and silicon contents than we have used, but not greatly outside the range of our investigations, the η phase of the iron–silicon system also enters, but in what manner we do not exactly know.

With regard to the identification of the α phase, we identify the α iron because it is a continuous phase with the constituent which separates when iron–copper alloys are cooled. It seems to be identical in all its constitutional properties with that phase, and I therefore call it α iron: we did not put in the change from γ to α iron, partly because we did not investigate it, and partly because the diagram is so constructed on that edge of the system that there is no proper room to indicate the main solubility lines clearly without a greatly exaggerated scale. The change seems of secondary importance from the immediate point of view, and we have not made any reference to it. There cannot be any considerable change of solubility when iron changes from γ to α, since the solubility of each is very small at this temperature.

TRANSFORMATIONS IN THE COPPER–PALLADIUM ALLOYS.*

By R. TAYLOR,† B.A., B.Sc., MEMBER.

SYNOPSIS.

Copper–palladium alloys up to 55 atomic per cent. of palladium have been examined by thermal, micrographic, and electrical resistance methods. The determination of the electrical resistance-temperature curves has been carried out with a much slower change of temperature than had previously been used. The occurrence of two transformations at 10–30 atomic per cent. and 35–50 atomic per cent., respectively, and associated with different types of electrical resistance curve has been confirmed. The results are compared with those of earlier workers and the mechanism of the transformations is discussed.

INTRODUCTION.

THE transformations which occur in the copper–palladium alloys have been previously examined by many methods.[1-8] The X-ray work of Holgersson and Sedström[2] and of Johansson and Linde[3, 4] makes it clear that at high temperatures alloys of all compositions possess a face-centred cubic lattice, but no regular arrangement of the two kinds of atoms has as yet been detected. On cooling to lower temperatures, alloys containing between 10 and 30 and between 38 and 50 per cent.‡ of palladium undergo transformations. The lattice in the former range is unchanged, but the atoms take up a regular distribution based on the ratio 3 Cu : 1 Pd, with the palladium atoms occupying the cube corners, and the copper atoms the centres, of the faces. According to Borelius, Johansson, and Linde,[5] the super-lattice lines in the X-ray photographs, which indicate the regular atomic distribution, are strongest at about 17 per cent. In the range 38–50 per cent. at low temperatures there is a change to a body-centred cubic lattice, with a regular arrangement of the atoms based on the 1 : 1 ratio, each component being at the points of a simple cubic lattice, as in CsCl.

---

* Manuscript received October 13, 1933. Presented at the Annual General Meeting, March 8, 1934.

† Downing College, Cambridge.

‡ Compositions are throughout expressed in atomic percentages and alloys are referred to by their nominal palladium content.

The electrical resistance measurements carried out at room temperature by Sedström,[1] Johansson and Linde,[3, 4] and Svensson [6] show that a low value of the specific resistance is associated with the ordered arrangement of the atoms. The minimum values in the two ranges are displaced from the simple atomic ratios, occurring respectively at 16–18 per cent. and at 47 per cent. The values of the specific resistance for alloys with an irregular distribution of atoms lie on a comparatively smooth curve and attain a maximum at about 60 per cent. of palladium.

EXPERIMENTAL.

Preparation of Alloys.

The alloys were prepared from electrolytic copper (the only impurity found was 0·002 per cent. iron) and palladium sponge of approximately the same purity. They were made up at 5 per cent. intervals from 5 to 55 per cent. of palladium, except that, for the micrographic and electrical resistance work, additional alloys were prepared near 40 per cent.

TABLE I.—*Composition of Alloys.*

Nominal Atomic Per Cent. Palladium.	Weight Per Cent. by Analysis.		Atomic Per Cent. Palladium.
	Pd.	Cu.	
5	8·05	91·95	4·96
10	15·65	84·35	9·95
15	23·10	76·90	15·18
20	29·50	70·50	19·95
25	36·08	63·92	25·17
30	41·96	58·04	30·11
35	47·74	52·26	35·26
38·5	52·50 *	47·65	39·62
40	52·57	47·43	39·77
41	54·69 *	45·45	41·75
42·5	56·59 *	43·49	43·67
45	58·21	41·79	45·36
48	62·01 *	38·08	49·24
50	63·02	36·98	50·38
55	67·49	32·51	55·31

Atomic weights : Palladium . . . 106·7
Copper . . . 63·57

* By analysis (in other cases only copper was estimated).

The alloys were made in high *vacuo*, using a high-frequency induction furnace, and were twice remelted before the final cooling. The crucibles used were made from Alundum tube and the ingots obtained were cylindrical, 1–1·5 cm. long and 0·8 cm. in diameter, and weighed about 12 grm. These ingots were used directly for the thermal investig-

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

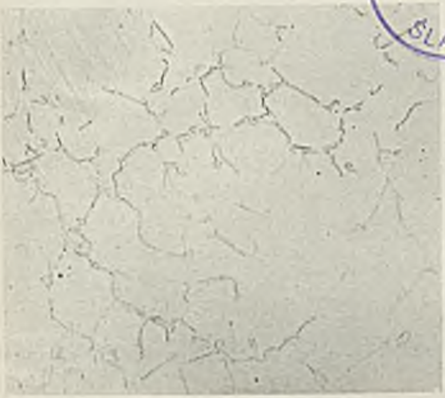


FIG. 5.—40 per cent. Palladium. Quenched from 600° C. × 150.

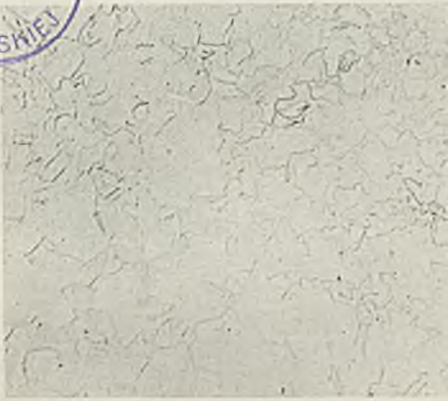


FIG. 6.—40 per cent. Palladium. Quenched from 594° C. × 150.

FIG. 7.—42·5 per cent. Palladium. Quenched from 594° C. × 75.

FIG. 8.—42·5 per cent. Palladium. Quenched from 590° C. × 75.

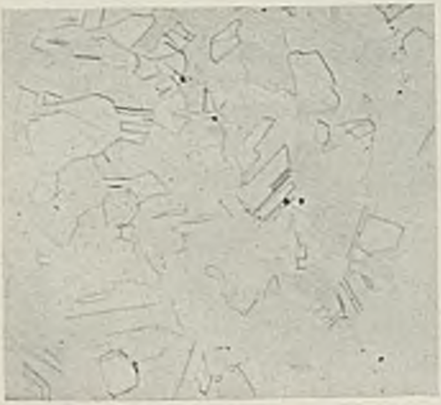


FIG. 9.—45 per cent. Palladium. Quenched from 599° C. × 150.

FIG. 10.—45 per cent. Palladium. Quenched from 598° C. × 50.

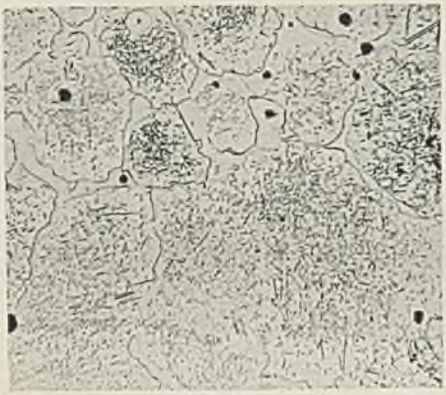


FIG. 11.—45 per cent. Palladium. Quenched from 594° C. × 100.

FIG. 12.—50 per cent. Palladium. Quenched from 556° C. × 75.

FIG. 13.—35 per cent. Palladium. Quenched from 300° C. × 200.

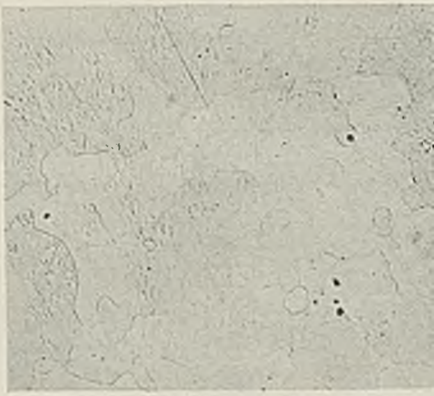


FIG. 14.—40 per cent. Palladium. Quenched from 300° C. × 75.

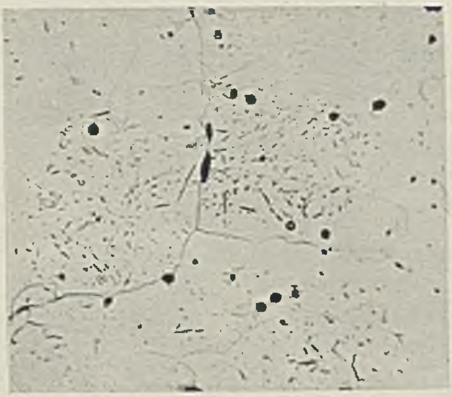


FIG. 15.—45 per cent. Palladium. Quenched from 300° C. × 200.

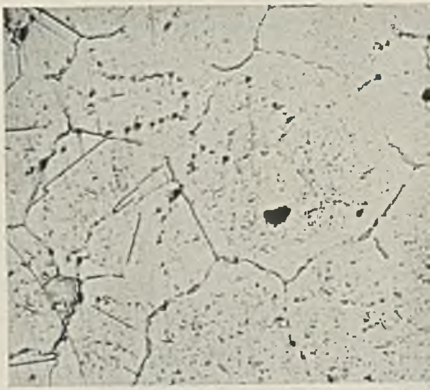


FIG. 16.—50 per cent. Palladium. Quenched from 300° C. × 150.

ation after holes had been bored in them to take the necessary thermocouples, with the exception of the 25 per cent. alloy, which had to be softened by quenching before it could be drilled. The same ingots were afterwards used in the micrographic investigation. Specimens similarly prepared were drawn down, first through Widia dies and then through diamond dies, to suitable wires for the electrical resistance work.

The compositions of the alloy wires are given in Table I. Samples from different parts of each wire were analysed and the results were in close agreement.

Thermal Investigation.

The specimens were heated in an electrical resistance tube furnace controlled by a thermo-electric thermostat, in an atmosphere of hydrogen or nitrogen. In taking heating curves a steady current was maintained through the furnace of such magnitude as to give a change of temperature of 1·5°–3° C. per minute over the critical range. Cooling curves were, in general, taken with no current passing, and the rate of cooling was therefore greater the higher the temperature; over the critical ranges it varied from 2° C. to 4° C. per minute.

It was found necessary to use a differential method in order to detect the evolution or absorption of heat accompanying the changes in the alloys. The neutral was a short piece of pure copper rod of the same size as the specimen. A Chromel–Alumel differential couple was used in conjunction with a " water-dropper." The short wire of this couple was of Alumel, which had periodically to be renewed, as it was embrittled by nitrogen in the absence of oxygen. The temperature of the alloy specimen was measured with a platinum/platinum–rhodium thermocouple and a millivoltmeter.

In tracing the temperature difference–time curves on the screen, the time was calibrated by marking the position of the spot of light every 2 minutes: the millivoltmeter was read every 4 minutes. The temperature difference–temperature curves could then be constructed if desired, although in most cases the temperature of a change was determined directly from the experimental tracings.

The specimens were usually given a preliminary anneal between 600° and 700° C. for some hours before cooling and heating curves were taken. Reproducible results could then be continuously obtained without further annealing.

Micrographic Analysis.

The specimens were annealed in an atmosphere of nitrogen in the furnace used for the heating and cooling curves, with the exception that, towards the end of the investigation, a triple furnace [9] with hydrogen was employed. A thread recorder was used to detect any irregularity in the temperature control. Two sets of very slowly cooled specimens were obtained by using an aluminium block furnace heated by gas, the flow of which was controlled by a crude form of thermostat. Cooling from 500° to 300° C., at which temperature one set was quenched, was spread over 23 days, and the further cooling to room temperature took 16 days. In this experiment the specimens were sealed in evacuated Pyrex tubes.

The initial heat-treatment of nearly all the specimens was an anneal for at least 2 hrs. in the neighbourhood of 800° C. The temperature was then lowered to that required, and was maintained for several hours before the specimen was removed and quenched in cold water.

A 1 per cent. solution of bromine in alcohol proved to be a satisfactory etching reagent for the alloys with more than 30 per cent. of palladium. A more dilute solution was used for the other alloys, which were rather easily stained and pitted. On the advice of Mr. E. M. Wise,* a mixture of equal volumes of 10 per cent. solutions of ammonium persulphate and potassium cyanide was tried. This was somewhat slower in action, and produced the same result on the higher palladium alloys as the bromine reagent.

Electrical Resistance Measurements.

In order that several alloys might be examined together, a large tube furnace was constructed. This furnace was wound in five sections with Nichrome tape, and, by arranging external resistances in parallel with the inner sections, a length of 15 cm. was obtained in which the temperature variation was less than 3° C. The furnace was fitted with a triple Chromel–Alumel couple for the thermostat control.

The alloys were examined *in vacuo* by the following arrangement: copper wires, about 33 cm. in length, were joined to the ends of about 45 cm. of alloy wire by means of small beads of silver. Tungsten wires, 7–8 cm. long, were brazed to the free ends of the copper wires, and copper leads were similarly joined to them. The tungsten wires were cleaned, oxidized slightly in a flame, and coated with a film of Pyrex glass. The alloy wire was wound, in the form of a spiral, round narrow Pyrex tubing, one lead passing up the inside of the tube. The specimen was then placed in a wider Pyrex tube, one end of which was sealed by pinching the hot glass round the tungsten wires. After the other end had been drawn down, the tube was evacuated and sealed off. For each

---

* Private communication. See also E. M. Wise and J. T. Eash, "The Rôle of the Platinum Metals in Dental Alloys.—III," *Trans. Amer. Inst. Min. Met. Eng.*, 1933, **104**, *Inst. Metals Div.*, p. 303.

alloy a similar specimen was prepared, but with only 5–10 cm. of alloy wire. By this means it was possible to eliminate the resistances of the leads.

It was possible to get twelve of these tubes in the furnace together, and six alloys could thus be examined at one time. The tubes were placed so that the whole of each alloy was within the range of constant temperature; the inside copper–tungsten junctions were then near the end of the furnace and the seal was just outside it.

The resistances of the specimens were measured by a potentiometric method. A lead accumulator and a 200-ohm coil were connected in series with a standardized Manganin coil and with a specimen. The fall of potential across the specimen was compared with that across the Manganin coil using a Pye potentiometer. The current through the specimen was then reversed and the readings were re-taken. The average value was used. The examination of a specimen was followed immediately by that of the corresponding subsidiary specimen. Measurements were made at various temperatures, the furnace being kept at each temperature until the resistances ceased to change. Outside the range of transformations, 3–6 hrs. was sufficient for this, but about 24 hrs. was given when a transformation was in progress. The result of longer annealing is considered on p. 267. The temperature was changed in steps of 30°–50° C. at low temperatures and 8°–15° C. through the transformation ranges. A Foster quadruple strip recorder was used to follow the changes in the temperature and in the resistances of three of the alloys. This gave an indication of the approach to equilibrium. The recorder was also used in two series of experiments to determine the temperatures of the transformations during continuous heating and cooling. The chart was calibrated for temperature by taking readings of the millivoltmeter at intervals, and the transformations were indicated by marked changes in direction on the resistance curves.

Results.

(a) 0–30 *Per Cent. of Palladium.*

Satisfactory evidence of a transformation in this range was obtained in only three of the six alloys which were examined by the thermal method. For the alloys containing 15, 20, and 25 per cent. palladium, curves were obtained similar to those shown for that containing 15 per cent. (Fig. 1 (I, II)). These curves have been derived from the experimental tracings by changing the time ordinate to a temperature ordinate (p. 257), and the scale of the alloy/neutral temperature difference has been reduced to one-third in reproduction. (Curves III, IV have been obtained similarly.) It should be noted that the alloys containing 20 and 25 per cent. palladium gave no indication of the smaller change point shown in the heating curve for that containing 15 per cent., nor did this point appear on cooling curves of that alloy. The curves for the alloy containing 5 per cent. palladium showed no transformation, whilst evidence with those containing 10 and 30 per cent. was indefinite. The effect of the gas in contact with the specimens was examined with the 20 and 25 per cent. palladium alloys. With the temperature of the furnace steady, a curve was traced while nitrogen was removed from the tube and hydrogen was admitted. No indication of any heat change was obtained; further, results obtained in hydrogen were in good agreement with those in nitrogen.

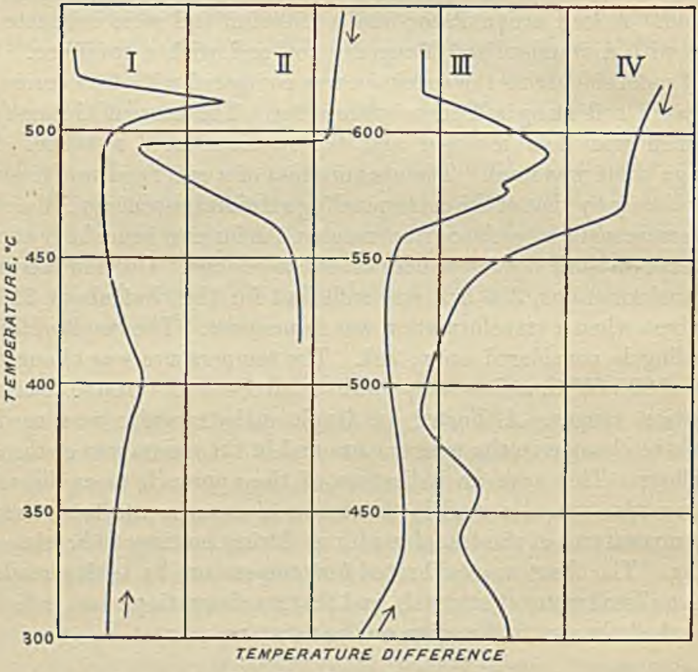


Fig. 1.—Thermal Curves.

The temperatures at which the transformations commenced and where the temperature difference was greatest are given in Table II. Where only one value is given, two or more experiments gave results to ± 3° C. The temperature–composition curves are irregular, and will be considered with the results of the work on electrical resistance.

A micrographic examination of these alloys yielded no results. Both the slowly cooled specimens and those quenched from 580° C. showed the typical polygonal grains of a solid solution. The alloy containing 25 per cent. palladium was examined at intervals of 20° C. from 520° to 460° C., and no indications of a duplex structure were obtained.

Examples of the electrical resistance–temperature curves are shown in Fig. 2 (I, II). The typical curve for this range is made up of three

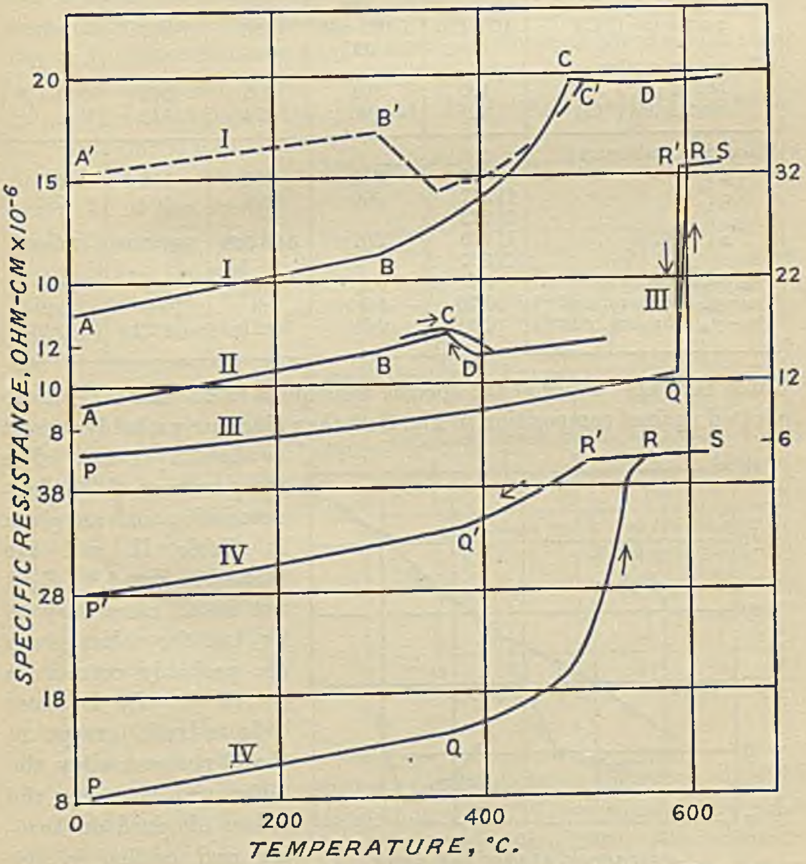


FIG. 2.—Electrical Resistance Curves. I, 20 per cent. Palladium; II, 10 per cent. Palladium; III, 41 per cent. Palladium; IV, 48 per cent. Palladium.

parts: (*a*) a linear increase of resistance with temperature to about 300° C. (*AB*); (*b*) a more rapid increase, with a continually increasing temperature coefficient, over a range of 100°–200° C. up to a sharp peak (*C*); (*c*) a small but definite decrease in resistance to a flat minimum (*D*), followed by a slow but steady increase. The changes in specific resistance between *B* and *C* and *C* and *D*, respectively, are given in

TABLE II.

	10% Pd.	15% Pd.	20% Pd.	25% Pd.	30% Pd.
Thermal investigation :					
Change on heating :					
began (° C.) . .	300–340	i 336–365 ii 488	455–475	440	336
maximum (° C.) .	400–420	i 400–440 ii 512	488	477	410
Change on cooling :					
began (° C.) . .	480	504	505	518	460–470
maximum (° C.) .	...	490	474	443	...
Electrical resistance :					
T_B (° C.) . . .	300	312	300	312	278
T_C (° C.) . . .	H 357 C 372	500	490	460	382
T_D (° C.) . . .	H 430 C 397	507	540–560	530–540	470–480
ρ_{20} (ohm-cm. × 10^{-6}) .	9·2	8·1	8·64	9·7	19·9
$\rho_C-\rho_B$ (ohm-cm. × 10^{-6})	0·76	5·3	8·3	10·8	2·9
$\rho_C-\rho_D$ (ohm-cm. × 10^{-6})	0·81	0·18	0·21	0·22	0·10

Table II. The values of the specific resistances at 20° and 600° C. are plotted against composition in Fig. 3 : * the values are probably correct to about 2 per cent. The temperatures of the characteristic points are given in Table II and are plotted in Fig. 4.* T_B is not in all cases easy to fix, but the values given are probably correct to ± 10° C. T_C is more definite and, except in the 10 per cent. alloy, the difference between the values obtained on heating and cooling is less than ± 3° C. In the alloys containing 20–30 per cent. palladium the minimum extends over a considerable range of temperature, the upper limit of which is plotted in the figure. There is no discontinuity of any kind on the curve for the alloy containing 5 per cent. palladium and whilst the heating curve for that containing 10 per cent. (Fig. 2, II) seems to indicate a departure from the typical

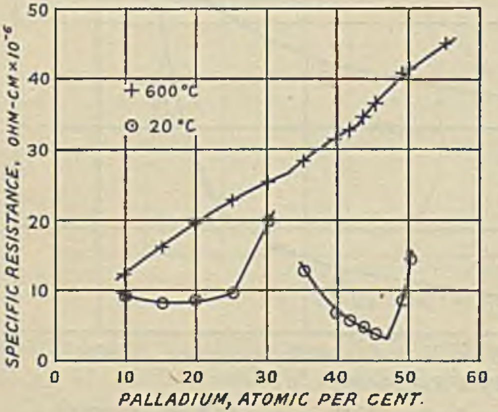


FIG. 3.

---

* In order to save space, the results for all the alloys are shown in these figures.

curve described above, the cooling curve conforms. The comparatively sharp rise from the minimum to the peak occurs again in the 15 per cent. palladium alloy.

The specimens were usually annealed for at least one day at 400°–500° C. and then cooled slowly in the furnace before an investigation was commenced, but one group of specimens was examined from the start, the results in this case for the 20 per cent. alloy being indicated in Fig. 2, I. The resistance was comparatively high at the start (A') and increased along the broken line until the temperature reached 300° C. (B'). There was then a fall, probably due to the removal of the work-hardness introduced in preparing the wires, followed by a rise to the peak C' at 500° C. From this point to the end of the examination, which included (*a*) heating to 630° C. and cooling to room temperature, (*b*) determining T_C with the recorder, and (*c*) heating from 330° to 616° C. and cooling to room temperature, all the readings for which the heat-treatment had been sufficient (nearly 50) lay very close to the curve *ABCD*.

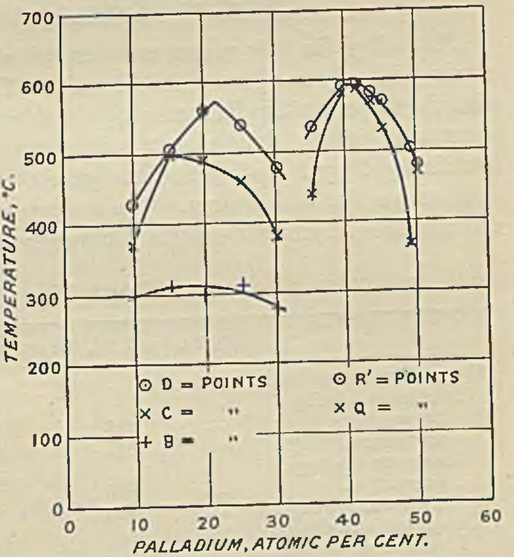


Fig. 4.

The decrease of resistance from the peak on cooling was found to be a comparatively slow process; for example, in the curve obtained with the recorder for a rate of cooling of 0·25° C. per minute there was a depression of 6° C. in the value of T_C for the 15 and 20 per cent. palladium alloys. The resistance of the 20 per cent. palladium alloy wire at room temperature was 0·544 ohm and 0·516 ohm, respectively, after the treatments (*a*) and (*c*) above. The difference was even greater in the alloy containing 25 per cent. palladium. As the only difference in the treatments was that the furnace had cooled freely from 350° C. in (*a*) and from 210° C. in (*c*), it seems probable that the more rapid cooling from the higher temperature had some quenching effect.

The results of the thermal investigation do not bear a very close relation to those of the work on electrical resistance. It will be seen from Table II that in the heating curves the absorption of heat commences between the *B* and *C* points and the maximum deflections correspond satisfactorily with the *C* points if allowance be made for slight superheating. The changes as shown by the cooling curves start between the *D* and *C* points, and the maximum deflections occur 10°–20° C. below the *C* points. As this may be entirely due to the rate of cooling employed, it is reasonable to conclude that the greatest change of energy occurs at about the *C* point, whilst both the *B–C* and *D–C* changes of electrical resistance are accompanied by small energy changes.

(b) 35–55 *Per Cent. of Palladium.*

Five alloys in this range were examined by heating and cooling curves, and only two gave definite results. The types of curve obtained with the 45 per cent. palladium alloy are shown in Fig. 1 (III, IV). The occurrence of the double points is difficult to explain. The alloy containing 40 per cent. palladium gave a very large and sharp peak both on heating and cooling. The temperatures at which the changes commenced and where the deflection was greatest are given in Table III.

Table III.

	35% Pd.	40% Pd.	42·5% Pd.	45% Pd.	50% Pd.	55% Pd.
Thermal investigation :						
Change on heating :						
began (° C.) .	...	618	...	538	...	...
maximum (° C.) .	...	642	...	592	...	...
Change on cooling :						
began (° C.) .	...	592	...	576	...	...
maximum (° C.) .	...	579	...	492	...	...
Micrographic analysis :						
Limits of upper phase boundary (° C.) .	540–550	604–613	604–613	594	572–575	521–537

The results of the micrographic examination can be divided into two parts, dealing respectively with the determination of the upper phase boundary and with the changes at lower temperatures. Except where one phase was present in only a small quantity, it was often difficult to distinguish between the phases under the microscope.

In the alloys containing 35, 50, and 55 per cent. palladium the separation of the second phase in the grain boundaries could be detected readily and the temperature of its appearance was obtained within satisfactory limits, which are given in Table III. Fig. 12 (Plate XX) shows the separation of the second phase in the 50 per cent. alloy about 20° C. below the boundary, where it has begun to appear in the grains as well as along the grain boundaries. Early experiments placed the boundary between the one-phase and two-phase areas at 598°–602° C. for both the 40 and 45 per cent. palladium alloys; Fig. 10 (Plate XIX) shows the presence of the second phase at 598° C. in the alloy containing 45 per cent. palladium and Fig. 11 (Plate XX) the marked increase in quantity at only 4° C. lower. A 42·5 per cent. palladium alloy was therefore prepared to determine the course of the curve between 40 and 45 per cent. palladium, specimens of all three compositions being annealed and quenched together. Considerable difficulty was experienced in interpreting the structures shown by the specimens quenched from the neighbourhood of 600° C. and, discrepant results being obtained, the following experiment was carried out: nine specimens, three of each composition, after being annealed for 18 hrs. at 870° C., were heated to 900° C., quenched in cold water, and then hammered. The specimens, in sets of three, were then annealed in the triple furnace at 604°, 600°, and 594° C., respectively, for 43 hrs., and quenched. The specimens of the alloys containing 40 and 42·5 per cent. palladium showed two phases at all temperatures, the quantity of separating phase being greater the lower the temperature and, at a given temperature, being greater in the 42·5 per cent. palladium specimen. The effect of temperature is shown in Figs. 5, 6 (Plate XIX), and of composition in Figs. 6, 7 (Plate XIX); in the latter case, the predominant phase is believed to be that separating with fall of temperature. Fig 8. (Plate XIX) shows this at a later stage of development. Two of the specimens containing 45 per cent. palladium were uniform (Fig. 9, Plate XIX) and that quenched from 594° C. showed only traces of a second phase. The limits given in Table III are based on the above results.

In order to determine what happens when the alloys are cooled to lower temperatures, specimens were quenched from 521°, 400°, and 300° C., and one set was slowly cooled to room temperature, the two last being treated in the aluminium block furnace. Figs. 13–16 (Plate XX) show the structures of the 35, 40, 45, and 50 per cent. palladium alloys quenched from 300° C. Fig. 13 shows the largest quantity of second phase seen in any 35 per cent. palladium alloy, and even here there are only traces of it. Only the 40 per cent. palladium alloy showed a uniform structure at low temperatures. In the alloys containing 45, 50, and 55 per cent. palladium the quantity of the second phase seemed to increase and then to decrease as the temperature was lowered. The greatest amount observed for each composition was at 550°, 521°, and 400° C., respectively.

The type of electrical resistance–temperature curve obtained in this range differs from that in the copper-rich alloys (Fig. 2). Curve III was obtained for the 41 per cent. palladium alloy and curve IV for the 48 per cent. palladium alloy. The characteristics of these curves are: (*a*) a steady increase of resistance over a considerable range of temperature (PQ); (*b*) a large increase of resistance over a comparatively short range of temperature (QR); (*c*) a further steady increase with a very small temperature coefficient (RS). The curve is not completely reversible on cooling. The retardation, RR', varied from 6° to 50° C. in the alloys examined, and while in some alloys the resistance then fell to, and continued along, the line QP (curve III), in others it fell only a fraction of its rise, and then smoothed out to a curve $Q'P'$ almost parallel to QP (curve IV). The temperatures of the Q, R, R', Q' points and the changes in resistance between these points are given in Table IV, together with the specific resistances at 20° C. before and after the experiments. The lower values at 20° C. and the values at 600° C. are plotted in Fig. 3, and the Q, R' points in Fig. 4.

TABLE IV.

	35% Pd.	38·5% Pd.	40% Pd.	41% Pd.	42·5% Pd.	45% Pd.	48% Pd.	50% Pd.	55% Pd.
Temperatures (° C.):									
T_Q . . .	440	582	596	588	570	531	368	472	...
T_R . . .	570	598	606	600	596	598	542	528	...
$T_{R'}$ . . .	535	592	591	594	584	570	504	480	...
$T_{Q'}$ . . .	440	580	585	588	550	490	380	408	...
Specific resistance (ohm-cm. $\times 10^{-6}$):									
ρ_{20} before . .	12·7	6·7	6·7	5·6	5·0	4·0	8·3	14·4	43·5
ρ_{20} after . .	22·9	6·7	6·7	5.6	4·8	3·7	28·2	36·1	43·8
$\rho_R - \rho_Q$ . .	11·5	18·4	18·4	20·2	21·2	24·0	26·3	17·0	...
$\rho_{R'} - \rho_{Q'}$ . .	2·5	18·5	18·6	20·2	22·4	25·8	6·2	1·5	...

The effect of continuous heating and cooling on the temperatures of the transformations was examined with the 40 and 45 per cent. palladium alloys. The results are collected in Table V, and comparison with

TABLE V.

Alloy Palladium Per Cent.	Rate of Change of Temperature ° C. per Minute.	Transformation	
		Began ° C.	Ended ° C.
40	Heating 0·3	596	607
	0·23	596	606
	Cooling 1·0	586	577
	0·03	591	585
45	Heating 0·4	557	598
	Cooling 0·4	518	...
	0·06	546	below 480

Table IV shows that the method of long-time annealing is almost essential for obtaining stable equilibrium during a transformation, especially in alloys away from 40 per cent. palladium. During the transformation of a 50 per cent. palladium alloy wire, its resistance increased from 1·033 to 1·260 ohms in the first 24 hrs. and to 1·290 ohms after a further 20 hrs., the temperature being kept constant. Annealing for only 24 hrs. thus yields a result about 3 per cent. too low, which has the effect of extending the temperature range of the transformation. Owing to the steepness of the curves in these experiments, it is unlikely that errors greater than 3° C. have been introduced as the result of insufficient annealing.

The resistance of the 55 per cent. palladium alloy increased by 1·5 per cent. on heating from room temperature to 250° C., and then remained constant to ± 0·5 per cent. up to 620° C. On cooling, the resistance was constant down to 200° C., and then decreased by 1·5 per cent. to the value at room temperature.

The low resistances of the 35, 48, and 50 per cent. palladium alloys after the preliminary anneal, in contrast to the high values after cooling slowly from above the transformation range, led to an investigation of the effects of quenching and rolling the wires. The resistances of the "as received" wires were respectively 7, 29, and 3 per cent. higher than the resistances of the slowly cooled wires given in Table IV (ρ_{20} after) for these compositions.

(a) *Rolling.*—35 and 50 per cent. palladium alloy wires in the slowly-cooled state were reduced by about a third, and their resistances were examined as before at various temperatures. There was little sign of a decrease in resistance due to the removal of the work-hardness, and the increases due to the transformation were only 14 and 5 per cent., respectively, of the increases obtained with the annealed alloys.

(b) *Quenching.*—35, 48, and 50 per cent. palladium alloy wires in the slowly-cooled state were heated to 620° C. for 1½ hrs. and quenched in cold water. The resistances were then 2–3 per cent. higher than in the "as received" condition. After treatment similar to the preliminary anneal, the resistances had decreased by amounts equal to 12, 14, and 3 per cent., respectively, of the corresponding decreases with the "as received" wires.

(c) *Quenching and Rolling.*—A length of the 48 per cent. palladium alloy wire was annealed at 615° C. for 1½ hrs., quenched, and then rolled to a 66 per cent. reduction in thickness. On annealing, the resistance fell 49 per cent., compared with 77 per cent. for the "as received" wire. It appears, therefore, that to produce a wire of low resistance requires both quenching and cold-work. It is probable that in the preparation of the alloys the cooling was comparatively fast and that the cold-work in preparing the wires was considerable, but since this treatment may not have been the ideal, it is possible that still lower values for the resistance of these alloys in the ordered arrangement may be obtained, in which case the transformations will commence at a lower temperature.

DISCUSSION OF RESULTS.

The general form of the electrical resistance–temperature curves is in agreement with the work of Borelius, Johansson, and Linde,[5] who used a rate of change of temperature of 50°–100° C. per hr., a rate which the present work has shown to be much too great for the maintenance of equilibrium conditions. As a result, they found the *B* points in the copper-rich range indefinite with T_B about 50° C. above the values given here, and the resistances below the *B* points considerably too high. Similarly in the 35–50 per cent. range the temperatures of the changes on heating were much higher than those given here. In this connection it is to be noted that the results of the present thermal investigation, obtained with a greater rate than the above, are, with one exception, in good agreement with the present electrical resistance work. Borelius, Johansson, and Linde obtained a considerably sharper transformation, but the hysteresis was much more pronounced. The resistance of their 49·8 per cent. palladium alloy decreased from the high value right down to the values on the heating curve at low temperatures, whilst in the present work only partial falls were obtained with both the 48 (by analysis 49·24) and 50 per cent. palladium alloys. Svensson [6] states that he was unable to obtain the regular arrangement of the atoms in a 49 per cent. alloy in spite of annealing it for several weeks between 700° C. and 300° C., and he considers that the 49·8 per cent. alloy, which Sedström and Johansson and Linde obtained in the ordered condition, was not completely homogeneous. The experiments with quenched and rolled wires suggest that the previous treatment may also have played a part.

The specific resistances (Fig. 3) corresponding with the ordered arrangement at 20° C. are all lower than values previously obtained, due, no doubt, to the treatment employed. In the copper-rich range the differences are not appreciable except at 30 per cent., and the present results are not in disagreement with the occurrence of the minimum specific resistance at 16–18 per cent. of palladium. Low values of the specific resistance have been obtained over a wider range of composition than before in the range 35–50 per cent. palladium, but the position of the minimum is in agreement with the work of Svensson. The specific resistance–composition curve at 600° C. shows two breaks at 32·5 and

42 per cent. of palladium, respectively, differing from the smooth curve up to 50 per cent. given by Borelius, Johansson, and Linde, and from Svensson's curve for quenched alloys, which has a point of inflection between 30 and 35 per cent. of palladium.

In the temperature-composition diagram (Fig. 4) the curve of the D points differs essentially from that of Borelius, Johansson, and Linde in placing the maximum at 22 per cent. instead of at the simple atomic ratio 3 Cu : 1 Pd. The course of the curve for the B points is tentative. In the range 35–50 per cent. palladium, only the beginnings of the transformations on heating and cooling are plotted (Q, R' points), representing the upper limit of existence of the pure body-centred cubic phase and the lower limit of the pure face-centred cubic phase, respectively, when the previous treatment of an alloy has ensured that the stable phase is alone present. The maximum near 40 per cent. palladium and the R' points above the Q points are in marked contrast to the earlier results, and emphasize the deficiencies of the method.

The composition limits of the two transformations cannot be accurately fixed by the present work. The copper-rich transformation probably begins very little below 10 per cent. and ends above 30 per cent. palladium. There is probably a region with no transformation between 30 and 35 per cent. palladium although there is at present no experimental proof available. The upper limit of the second transformation is very close to, but definitely above, 50 per cent. palladium. This indicates, as has been noted previously,[4] that the palladium atoms are unable to replace the copper atoms in the ideal body-centred cubic lattice of the CsCl type to any appreciable extent.

Theoretical Considerations.

The occurrence at 17 per cent. of palladium of the minimum specific resistance and the maximum intensity of the super-lattice lines in the X-ray photographs of slowly-cooled alloys was explained by Borelius, Johansson, and Linde in terms of the splitting up of the crystallites into small zones during the ordering of the atoms. So far as the electrical resistance is concerned, there is another explanation for the displacement of the minimum away from 25 per cent. Two opposing factors combine to determine the value of the specific resistance: the regularity of the atomic arrangement favours a low resistance; the dilation of the copper lattice by the addition of palladium atoms produces an increase of resistance. As the 600° C. isotherm (Fig 3) shows, this latter effect is very considerable—atom for atom, palladium is nearly twice as effective as gold in increasing the resistance of copper. As a result, the first factor is outweighed by the second, and, while the decrease of resistance due to the ordering of the atoms ($\rho_C - \rho_B$, Table II) is greatest at 25 per cent., the minimum resistance is displaced to the copper-rich side.

The temperature–composition diagram for the copper-rich alloys does not have the same significance as the usual equilibrium diagram, since it represents stages in a uniphase rearrangement of atoms which, even at the composition of the simple atomic ratio, takes place over a considerable range of temperature. An interpretation of the resistance–temperature curves is necessary to determine the stages associated with the *B*, *C*, and *D* points. From the X-ray work, the structure of the alloys at low temperatures is considered to be ordered in terms of the Cu_3Pd structure (p. 255). Thus the 25 per cent. palladium alloy should have the ideal arrangement; in alloys richer in copper, the excess atoms should occupy cube corners; on the other side, the excess of palladium atoms should go to the centres of the cube faces. The high-temperature arrangement is an irregular distribution of the atoms on the points of a face-centred cubic lattice. The following suggestions are based mainly on the results for the 15–25 per cent. palladium alloys. From *A* to *B* (Fig. 2, I) the resistance increases steadily with temperature as in a pure metal, due to the normal expansion of the space-lattice. At *B* the change of slope is taken to indicate that the ordered arrangement of the atoms has begun to be upset. If it be assumed that, away from the 25 per cent. palladium alloy, the ordered arrangement of the atoms consists of small groups with the Cu_3Pd structure distributed throughout the whole, then in the production of the uniform irregular distribution the local change of composition is less at 25 per cent. palladium than on the copper-rich side. The transformation should therefore be completed there more readily, *i.e.* at a lower temperature. The *C* point may thus correspond with the conclusion of the atomic redistribution. It is suggested that this process produces a distortion of the lattice, the rectification of which, taking place between *C* and *D*, causes the observed small decrease in resistance. The values of $\rho_C - \rho_D$ for the 15–25 per cent. palladium alloys indicate that the greatest distortion is at 25 per cent., and the range of temperature of the change supports this. Above *D* the normal increase of resistance is resumed.

In the case of the 10 per cent. palladium alloy, where only 40 per cent. of the atoms need be concerned in the ordering, it is conceivable that the resistance when these atoms are arranged statistically among themselves in groups is greater than when the palladium atoms are distributed uniformly at random. There is thus the possibility of a two-stage process, which would also account for the lag on cooling.

On the palladium side of the simple ratio, the conditions differ, in that the excess atoms are the larger (atomic radii :—copper 1·28 A., palladium 1·38 A.). In the ordered state, these larger atoms must go to the centre of a cube face, and thus be closer to a neighbouring palladium atom than on the copper-rich side. With the lattice spacing larger, the palladium atoms may conceivably be able to move more freely, and the change begin and end at a lower temperature: the distortion too would be correspondingly reduced.

The temperature–composition diagram may now be construed. (i) The *D* line marks the lower limit of the undistorted face-centred cubic lattice with the atoms irregularly arranged; (ii) between the *C* and *D* lines the lattice is distorted, with an irregular arrangement of atoms; (iii) between the *B* and *C* lines the diffusion of the atoms from the ordered to the irregular arrangement is taking place, accompanied by a distortion of the lattice; (iv) the *B* line marks the upper limit of the ordered face-centred cubic structure.

The hysteresis obtained in the resistance–temperature curves of the range 35–50 per cent. palladium seems to be a definite characteristic of these alloys. The loop is small in the alloys near 40 per cent. of palladium, and it is only some 50° C. wide at the limiting compositions. It is therefore possible that a modified form of under-cooling is responsible for its occurrence. The thermal and electrical resistance results with alloys near the limiting compositions indicate that the difference in energy content of alloys in the two states is small. Thus quite small factors should be able to retard the change.

SUMMARY.

1. In the range 10–30 per cent. of palladium, the electrical resistance–temperature curves for the transformation from an irregular to a regular distribution of the atoms on the points of a face-centred cubic lattice are explained on the assumption that a lattice distortion, which produces a small increase in resistance, is followed by the ordering of the atoms which causes a large diminution in resistance.

2. The highest temperature for the commencement of the first stage is about 570° C. at a composition near 22 per cent. of palladium. The corresponding figures for the second stage are 500° C. and 15 per cent.

3. The minimum specific resistance in the ordered state is $8·1 \times 10^{-6}$ ohm-cm. at 20° C. in the 15 per cent. palladium alloy. The increase due to the transformation is greatest at 25 per cent. palladium.

4. In the range 35–55 per cent. palladium, the transformation from a face-centred cubic lattice with the atoms arranged irregularly to a body-centred cubic lattice with an ordered distribution of the atoms takes place completely near 40 per cent., but only partly on cooling in alloys near the limiting compositions. The change in the latter case

can be made more complete by quenching from 600° C., cold-rolling, and then annealing at 450° C.

5. In no case has the transformation been found to take place at constant temperature, the range being smallest and the temperature highest at 40 per cent. palladium.

6. The specific resistance in the ordered state is a minimum at 47 per cent. of palladium ($3{\cdot}1 \times 10^{-6}$ ohm-cm. at 20° C.).

7. There are two breaks in the specific resistance–composition curve for the irregular arrangement of the atoms, at 32·5 and 42 per cent. palladium, respectively.

ACKNOWLEDGMENTS.

The author wishes to express his thanks to Messrs. the Mond Nickel Company, Ltd., for a grant which enabled this work to be started, and to the Department of Scientific and Industrial Research for a grant which enabled it to be continued for a second year. The alloys were made and analyzed at the Acton Refinery and Research Laboratory of Messrs. the Mond Nickel Company, Ltd., and much valuable assistance was obtained from the Acton staff, in particular from Major C. Johnson, M.B.E., M.A., Captain R. H. Atkinson, M.A., and Mr. A. R. Raper, M.A. The author also wishes to thank Dr. D. Stockdale, M.A., for his advice and encouragement.

REFERENCES.

[1] E. Sedström, Dissertation. Stockholm : **1924.**
[2] S. Holgersson and E. Sedström, *Ann. Physik*, 1924, [iv], **75**, 143.
[3] C. H. Johansson and J. O. Linde, *Ann. Physik*, 1925, [iv], **78**, 439.
[4] C. H. Johansson and J. O. Linde, *Ann. Physik*, 1927, [iv], **82**, 449.
[5] G. Borelius, C. H. Johansson, and J. O. Linde, *Ann. Physik*, 1928, [iv], **86**, 291.
[6] B. Svensson, *Ann. Physik*, 1932, [v], **14**, 699.
[7] J. O. Linde, *Ann. Physik*, 1932, [v], **15**, 249.
[8] H. F. Seemann, *Z. Metallkunde*, 1932, **24**, 299.
[9] D. Stockdale, *J. Inst. Metals*, 1932, **49**, 276.

THE GOLDSMITHS' LABORATORY,
THE UNIVERSITY OF CAMBRIDGE.
September 1933.

DISCUSSION.

DR. J. L. HAUGHTON * (Member of Council): With regard to the method of measuring electrical resistivity, I am not quite sure that I have the idea right, but if I have I think that it is slightly open to criticism. If I understand it correctly, the arrangement is as follows: a spiral of the alloy approximately 45 cm. long is welded to a copper lead approximately 33 cm. long. To this is fastened a small tungsten wire, roughly 8 cm. long, to which the copper

---

* Principal Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory.

leads are attached. In series with this is a standard resistance, an accumulator, and a swamping resistance. The voltage drop across the standard is compared with the voltage drop across the system composed of the copper and tungsten wires and the specimen. Then an exactly similar arrangement, except that there is only 10 cm. of alloy, is used to find the resistance of the leads.

It seems to me that in that case very accurate measurements of the lengths of the wires are required, and it is necessary to be quite sure that all the leads up to the specimen are exactly the same. Would it not have been possible, without introducing any excessive complication, to bring the potential contacts in to the end of the specimen? It would need another pair of copper–tungsten–copper wires going through the glass. In that case only the resistance of the specimen itself would be measured. Whether the complication of the extra pair of leads in each of the specimens would have been too great, and whether it would be worth it or not—because it is possible that the method used is sufficiently accurate—I do not know, but personally I should be very frightened of errors that might be introduced by the compensating arrangement.

The AUTHOR (*in reply*): It would have been more complicated to have these extra leads. With only 2 leads I was able to use a tube that was less than 1 cm. in diameter and to get 12 such tubes into my furnace at once. The actual values of the resistance may not be accurate, but the main inaccuracy came in measuring the diameters of the wires; the errors there were greater than the errors brought in elsewhere. As the main object was to determine the temperatures of the change, my method was sufficiently accurate.

ALLOYS OF MAGNESIUM RESEARCH. PART I.—THE CONSTITUTION OF THE MAGNESIUM-RICH ALLOYS OF MAGNESIUM AND NICKEL.*

By JOHN L. HAUGHTON,† D.Sc., MEMBER OF COUNCIL, and RONALD J. M. PAYNE,‡ B.Sc., MEMBER.

SYNOPSIS.

The constitution of magnesium alloys containing up to 50 per cent. nickel has been studied by thermal and microscopic methods. Magnesium forms a eutectic with the compound Mg_2Ni at a temperature of 508° C. and a composition of 23·5 per cent. nickel. The solubility of nickel in solid magnesium is less than 0·1 per cent.

I.—INTRODUCTION.

THIS paper describes the results of the first part of a research on the constitution and properties of alloys of magnesium which is being carried out in the Metallurgical Department of the National Physical Laboratory under the general supervision of Dr. C. H. Desch, F.R.S. The research is being conducted in a manner similar to those on alloys of iron and alloys of aluminium which have been proceeding for many years in this Laboratory.

The work is being carried out under the auspices of the Alloys Sub-Committee of the Aeronautical Research Committee, with the object of improving alloys of magnesium for use in aircraft, and the study of the constitution of the alloys is being undertaken simultaneously with the investigation of their mechanical properties.

II.—PREVIOUS WORK.

A comprehensive study of the constitution of the alloys of nickel and magnesium was made by Voss § in 1908. A part of the diagram he

---

* Manuscript received November 9, 1933. Presented at the Annual General Meeting, March 8, 1934.

† Principal Scientific Officer, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

‡ Assistant III, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

§ *Z. anorg. Chem.*, 1908, 57, 61.

obtained is given in Fig. 1. Some of his thermal curves, however, were obtained from alloys contained in silica vessels, and, as was admitted, the attack of the alloy on the crucible was severe, and must have resulted in very serious contamination of the melt and alteration in its composition.

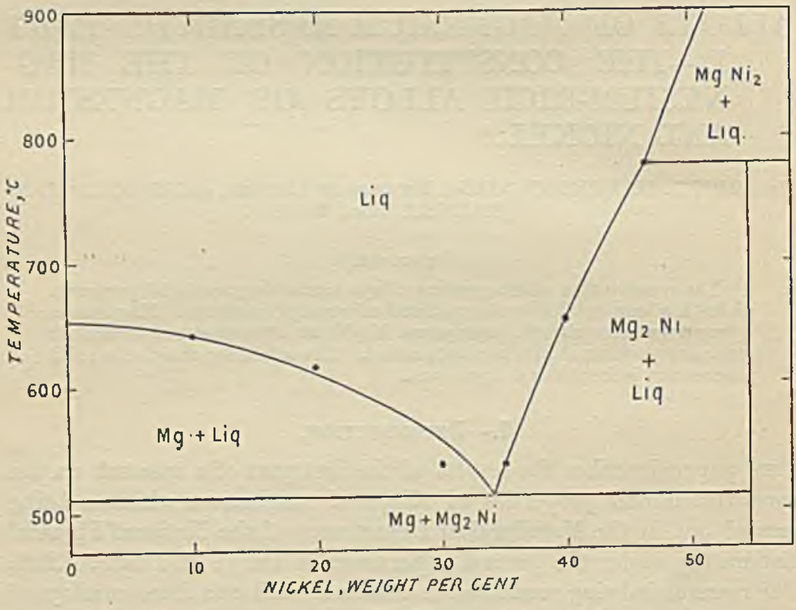


FIG. 1.

III.—PRESENT WORK.

The primary object of the present work was the study of the constitution of alloys of magnesium with small quantities of nickel, mainly in order to determine whether they were likely to exhibit age-hardening properties. For completeness, however, the investigation has been carried to the limit of existence of the α-phase, namely, up to about 55 per cent. nickel.

Materials Used.

For the greater part of the research, commercial magnesium of about 99·93 per cent. purity was employed. A representative analysis of the several batches from which supplies were taken is as follows:

	Per Cent.
Iron	0·043
Aluminium	0·021
Copper	0·008
Magnesium (by difference)	99·928
	100·000

The nickel used was specially supplied by The Mond Nickel Company, Ltd., and contained:

	Per Cent.
Copper	0·008
Iron	0·028
Carbon	0·011
Silicon	0·004
Nickel	99·949
	100·000

For making up the alloys used for determining the solubility limit, specially pure magnesium was employed. This was prepared from the commercially pure material by a three-fold sublimation at a temperature of about 580° C. under a pressure of 0·01 mm. of mercury. Chemical analysis showed that it contained about 99·97 per cent. magnesium (obtained by difference), and the spectroscope indicated that the impurities had to a great extent been removed. Sublimation appears to remove iron more effectively than it removes copper.

Preparation of the Alloys.

Two high-nickel alloys, containing about 22 per cent. and 47 per cent. nickel, respectively, were prepared by dissolving nickel in magnesium in an iron crucible under a flux. The alloy containing 47 per cent. nickel requires a temperature of about 900° C. and a long time to dissolve.

These basis alloys were employed in making up all the other melts (except those for solubility determinations), an iron crucible and a flux again being used. The flux first employed contained:

Sodium fluoride	30 grm.
Calcium fluoride	20 ,,
Potassium chloride	160 ,,
Magnesium chloride	450 ,,

This flux, which is very mobile when molten, but which tends to seek the sides of the crucible, is suitable for the low-melting point alloys, but the commercial flux "Elrasal," which forms a protective layer over the surface of the metal, is preferable for use with alloys of high melting point.

Thermal Analysis.

The thermal analysis of magnesium-rich alloys presents some difficulties. With such a reactive material as magnesium it is almost imperative that a liquid flux be used if oxidation of the metal is to be avoided completely, and a liquid flux, in turn, necessitates the employment of a metal crucible, such refractory crucibles as are resistant to the attack of magnesium being usually porous and absorbing the flux. A thin-walled crucible of mild steel is satisfactory except that it scales at high temperatures. Crucibles of stainless iron were found to be slightly superior in this respect, and were used for this research. No serious contamination of the contents resulted from the use of such a crucible until the nickel content exceeded 25 per cent., and then only when the temperature was raised above about 800° C.

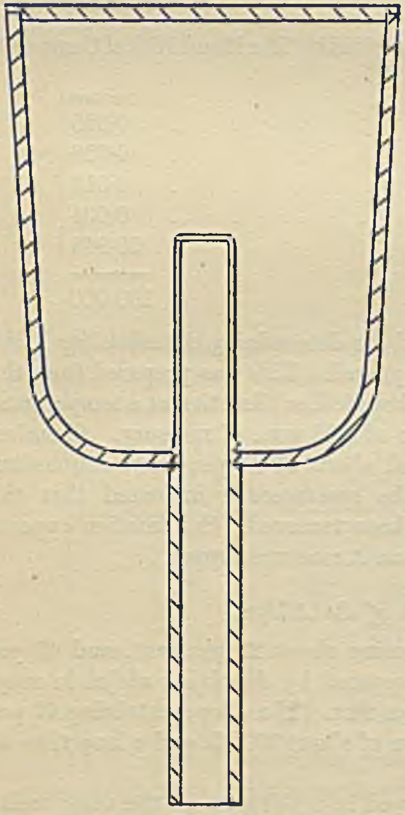


Fig. 2.

The design of the crucible requires a little consideration. The marked tendency of the flux to creep out of the crucible, and its volatile nature and electrically-conducting properties, made efficient shielding of the thermocouple essential. Fig. 2 shows the form of crucible found to be most satisfactory. The crucible itself is a stainless iron pressing, with a close-fitting stainless iron lid. The couple protector, the end of which is closed by welding, is made from stainless iron tube and is screwed into the bottom of the crucible. The thermocouple is placed in a "Pythagoras" tube which fits the metal protecting tube fairly closely. A platinum/platinum-rhodium couple is used for the temperature measurement.

The thermal analysis of alloys rich in magnesium was carried out in a gradient furnace * arrangement in which the furnace moves past the specimen; with this the thermocouple does not pass through the hottest part of the furnace tube, and, further, it is shielded to some extent by the tube supporting the crucible.

(a) *Melting Point of Pure Magnesium.*

Some doubt appears to exist as to the actual melting point of pure magnesium: the accepted figure is 651° C., but competent workers have obtained values varying between 647° and 652° C. A quantity of the specially purified metal was therefore melted in a crucible of the kind just described and its melting and freezing points were very carefully determined, using a couple which was calibrated in the Metallurgy Department before the curves were taken, and checked afterwards in the Heat Department of the Laboratory against the melting point of specially purified antimony. From this work it can be stated that the melting point of pure magnesium is 649° C. ± 0·5° C.

(b) *Alloys Containing Less than* 45 *Per Cent. Nickel.*

Difficulties were early encountered when a systematic attempt was made to determine the liquidus of the system. Starting from pure magnesium, the melting point was found to be progressively depressed by the addition of nickel, but the arrest point was also found quickly to become ill-defined, and by the time 20 per cent. nickel had been added it had become so small and indefinite as to be very doubtful, or even non-existent. An attempt was then made to work back across the diagram from the neighbourhood of the compound Mg_2Ni; here again it was found that the more the alloy differed in composition from that of the compound the more diffuse the liquidus halt became. Only the smallest indication of an arrest point was obtained with the alloy containing 35 per cent. nickel, whilst those with a composition between 20 and 35 per cent. nickel showed only the eutectic halt. The diffuseness or absence of the arrest at once suggested inhomogeneity of the specimen. (With all alloys the eutectic arrest was found to be very well defined and to occur at sensibly the same temperature.)

On two cooling curves, obtained from alloys containing 31·2 and 33·3 per cent. nickel, well marked but small arrests were found at temperatures of 745° and 738° C., respectively; they were also found on heating at 754° and 752° C. This would seem to suggest the presence of a hump between the two branches of the liquidus already established,

---

* J. L. Haughton, "Appareil pour l'analyse thermique des échantillons métalliques." Treizième Congrès de Chimie Industrielle, Lille, 1933, Sept.

but this suggestion was not borne out by the microstructure, which was that of a simple eutectiferous series right across the diagram.

In order to determine whether the liquidus did, in fact, attain a maximum at some point between 20 and 35 per cent. nickel, an alloy containing 31·2 per cent. nickel was melted in a mild steel pot and a steel stopper was forced in. The crucible and contents were then annealed at various pre-determined temperatures and quenched in water. Care was taken in quenching not to disturb the metal in the pot. A vertical section of the crucible and contents was then made, and the face polished and etched. It was hoped to detect whether the alloy had been wholly or partly liquid at the temperature of quenching by examining the section for the presence of large and possibly segregated crystals of a primary separation. No conclusive results were obtained from these experiments, although annealings were conducted at temperatures between 530° and 900° C.; *all* specimens on quenching showed segregation of primary crystals. The segregation, especially that occurring on annealing at the lower temperatures, was very marked, and confirmed the authors' belief that the absence of liquidus arrests might be due to this cause.

Further samples of the same alloy (31·2 per cent. nickel) were next poured into a thin, wedge-shaped copper mould immersed in a freezing mixture of ice and salt. It was found on sectioning the wedge that the tip always possessed a very fine structure when pouring was carried out above 650° C.; this indicated that the alloy was completely molten above this temperature.

Thermal curves were then taken on some of the same alloy in the same stainless iron crucible, but with an iron stirring rod introduced through a hole in the lid. After melting, the alloy was stirred continuously while a cooling curve was taken almost down to the eutectic temperature, and a well-defined liquidus arrest was obtained; the arrest was also reproduced on heating. The remainder of the alloys between 20 and 35 per cent. nickel were then treated similarly, and repeat curves were obtained for alloys which yielded ill-defined points when not stirred. The liquidus thus obtained is shown in Fig. 3.

With alloys containing more than about 40 per cent. nickel the method of stirring with an iron rod was not very satisfactory, as metal sticking to the rod caught fire when it was carried through the hole in the lid of the crucible, and not only was the composition of the alloy altered, but the stirring rod tended to jam in the hole. A piece of apparatus was therefore made up in which the tendency to segregate was greatly reduced by continuously rotating the specimen about a horizontal axis while observations for heating and cooling curves were being made. The method was used by Bingham and Haughton when studying the copper–nickel–aluminium alloys.* In the present form of the apparatus the thermocouple and its sheath rotate with the crucible, instead of being stationary, as in the earlier form. The much closer fit of the couple sheath in the crucible which can be thus obtained will tend to keep small the thermal lag between alloy and couple. A further improvement consists in the introduction into the crucible of a scoop, which further checks segregation. The apparatus has been described in detail by one of the authors elsewhere.†

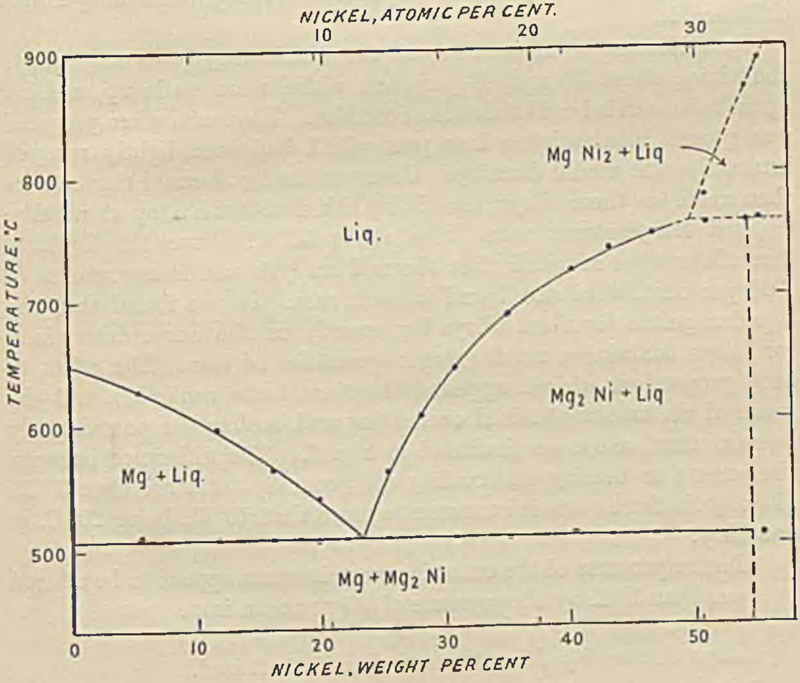


FIG. 3.

At this stage of the work it was found that in alloys containing more than 25 per cent. nickel some iron had been dissolved from the crucible. All these alloys had been taken to a high temperature, of the order of 900° C., in the earlier attempt to determine the liquidus, and some of them had been heated and cooled under these conditions many times. It was not surprising, therefore, to find that they had an iron content increasing from less than 0·2 per cent. iron when about 30 per cent.

---

* K. E. Bingham and J. L. Haughton, *J. Inst. Metals*, 1923, **29**, 71.

† R. J. M. Payne, *J. Sci. Instruments*, 1934, **11**, 90.

nickel was present, to almost 0·5 per cent. iron when the alloy contained 45 per cent. nickel. It was proposed, therefore, to redetermine the liquidus from 25 per cent. nickel upwards, taking the utmost precaution to avoid contamination. As a starting point, a fresh stock alloy was made up. The melting together of the nickel and magnesium was carried out with difficulty in a hard alumina crucible. Large amounts of flux were added continuously to make up for losses by absorption by the crucible. The alloy was then poured (burning meanwhile) into a chill mould.

By additions of magnesium to the stock alloy, two new alloys containing about 30 and 40 per cent. nickel were made up, melting again being carried out in alumina crucibles. The metal when prepared was poured into stainless iron pots which had been lightly sprayed internally with mould dressing. Observations for thermal curves were then made on these alloys, care being taken that the alloy at no time reached temperatures more than about 30° C. above the liquidus. The alloys were sampled after thermal analysis and iron contents of 0·08 per cent. were also found in each case. It was found that the liquidus points for these alloys lay exactly on the curve determined for alloys containing much greater quantities of iron. The effect of such proportions of iron appears, therefore, to be negligible, and the mean of the arrests obtained on heating and cooling for considerably contaminated alloys are included in Fig. 3. The difference between the arrests on heating and cooling was generally not more than 5° C., although in three cases it increased to more than 10° C., being 20° C. in one alloy.

The temperature of the eutectic arrest does not appear to be altered by more than 1° C. by the presence of 0·5 per cent. iron.

(c) *Alloys Containing More than* 45 *Per Cent. Nickel.*

Four alloys containing 47, 51·3, 54·7, and 55·5 per cent. nickel were examined in this area. Thermal curves of the two alloys with 51·3 and 54·7 per cent. nickel were first taken without stirring, and showed only one arrest above the eutectic temperature (the peritectic arrest). On stirring, however, all alloys showed a liquidus point in addition to the peritectic. Owing to the high temperature to which the alloys had to be taken, it was impossible to avoid contamination with iron, the amounts present being 0·49, 0·52, 1·27, and 1·34 per cent., respectively. For this reason the diagram has been shown dotted in this area, although, in view of the negligible effect of iron on the rest of the diagram, it is unlikely that any serious error is introduced by its presence here.

Solid Solubility of Nickel in Magnesium.

An alloy containing 1 per cent. nickel was first made up by dissolving pure nickel foil in sublimed magnesium, which was carefully melted under flux in a stainless steel crucible. Alloys containing less nickel were prepared by additions of magnesium. Samples of the alloys were then annealed at various temperatures. For this treatment the samples were wrapped in thin sheet iron (to prevent contact between alloy and tube) and sealed *in vacuo* in a " Pyrex " glass tube. At the end of the annealing the tube was broken under water and the sample examined microscopically. It was found that even at 500° C. the solid solubility of nickel in magnesium is less than 0·1 per cent. nickel.*

Microstructure.

The structure of all the alloys was found to be normal, except that, even after prolonged annealing, alloys the compositions of which fall within the peritectic range showed the presence of three phases (Mg, Mg_2Ni, $MgNi_2$), owing to the formation of a sheath round the primary crystals and to slow diffusion.

CONCLUSIONS.

Magnesium and Mg_2Ni form a simple eutectiferous system with practically no solid solubility. The eutectic temperature is 508° C., which agrees very well with the figure obtained by Voss (512° C.), who found the eutectic composition to be at 33 per cent. nickel, whilst the present authors show it to be at 23·5 per cent. nickel. In view of the very great contamination of Voss's alloys, the agreement in eutectic temperature is remarkable. The presence of a few tenths of 1 per cent. of iron seems to have little or no effect on the constitution of the series.

ACKNOWLEDGMENTS.

The authors wish to express their thanks to Dr. W. Rosenhain, F.Inst.Met., F.R.S., under whom the work was started, and to his successor, Dr. C. H. Desch, F.R.S. They also are indebted to Messrs. W. H. Withey and P. Ward for carrying out the analysis of the alloys and to The Mond Nickel Company, Ltd., and the British Maxium Company for supplying the nickel and magnesium, respectively, used in the research.

---

* J. A. Gann (*Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, **1929**, 309) has shown that a large amount of free Mg_2Ni is present in an annealed alloy containing 0·25 per cent. nickel.

CORRESPONDENCE.

The Authors: In a private discussion, Dr. Rosenhain suggested that it would be worth while carrying out some age-hardening experiments on the magnesium–nickel alloys, as it was often possible to determine sloping solubility lines by this method, even when the solubility was too small to be readily established by micrographic methods. We intended to act on this suggestion until we found that Gann * had already shown that in the alloys he had investigated there was no sign of age-hardening, and, whilst his alloys were not quite so pure as ours, it did not seem worth while to repeat his experiments.

---

* J. A. Gann, *loc. cit.*

ANNUAL MAY LECTURE.

At a General Meeting of the Institute held in the Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, London, S.W.1, on the evening of Wednesday, May 9, 1934, Dr. Harold Moore, C.B.E., President, in the Chair, Professor E. K. Rideal, F.R.S., delivered the Twenty-Fourth May Lecture (see pp. 287–312).

The Chairman proposed, Professor D. Hanson, D.Sc., seconded, and there was carried with acclamation, a hearty vote of thanks to Professor Rideal for his lecture.

The Minutes of the Annual General Meeting, held in London on March 7 and 8, 1934, 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 5 and May 9, 1934.

Members Elected on April 5, 1934.

Bain, H. Foster, Ph.D.	New York City, U.S.A.
Hauser, Alexander	Wien, Austria.
Hayes, Joseph	Stoke-on-Trent.
Hoblyn, Edward Henry Treffry, Ph.D., D.I.C., A.R.C.S.	Luton.
Hoesen, Henry B. Van, Ph.D., A.B., A.M.	Providence, R.I., U.S.A.
Lodder, Leslie Arthur John, B.Sc., A.R.C.S.	Avonmouth.
Savage, Herbert	Isleworth.
Schneider, William George, E.M., B.S.	New York City, U.S.A.
Wood, Ernest, Assoc.Met.	Bristol.

Student Members Elected on April 5, 1934.

Buckley, Frank, B.Sc.	Rugby.
Chard, John Edwin	Beckenham.
Gegg, Christopher Coghlan	London.
Hallowes, Arthur Patrick Collis	Leek.
Harris, Jacob Henry	London.
Hopkin, Norman Maynard	London.
Hora, John Marcel Raymond	Hove.
Keeble, Hubert William	Stockport.
MacGregor, Ian Kinloch	Glasgow.
McIntosh, Alexander Benjamin	Glasgow.

Members Elected on May 9, 1934.

Bews, William James Linklater	Antwerp, Belgium.
d'Auvigny, Henry Antoine	Paris, France.
Davies, Ernest Allen, M.C.	Whaley Bridge.
Jacques, Frank	Manchester.
Kirsebom, Gustaf Newton, M.A.	Bristol.
Rice-Oxley, Francis Bowyer, B.A.	London.
Sanders, Alexander	Avonmouth.
Welsh, William Cameron, B.Sc., A.R.S.M.	Eaglescliffe.
Zwanzig, Walter, Dr.-Ing.	London.

Student Members Elected on May 9, 1934.

Armstrong, Denys George	Bedford.
Ashby, Cyril Lawrence George, B.Sc.	London.
Bradley, Alan Ludwig	Sheffield.
Forrest, George Kenneth	Birmingham.
Readman, John Abercromby	Lockerbie.
Sallitt, Lieut. William Baines, B.A.	London.
Whitworth-Jones, Henry Lewis	London.

MAY LECTURE, 1934.

GASES AND METAL SURFACES.

By Professor E. K. RIDEAL,* M.B.E., D.Sc., Ph.D., M.A., F.R.S.

TWENTY-FOURTH MAY LECTURE TO THE INSTITUTE OF METALS, DELIVERED MAY 9, 1934.

Synopsis.

Attention is directed to the complex nature of the surface structure of a metal and the influence of the structure on the equilibria and the rate of attainment of equilibrium of a metal with a gas. Various types of adsorption processes are shown to exist and a differentiation is made between van der Waals' adsorption and chemi-adsorption where an electron switch has taken place. The existence of an energy of activation in the latter type of adsorption may give rise to the slow process of activated adsorption. The formation of bimolecular layers is shown to be of frequent occurrence and the phenomenon of two-dimensional mobility is discussed. It is shown that a high surface mobility in the second adsorbed layer plays an important part in the dynamics of the formation of the surface phase.

Different types of surface layers are shown to exist which may be compared to three-dimensional phases; the experimental methods for observing two-dimensional phase changes are reviewed. The evidence for the existence of an internal surface existing between the crystallites of the metal is considered, and it is demonstrated that such a surface plays an important part in adsorption processes. The differences between the internal surface and the uniform bulk lattice are discussed, and it is made clear that the heats of adsorption and energies of activated migration on the internal surface are quite distinct from the heats of formation of compounds and energies of activated solution in the lattice. The experimental evidence in the case of copper for the gases hydrogen and oxygen is briefly reviewed. The properties of surface compounds and the effect of metallic dispersion and lattice spacing are discussed.

When your Council honoured me by extending an invitation to deliver this May lecture I was doubtful whether I had anything to say which might be of interest or of utility to the members of the Institute of Metals.

As you are aware, the attention which has been devoted to the interaction of metals with gases by a number of physicists and chemists arises chiefly by reason of the remarkable properties exhibited by some metals of effecting a catalytic acceleration of many gaseous reactions.

---

* Professor of Colloid Science, Cambridge University.

From the point of view of the metallurgist these are all low-temperature reactions, and I thought at first might be of little interest to you, but I note that no less than four metallurgical bodies—the British Non-Ferrous Metals Research Association, the Metallurgy Research Board, the Iron and Steel Institute, and the National Physical Laboratory—are devoting no little part of their interest to the problems connected with gas unsoundness in metals, the effects of gases in cast iron, steel, aluminium, copper, nickel, and zinc. By studying the processes at work in the interaction of gases and metals at relatively low temperatures, some insight may be obtained into the factors operative at high temperatures.

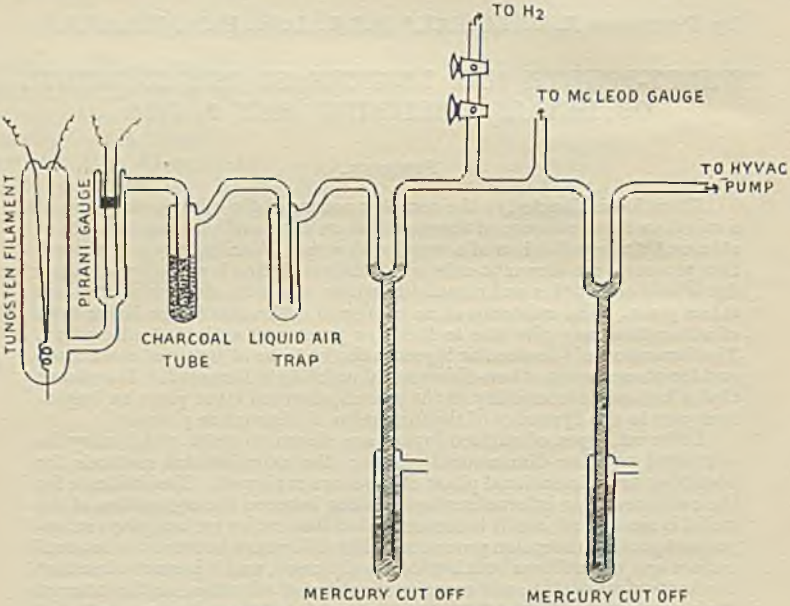
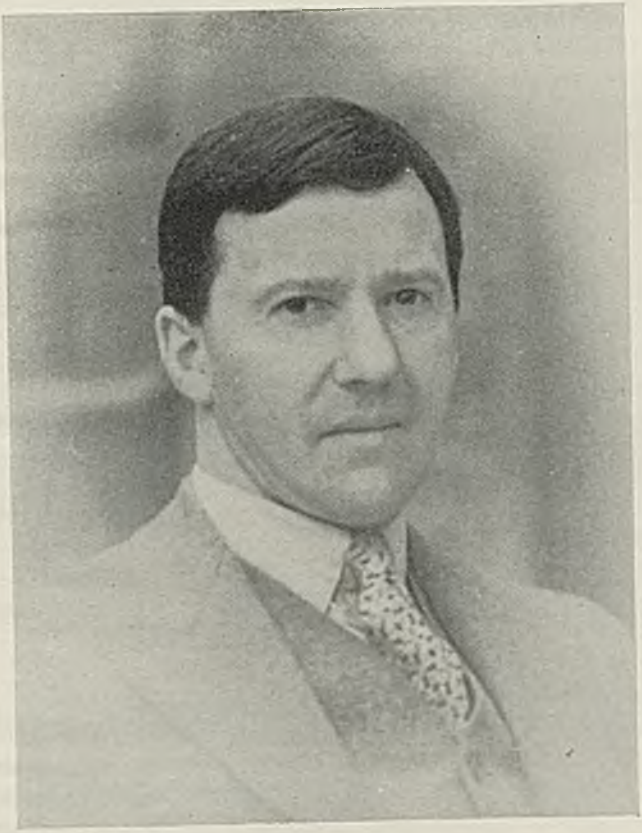


Fig. 1.

The physico-chemical study of the adsorption of gases by metals has during the last quarter of a century been pursued by two entirely different methods of attack. In one, the interaction of the gas and metal is studied when the latter is in the form of a filament, a method particularly suitable for studying systems in which the gases attack the metal and form volatile products, or in conjunction with suitable physical methods of investigation for those systems in which a surface film is formed. We are indebted to Irving Langmuir * for the elabora-

---

* Langmuir, *J. Amer. Chem. Soc.*, 1912, 34, 1310; 1913, 35, 105, 931; 1919, 41, 167.



PROFESSOR E. K. RIDEAL, M.B.E., D.Sc., Ph.D., M.A., F.R.S.
May Lecturer, 1934.

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

[*To face p.* 288.

tion of this elegant method, and it is somewhat surprising that, apart from research laboratories connected with the electric-lamp industry, more general application of the method has not been made.

The other and more usual method of investigation employs the metal in a form more akin to that in catalytic industrial use as granules up to 1–2 mm. in diameter, and prepared in as porous or spongy a state as is compatible with strength. Since the specific surface of the metal available for examination by this method is relatively large, the method lends itself particularly well to the study of the adsorption of gases by metals, although even with the filament or hairpin technique micro methods are frequently applicable. The chief disadvantage of this method lies in the extreme difficulty of removing all the gas from the system.

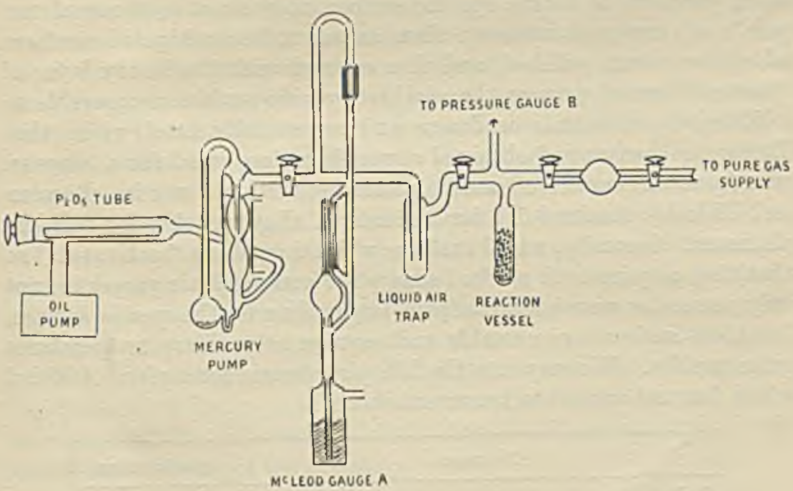


Fig. 2.

Figs. 1 and 2 show the general experimental arrangements for the two methods in their most primitive forms.

The Surface Structure.

In considering the general problem of the adsorption of gases by metallic surfaces, it is evidently important to know what the exact configuration of a metallic surface is like. Since no surfaces are optically smooth, the actual area must always be greater than the apparent macro-geometrical area, thus introducing the concept of specific surface as a ratio of true to apparent areas. It is clear that the evaluation of the true area of a surface will depend on the yard-stick employed for such measurement, and it has been found customary to employ molecular yard-sticks for the purpose in the form of the determination of the molecular area multiplied by the number of molecules required to form a closely packed unimolecular layer on a macro-geometrical square centimetre of surface; or, alternatively, by a comparison of the relative number of molecules adsorbed on or dissolved off in unit time a square centimetre of the surface under investigation with the numbers obtained under identical conditions for what is considered to be a plane surface. Chemical, electrical, electrolytic, and optical methods have been devised for this purpose. Whilst no one of these methods can give us an exact value for the specific surface, they do at least reveal two points of very great interest: first, as was to be anticipated, surfaces which have been polished, and thus covered with the Beilby layer of "flowed" metal, possess the smallest specific surface, comparable to solidified liquid metals or drawn and superficially fused wires, thus Taylor and Langmuir * obtained a specific surface of 1·3 for a tungsten wire from the number of cæsium atoms required to cover it. Bowden and Rideal † obtained 1·4 for a solidified alloy and 2·1 for polished platinum. Secondly, metal surfaces which have been "activated" so that they acquire both marked adsorptive and catalytic properties not only possess, as we might anticipate, large values for the specific surface, but these surfaces are unstable and contract at ordinary temperatures quite rapidly. We may cite the following figures for a piece of nickel which has undergone the treatment shown:

Treatment.	Specific Surface.
Rolled	3·5
Do. annealed	7·7
Do. sand papered	9·7
Freshly "activated" by oxidation and reduction	46
Do. 24 hrs. old	29

Whilst great adsorptive powers and high catalytic activity are clearly related to the extent of the specific surface, it is evidently desirable to learn more about the microtexture of the surface and its relationship to both the adsorption process and the chemical reactivity. Examination both by means of X-rays and by the diffraction of electrons are now widely employed for this purpose, and a great deal of valuable information has been obtained concerning the mean grain-size and structure of the micro-crystals present in, and near, the surface layer. The process of "activation" undoubtedly causes the surface to break up, the macro-

---

* *Phys. Rev.*, 1933, [ii], 44, 423–458.

† *Proc. Roy. Soc.*, 1928, [A], 120, 63.

crystals disappear, and the micro-crystals become smaller and smaller, until practically no traces of a regular arrangement of atoms are revealed by the method. The reverse process of sintering, the stage of collapse which merges into the ordinary process of annealing and grain-growth, is likewise readily demonstrated, and what is well known in the case of annealing, *viz.* the phenomenon of retarded grain-growth by suitable impurities which coat the grains and hinder the process of atomic diffusion of the metal, is noted also in the preliminary stages of sintering. The effect of potassium oxide and alumina forming spinels with iron oxide in retarding grain-growth in iron formed by reduction of the oxide, serves as an example of the technical application of the principle of endowing an active and unstable surface with a longer life.

Fissures exist in between the regular crystalline grains, containing irregularly placed aggregates of atoms and surface layers of atoms contracted by the surface tension (until recently termed the intercrystalline cement), and whether or no the case for the existence of the subcrystalline mosaic structure postulated by Smekal,[*] Lennard-Jones and Dent,[†] and Zwicky [‡] is regarded as fully established as yet, it is evident that the majority of metallic surfaces must present to the exterior the facets and edges of crystals both small and large, in which the atoms are set in regular array, and intercrystalline channels and cracks which are more porous to gases than the crystals themselves.

This irregularity in the nature of the surface has an important bearing on such factors as solution into the metal from the surface phase, migration of the adsorbed molecules across the surface, and on the chemical reactivity of the surface.

TYPES OF SURFACE COMPLEX. VAN DER WAALS' ADSORPTION.

It may be worth while to study the various possibilities which present themselves when a metal surface is exposed to a gas. At one time it was considered most probable that molecules impinging on the metal surface would remain there for a short period, and after a finite lifetime on the surface "the molecular *verweilzeit*" would re-evaporate. As a result of this a dynamic equilibrium between condensation on, and re-evaporation from, the surface ensues, and the surface attains an equilibrium when partly covered with gas—the adsorbed phase. This picture of the process of formation of the adsorbed phase we now know is not correct, for in point of fact some molecules are specularily reflected, especially those impinging on the surface at small angles.[§]

---

[*] *Physikal. Z.*, 1925, **26**, 700; 1927, **45**, 869.

[†] *Proc. Roy. Soc.*, 1928, [A], **121**, 247. [‡] *Proc. Nat. Acad. Sci.*, 1929, **15**, 253.

[§] Stern, *Z. Physik*, 1930, **61**, 95; Johnson, *J. Franklin Inst.*, 1930, **210**, 145.

We may picture the molecule undergoing adsorption as entering the attractive field of the surface, and due to the influence of the attractive field of the molecule and its mirror image, which here represent the so-called van der Waals' forces, it is drawn inwards until it encounters the repulsive fields; diagrammatically the molecule may be regarded as lying at the bottom of a potential valley oscillating about a mean distance from the surface (Fig. 3).

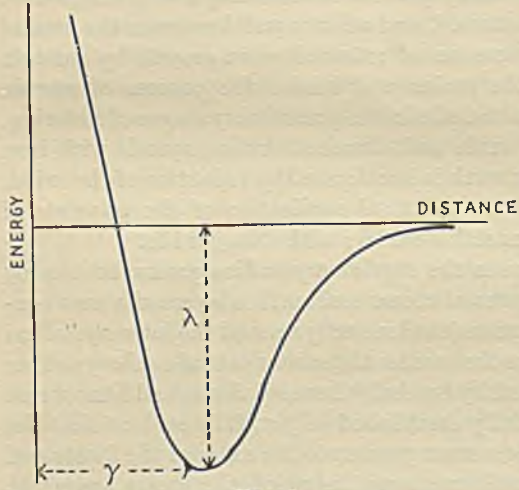


Fig. 3.

For simple molecules the attractive field outside a metal may, as shown by Lennard-Jones,* be taken as proportional to the magnetic susceptibility of the molecule. We may note in passing that the process of evaporation requires the supply of a definite amount of energy λ.

Chemi-Adsorption.

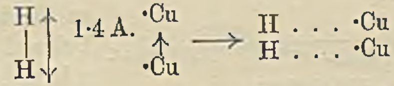
So far we have considered the case of molecules attracted and held by what are generally termed physical or van der Waals' attractive forces dependent on the mutual polarizability of the molecules. On the other hand, under suitable circumstances an electronic switch occurs, and a chemical reaction takes place between the adsorbed molecule and one or more molecules of the substrate forming a chemi-adsorbed complex. It is customary to consider chemical compounds as belonging to one or other of two extreme types; one where the stability of the compound is due to the operation of coulomb forces between ions, and the other, where a bond or a valency force in the form of a pair of electrons is shared between the two atoms in a binary compound. We know, in fact, that these two classes are not really quite distinct, in that a transition from one to the other can be effected. As examples of these various types of adsorption complexes we may cite the rare gases on mica, and perhaps on tungsten, for a typical van der Waals' adsorption, cæsium on tungsten for adhesion by means of coulombic

* *Trans. Faraday Soc.*, 1932, 28, 336.

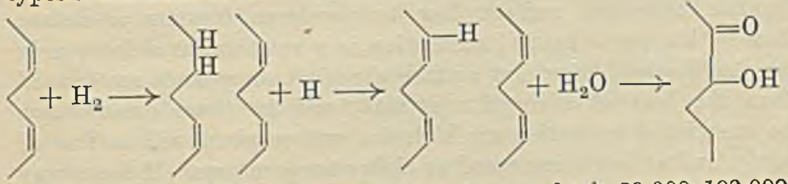
forces between ions, and oxygen on tungsten as typical of a covalent compound.

In some cases it is evidently possible to obtain more than one surface chemical combination between the gas and the substrate. We must now inquire how we can determine whether a molecule is held to the substrate by van der Waals' forces or by chemical reaction. We may note from a comparison of the relatively small latent heats of vaporization of liquids in which the molecular adhesion is due entirely to the mutual polarization of the molecules, with the relatively large values for the energies necessary to decompose chemical compounds or to break bonds, that the heats of adsorption may be used as a criterion for a distinction between the two types.

It does not necessarily follow that the total calorimetric heat of adsorption in chemi-adsorption should be high; thus the calorimetric heat of chemi-adsorption of a diatomic gas on a metal surface may be relatively small if surface dissociation into atoms occurs on the surface. It is possible that such is the case of, say, hydrogen on copper which might be depicted as



As an example of a different type we may take the chemi-adsorption of hydrogen and of water by active charcoal. X-ray examination reveals the fact that active charcoal consists of minute graphite-like plates somewhat more separated from each other (3·6 A.) than in natural graphite. The chemi-adsorption process apparently goes on round the edges of the plates, and we can describe pictorially the three simplest types of reactions as follows:



Taking the usually accepted heats of linkage, we obtain 39,000, 102,000, and 16,000 cal./grm.-mol. as the heats of formation of the three surface compounds.

Furthermore, if charcoals containing these compounds are heated in a vacuum of $P = 10^{-6}$ mm. appreciable decomposition will occur* when $\frac{\sqrt{2\pi mkT}}{P\sigma_0\tau_0} e^{-\frac{U}{kT}} \sim 1$. Spectroscopically we obtain the values of $\tau_0 = \frac{1}{\nu}$

---

* Frenkel, *Z. Physik*, 1929, **26**, 117.

the wave number, and can thus evaluate T_0°. These are found to be 300° C., 1200° C., and 0° C., respectively.

ACTIVATED ADSORPTION.

Chemical reactions in general both in gases and in liquids do not take place at every molecular collision; only a certain number are fruitful, and it is assumed that, in addition to a suitable orientation called the steric factor, a definite energy of activation is necessary. We should thus anticipate an energy of activation as necessary for the formation of the surface compound, which we can denote by E, and we can depict this as a potential barrier to be overcome (Fig. 4). If the molecule striking the surface is subject to the van der Waals' forces before entering into chemical combination, this has the effect of reducing E. Furthermore, as the investigations of Polanyi have shown, in a large class of reactions involving atoms, the energy of activation is negligibly small. Thus on *a priori* grounds we might anticipate that adsorption which takes place almost instantaneously (at a rate calculable from the Herz Knudson equation) and at low temperatures forming a surface phase with a small heat of adsorption, is a reaction involving purely van der Waals' forces; but surface chemical compounds are formed when the heat of adsorption is high, and in those cases where the energies of activation are high the surface phase will be formed slowly, and at increasing speed at higher temperatures. If the energy of activation is very small, chemi-adsorption will result even at low temperatures, and the speed may be comparable with that obtained for the process involving only van der Waals' forces. The complete curve for an isobaric adsorption involving a chemi-reaction with a relatively large energy of activation will consequently take the form shown in Fig. 5, where OA represents the van der Waals' adsorption decreasing with increasing temperature. At "A" the temperature is high enough to permit the process of chemical adsorption to proceed with

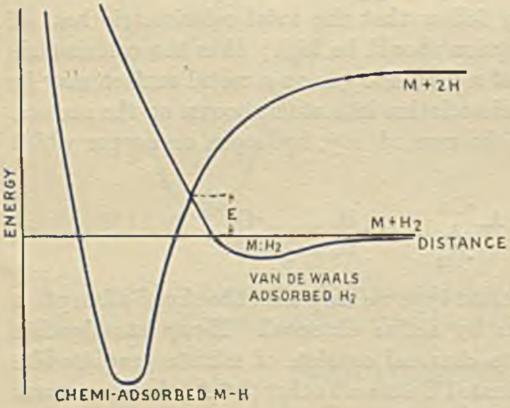


FIG. 4.

sufficient speed, so that in the time interval adopted for the experiment an appreciable chemi-adsorption occurs. *C–C′* represents the true equilibrium of the chemi-adsorption isobar, whilst over the temperature range T–T_1, where chemi-adsorption proceeds at a measurable rate, the process is termed "activated adsorption." Cases of this type for metals and gases were first obtained by Nikitin * later by Benton and White,† H. S. Taylor,‡ Garner and Kingman.§ These latter investigators have also extended their work to include various oxides, *e.g.* hydrogen on chromium oxide.‖ We shall have occasion to note that whilst curves of this type are obtained for gases like hydrogen on metals, other interpretations may be given for their origin. A similar type of curve would be obtained not only for the transition of a van der Waals' to a chemi-adsorbed complex when the energy of activation of the latter is large enough, but also from one type of chemi-adsorbed compound to another, provided that they differed sufficiently in their energies of activation.

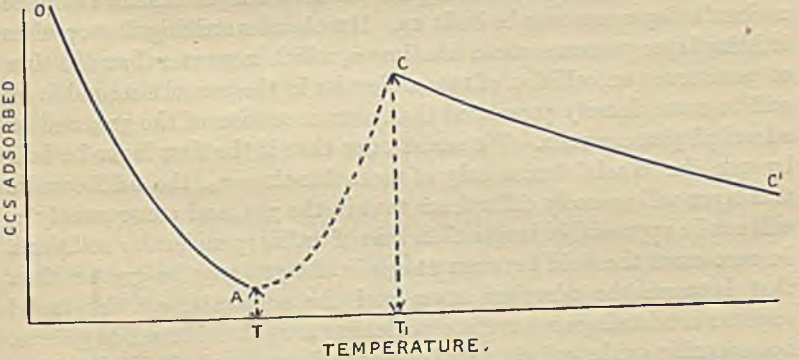


Fig. 5.

Chemi-adsorbed gases may undergo dissociation on heating, as is the case with the majority of hydrides and nitrides, or the strength of the union of the gas to the metallic substrate may exceed that of the metal gas complex to the metal and evaporation in the form of a metallic compound ensues. Frequently the surface film most readily volatilized is the most saturated compound, *e.g.* tungsten hexachloride resulting from the chemi-adsorption of chlorine on tungsten. The energy of linkage of the reacting molecule to the substrate decreases

---

* *Z. anorg. Chem.*, 1926, 154, 137.

† *J. Amer. Chem. Soc.*, 1930, 52, 2325.

‡ *J. Amer. Chem. Soc.*, 1931, 53, 578.

§ *Trans. Faraday Soc.*, 1931, 27, 322.

‖ Howard, *Trans. Faraday Soc.*, 1934, 30, 278.

as saturation increases, as is exemplified by the following data for iodine and platinum. The values are given in cal./grm.-mol. Pt—Pt 124,000. Pt—PtI 96,000. Pt—PtI_2 57,800.

MULTIMOLECULAR LAYERS.

So far we have considered the surface phase to consist of molecules which have arrived by direct impingement on the surface from the gas and exist there held by van der Waals' forces for a definite life-time τ_w. These molecules may also undergo chemical combination with the surface. The surface compound may dissociate again, giving a mean life for the surface complex τ_c. As we have seen, in general $\tau_c > \tau_w$, and also in suitable systems the two types of adsorbed molecules may exist side by side. We might inquire whether a layer thicker than one molecular layer can ever be built up. If molecules striking the top of an existing layer possess a mean life-time τ_2 which is greater than the time of persistence on collision of two molecules in the gas, the second layer will be more densely populated than a cross-section of the gas, and an adsorbed phase results. We see at once that if the first layer be held by van der Waals' forces only of mean life-time τ_w, the field outside this layer will scarcely differ from that in the gas, and consequently τ_2 will not be appreciably longer than that of ordinary molecular collisions. In rare cases the field between atoms in the gas may be greater than that between the adsorbed atom and the substrate, *e.g.* for metal vapours condensing on a surface possessing a weak field such as glasses, non-metallic oxides which may be regarded as chemi-adsorbed oxygen on metals or metals with adsorbed gas films. In this case a unimolecular layer will not be formed, but aggregates or nuclei result.

If, on the other hand, the life-time of the first layer is long and τ_c large, the forces holding the first layer are strong, as in the case of chemical reaction; the layer has now lost the properties of the gaseous molecules, and we might indeed expect the formation of a second layer. Several instances of this can be given; thus Langmuir found that oxygen could be adsorbed on a surface of tungsten which had already a chemi-adsorbed layer of oxygen on it. Dr. Whipp has investigated the adsorption of iodine on potassium iodide * and found that a bimolecular layer of iodine vapour can be formed on potassium iodide. In the case of the oxides referred to above which may be regarded as oxygen chemi-adsorbed on the metal, both hydrogen and nitrogen are readily adsorbed. In this latter case it is evident that the hydrogen may be adsorbed by van der Waals' forces, or may undergo reaction with the substrate forming chemi-adsorbed hydrogen or adsorbed water. The

---

* *Proc. Roy. Soc.*, 1933, [A], 141, 217.

form of the adsorption isotherm obtained when a bimolecular layer is built up will evidently depend on the relative lives of the molecules in each layer. In general $\tau_1 \gg \tau_2$, and each forms a Langmuir isotherm attaining saturation at very different regions of pressure. In some cases, *e.g.* iodine on *KI*, the discrepancies between the life-times are not so great, and we obtain a curve as in Fig. 6. Experiments on the adsorption of hydrogen on a really clean tungsten surface, recently carried out by Dr. Roberts,* show that the metal is always covered with a chemi-adsorbed layer so that any van der Waals' adsorption must take place on top of this.

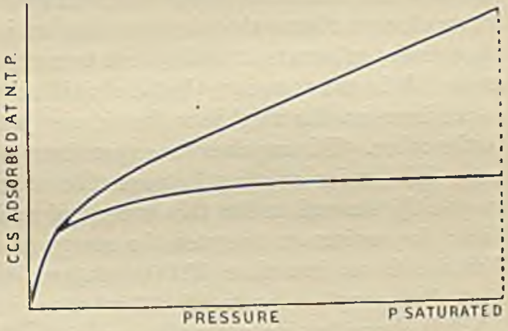


Fig. 6.

On Two-Dimensional Mobility.

In considering the formation of the adsorbed phase, it is pertinent to inquire whether a molecule striking the surface from the gas-phase possesses any lateral mobility over the surface, for, if such is the case, this must prove an important factor in the formation of the phase. Evidence for such lateral mobility was first provided by Volmer, who carried out a number of interesting experiments to demonstrate it. I might mention one of them which possesses many points of interest. If mercury vapour be supercooled, small flat hexagonal crystals of mercury grow from nuclei formed in the vapour; since the crystals consist of flat hexagonal plates, it is evident that the hexagonal surfaces grow more rapidly than the basal planes. Indeed, they grow more rapidly than can be accounted for by the rate of impingement of mercury atoms from the vapour phase, and we must conclude that they are fed by atoms striking the basal planes and migrating over the surface until they arrive at the edges. We have already recognized a distinction between molecules held by van der Waals' forces and chemi-adsorbed molecules, and, curiously enough, the power of lateral migration in the surface phase was first shown for the more firmly bound chemi-adsorbed atoms. Becker † has shown by measurement of the change in thermionic

---

* *Proc. Camb. Phil. Soc.*, 1934, 30, 79.

† *Phys. Rev.*, 1926, [ii], 28, 341; *Trans. Amer. Electrochem. Soc.*, 1929, 55, 153; *Bell Telephone Lab. Reprint*, B.-210, 1926, 21).

properties of a tungsten surface that adsorbed alkaline-earth metals such as barium as well as chemi-adsorbed oxygen will migrate over the surface. Langmuir and Taylor likewise measured the mobility of cæsium atoms adsorbed on tungsten.* Such lateral movement is not identical with the free movement of molecules in three dimensions, for we observe at once that if an atom is chemi-adsorbed to one particular atom in the substrate, in order for it to move a chemical reaction has to ensue. It is not necessary that it should evaporate into free space and re-condense on the neighbour, but it can jump or slide over from one to the other. This requires the expenditure of energy to jump over the potential barrier existing between the atoms of the substrate, and frequently the values for this energy of activation for migration are high; for cæsium on tungsten the energy of activation for this lateral diffusion is no less than 12,000 cal./grm.-mol., although the latent heat of evaporation is some 38,000 cal./grm.-mol.

It is clear that we can no longer picture our metallic surface as a uniform sheet, but must consider an atom held to an atom on the metallic substrate as in a sort of well surrounded by a potential barrier. From this well it can either evaporate into free space or with less, but sufficient energy, it can jump over the barrier into the well of a neighbouring atom.

Lennard-Jones † has developed the theoretical implication for activated migration in some detail.

It is also clear that a slight variation in the atomic spacing of the surface atoms will alter very profoundly the contour of the potential barrier which the adsorbed migrating atom has to pass over. Thus, it is easy to understand that a few single atoms or small clusters of atoms in any extent of surface may be isolated from their neighbours by a continuous high potential barrier.

We may cite as an example of this mobility Estermann's ‡ investigations on the deposition of silver on glass, for when only a monolayer was deposited the atoms collected into nuclei, each amounting to at least 1000 atoms.

This factor of lateral mobility is important in building up the surface phase. We have assumed that only molecules striking the surface are adsorbed; molecules striking that part of the surface which is already covered with a monolayer may build up a second layer which is, in general, only sparsely populated, because the field holding the second layer is much weaker than that holding the first. In spite of the short life in the second layer, the molecule is relatively so mobile that it

---

* *Phys. Rev.*, 1932, [ii], **40**, 463. † *Trans. Faraday Soc.*, 1932, **28**, 347.

‡ *Z. physikal. Chem.*, 1923, **106**, 403.

can travel very considerable distances over the surface until it finds a vacant hole in the incomplete first layer; thus the rate of building up the first layer may be greater than that calculated from the simple Herz Knudsen law. Langmuir has observed this phenomenon in the adsorption of oxygen on tungsten, and this was also found to be the case when iodine vapour condensed on potassium iodide.

With molecules held by van der Waals' forces alone we might anticipate a much greater surface mobility, for the energies of activation even for evaporation are only of the order of a few thousand cal./grm.-mol. Many experiments demonstrating this mobility have been devised by Volmer * and by Moll.† We may note that it plays an important part in another interesting property of the surface phase. So far we have considered it as ranging between a two-dimensional solid where no lateral mobility exists and a two-dimensional gas where the energy of activation for lateral migration is low, and have neglected the lateral attractive and repulsive forces between the adsorbed molecules in the adsorbed phase itself. It is evident that, as in three dimensions, both solid and liquid phases should exist as well as gaseous and vaporous phases, and transition phenomena might be expected where we should have on the surface at the same time two phases in equilibrium with one another.

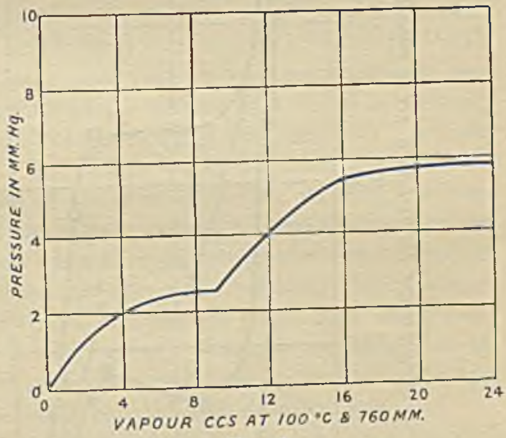


Fig. 7.

In order to demonstrate this phenomenon we require some method of examining the surface phase at different portions of the surface, an operation readily performed at high temperatures by means of thermionic emission. At low temperatures other methods have to be employed. Fig. 7 shows the adsorption isotherm of ethyl alcohol on thoria determined by Rideal and Hoover.‡ This form of curve is typical of the adsorption of vapours on numerous solid surfaces. The form of the curve is not a simple adsorption isotherm, for when a certain critical pressure is attained a relatively large quantity of vapour is adsorbed at almost constant pressure. This phenomenon is indicative of another

* *Z. Physik*, 1925, 35, 170. † *Z. physikal. Chem.*, 1928, 136, 183.

‡ *J. Amer. Chem. Soc.*, 1927, 49, 120.

condensation process commencing, and it is still a matter of very considerable doubt whether in any particular instance this condensation process consists in the filling up of the micro-capillaries in the solid, as occurs in the case of charcoal and possibly some gels, or whether it is the formation of a two-dimensional liquid phase, as may be the case in the condensation of vapours on metals such as gold.

Mr. Ouellet has examined by means of a photo-electric method the condensation of vapours on a gold surface, and Fig. 8 shows one of his curves.

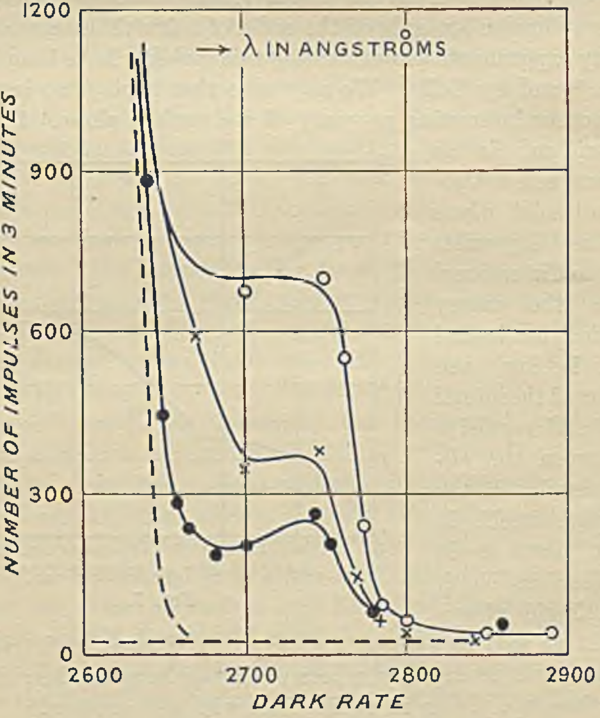


Fig. 8.

It is clear that on the gold surface there exist two distinct areas, the extents of which vary with the partial pressure of the vapour which possess different threshold values for photo-electric emission, and we may infer that these consist of the two-dimensional vaporous and liquid phases, respectively. Condensation of the two-dimensional vapours, as in C. T. R. Wilson's experiments in three dimensions, probably occurs most readily round impurities in the form of adsorbed ions forming small dipoles to which the polar molecules are attracted.

THE EFFECTS OF EXTRANEOUS GASES AND OF SOLUBILITY ON THE ADSORPTION ISOTHERM.

We have seen that the isobaric adsorption curve is frequently discontinuous, and that the two continuous portions of the curve can be interpreted as consisting of van der Waals' adsorption over the low-temperature region and chemi-adsorption over the high-temperature region; such, indeed, appears to be the case for the adsorption of hydrogen on various oxides. In the case of the adsorption of hydrogen on metals, we have to note that it is extremely difficult to obtain a clean metallic surface, owing to the almost continuous evolution of gas from the interior. Since, as we have noted, gas may be adsorbed on to a monolayer of gas already present if the temperature be low enough, evidence must be forthcoming that the original metal was perfectly clean before the curve *OA*, Fig. 5, may be truly identified with the van der Waals' adsorption on the metal. Of recent years several methods have been developed for the examination of the surface of a metal at ordinary temperatures, with the object of ascertaining whether or no it is really free from adsorbed gases. Both Rupp * and Davisson and Germer † have shown by the method of electron diffraction utilizing low-speed electrons that both nickel and copper exhibit marked changes in their electron diffraction patterns when brought into contact with hydrogen at partial pressures lower than 10^{-4} mm. and at ordinary temperatures, suggesting that chemi-adsorption of hydrogen takes place remarkably readily when the surface is really clean. We may conclude that the curve *OA* obtained with these metals really represents the adsorption of hydrogen on a surface already covered with adsorbed gas.

Another method of examining a surface at ordinary or low temperatures for the presence of an adsorbed film consists in measuring the threshold value for the wave-length of light necessary to effect photoelectric emission. Although the method is sufficiently sensitive for the purpose, it has not yet been employed for the specific purpose of controlling an adsorption isotherm of a gas, but the difficulties of obtaining a sharp threshold value even in high *vacua* for platinum which has been in contact with either oxygen or hydrogen do not support the view that van der Waals' adsorption is the characteristic form of adsorption, at any rate at ordinary temperatures. One of the most sensitive methods for examining surfaces is being undertaken by Dr. Roberts ‡ by observing the change in the accommodation coefficient of a wire when clean and when covered with an adsorbed film. Utilizing neon as a detector

---

* *Ann. Physik*, 1930, **5**, 453; 1932, **13**, 101.

† *Phys. Rev.*, 1927, [ii], **30**, 705.

‡ See *Proc. Camb. Phil. Soc.*, 1934, **30**, 79.

gas at room temperature, the accommodation coefficient for a clean tungsten wire is 0·07, which rises to 0·60 when the wire is covered with an adsorbed film. By this method it has been found that tungsten adsorbs hydrogen both rapidly and strongly at temperatures as low as 79° K. and at room temperature, suggesting that chemi-adsorption of hydrogen occurs with an energy of activation that cannot exceed 2000 cal./grm.-mol.

It is unfortunate that our information on the heats of adsorption as well as on the energies of activation for chemi-adsorption is so scanty, since their variation with the temperature should provide us with information respecting any effects due to an alteration in the lattice spacing on these thermal magnitudes.

THE INTERNAL SURFACE OF METALS.

By these methods of examination we are led to infer that the curve OA, Fig. 5, obtained in the isobaric adsorption of hydrogen on such metals as copper and nickel at low temperatures is not really a van der Waals' adsorption isobar on the metal, but a van der Waals' adsorption on a surface already covered with extraneous impurities or on chemi-adsorbed hydrogen which has not been previously desorbed. If this be the case, it is evident that the second portion of the isobar, *viz.* CC' (likewise the transitional region from A to C where an apparent temperature-dependent uptake of gas takes place) requires a new interpretation. It is clear that this cannot be caused by the desorption of an impurity and the re-adsorption of the hydrogen on the clean metal unless the impurity were in effect non-volatile or preferentially adsorbed on the walls of the container. It seems much more probable that some process of solution of the gas into the metal is taking place, the rate of which is enhanced by rising temperature, but the total amount of which decreases with rising temperature up to at least the temperature limits of these investigations.

We know already that gases are appreciably soluble in metals at high temperatures from the classical experiments of Sieverts.* It is also clear that the temperatures of the gases under consideration are so far removed from their critical points, and the internal pressures of the metals are so high, that the actual solubility of a gas in the simple molecular form as a true solution in a metallic lattice must be negligibly small. We must pre-suppose that the bulk of the gas stored in a metal is in some form or other which is not molecular. We note here that what may be termed the internal surface of a metallic granule must be an important factor in the whole mechanism of adsorption of gases, and

---

* *Z. physikal. Chem.*, 1910, 68, 115 *et seq.*

we shall now examine how we may obtain some information as to its nature and extent.

Several years ago Dr. Dunn commenced a series of investigations on behalf of the British Non-Ferrous Metals Research Association on the passage of zinc into copper and out of brass, and he found that the diffusion of this element obeyed, as was to be anticipated, the ordinary diffusion law of Fick, but that the diffusion process had the interesting property of possessing an exponential temperature coefficient like a chemical reaction. The migration of zinc in copper is thus similiar to the "*platzwechsel*" of ions in solid ionic electrolytes, and is not a continuous and steady movement, but a species of jumping from place to place of like configuration in the lattice, the energy of activation being a measure of the magnitude of the potential barrier existing between these places. The investigation was extended to examine the passage of a reactive gas into copper from the same point of view[*] and completed by Dr. Wilkins.[†] These investigations can be regarded as a study of the chemi-adsorption of oxygen by copper. When exposed to oxygen an ever-increasing thickness of cuprous oxide is formed on the metal, the thickness of which can be measured either by observing the change in electrical conductivity or by the beautiful method of Tammann based on the formation of Newtonian interference colours, a principle employed so extensively by U. R. Evans[‡] in his work on corrosion. In agreement with the classical experiments of Pilling and Bedworth,[§] it was found that the rate of penetration or chemi-adsorption of oxygen by copper obeyed the Fick diffusion law, but also that the diffusion process was again exponentially dependent on the temperature.

Analysis of the curves revealed the fact that two reactions were involved, each with definite energies of activation, the low-temperature one predominant below 600° C. having a value of $E = 9500$ cal./grm.-mol. Clearly the passage of oxygen through the ever-increasing thickness of cuprous oxide can be effected by two different methods. A clue to the nature of these two processes was found in examining the effects on the speed of the two reactions of an alteration in the gas pressure and of activating and annealing the copper. The conclusion was reached that at high temperatures the oxygen actually migrates through the lattice of the cuprous oxide, but at low temperatures the oxygen migrates with a lower energy of activation between the micro-crystals of the oxidized metal. This low-temperature activated migration is the one we are particularly interested in, for the rate of diffusion into the metal

---

[*] *Proc. Roy. Soc.*, 1926, [A], 111, 210.

[†] *Proc. Roy. Soc.*, 1933, [A], 128, 394.

[‡] "Corrosion of Metals."

[§] *J. Inst. Metals*, 1923, 29, 529.

is governed by the extent and number of the slip planes and intercrystalline channels, and by the amount of gas actually on the surface of the oxide.

It is not necessarily self-evident that the oxygen migrates along the slip planes in a manner analogous, say, to the diffusion of bromine through carbon tetrachloride, for a similar passage of oxygen would be obtained if the oxygen migrated by chain displacement in a manner originally suggested by Grotthuss and developed by Fowler and Bernal * for the movement of the hydrogen ion in water.

Another very interesting discovery was made in this investigation when studying the effect of oxygen pressure on the rate of oxidation. It was found that for any particular piece of copper the rate of oxidation was proportional to the amount of oxygen adsorbed on the oxide surface, the amount adsorbed being related to the gas pressure by means of the Langmuir adsorption isotherm. At a certain critical high pressure the surface becomes saturated, and the rate of oxidation is then no longer dependent on the oxygen pressure. Now it is found that the critical pressure is dependent on the nature of the original copper. The critical pressure is higher the more microcrystalline the copper and the greater the number of crystal boundaries; very low pressures suffice for well-annealed copper, as is evident from the following figures :

Treatment.	Limiting Pressure in mm. Hg.
Original foil . . .	9·5
One reduction and oxidation	25·2
Four do. . . .	55
Eight do. . . .	129·3
Sintered at 305° C. for 2 hrs.	26–43

We can conclude from these experiments that the adsorbed oxygen is not fixed on the cuprous oxide surface, but can undergo two-dimensional migration, and thus approach an inter-crystalline boundary along the surface. The surface is thus to be compared to a bucket with holes in the bottom, the more holes present the greater has to be the supply of water to keep the bottom covered with water. It is, of course, improbable that the oxygen migrates freely over the surface of the cuprous oxide, as imagined by Volmer, and we infer that it is more likely that an energy of activation, for migration from point to point is involved.

So far we have surveyed the evidence for the surface and intracrystalline migration of a gas, and the question might be raised as to the relationship between them. This problem might be formulated

---

* *J. Chem. Phys.*, 1933, 9, 516.

in another way. If we consider the passage of gas down a tube, we note that at relatively high pressures but low pressure differences, the gas flowing through the tube in accordance with the conditions of Newtonian flow, Poiseuille's law will be obeyed. At pressures so low that the tube diameter is of the order of a mean free path and the gas flows through suffering simple reflection at each collision with the wall, we obtain the conditions for Knudsen flow. If we imagine that the molecules condense whenever they strike the walls and re-evaporate at random, the rate of passage down the walls will now depend on the life-time of the adsorbed molecules, a state of affairs examined both theoretically and experimentally by Clausing. This may be regarded as the type of flow occurring through a wide crack. The mechanism of passage changes again when the tube becomes so narrow that the fields of the molecules forming the wall start to overlap.

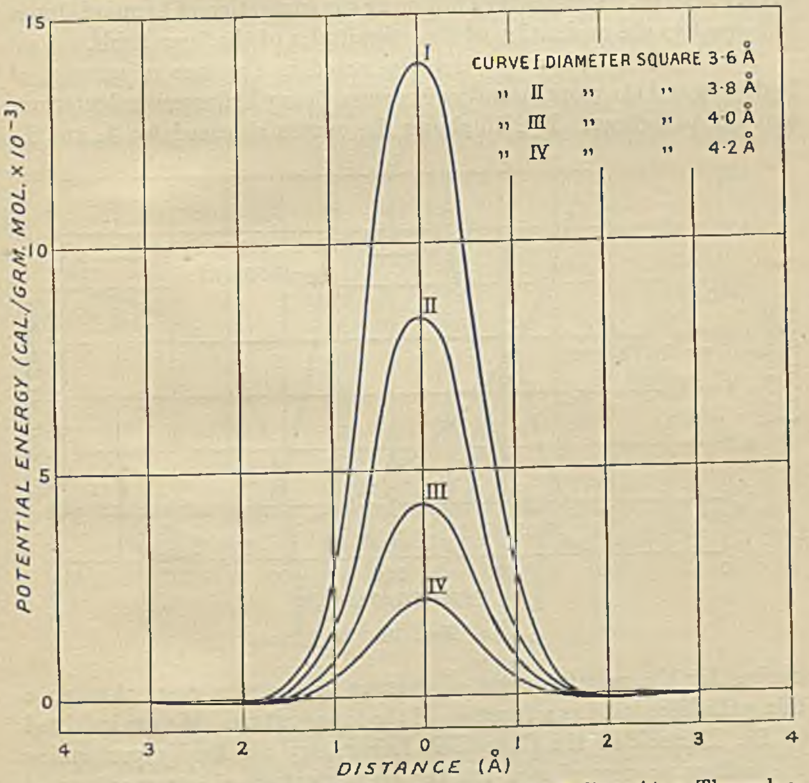


Fig. 9.—Potential Energy Curves for Migration of a Helium Atom Through a Square of Helium Atoms.

If we attempt to push a molecule through a single cross-section of the tube comprising a ring of atoms of the solid, then it is evident that the smaller the diameter of the ring the greater will be the potential barrier of the solid to the molecule attempting to pass through the ring. This case has been investigated by Mr. Barrer, who has made a detailed study of the passage of gases through quartz. Fig. 9 is one of the sets of curves which he has derived following the suggestion of Lennard-Jones in respect to the evaluation of the magnitudes of the force fields.

Another interesting case is to be noted in the case of passage of hydrogen and the more recently discovered heavy hydrogen or deuterium through palladium. Fig. 10 shows the curves obtained by A. and L. Farkas for the relative rates of passage of the two gases through a thin palladium tube as a function of the temperature. We are indebted to Dr. Harteck of the Cavendish Laboratory for kindly performing the tedious process of carrying the concentration of our specimen of heavy water through the latter and tedious stages.

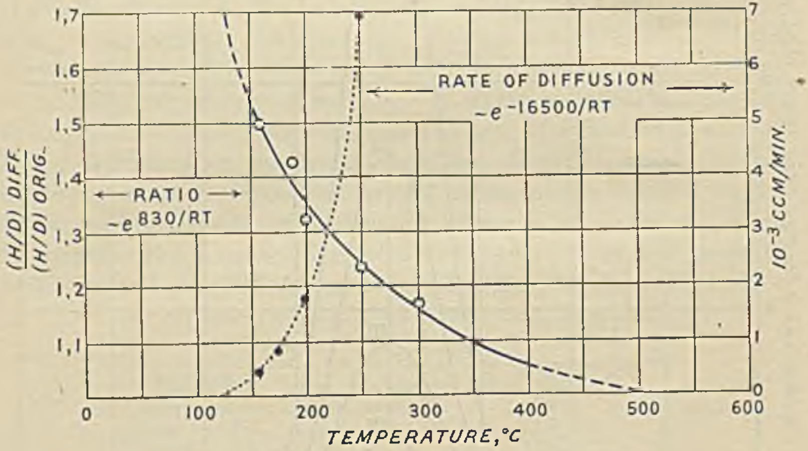


FIG. 10.

We note that the two hydrogens differ in their energies of activation for the passage through palladium of about 860 cals. These are two different examples of what McBain terms persorption or passage through molecular sieves. We may conclude with some degree of certainty that for a molecule to enter the metal either down a narrow crack or into the lattice from the adsorbed phase, whether it is held there by van der Waals' forces of polarization or is retained in the chemi-adsorbed state, a definite energy of activation is necessary. The extension of the investigation from oxygen which forms a visible layer of cuprous oxide on copper to hydrogen which, when chemi-adsorbed by copper, causes no marked change in colour and may not necessarily form a continuous phase, had to be undertaken by indirect means, namely by measurement of the rates of uptake and gas liberation as a function not only of the gas pressure, but also of the surface concentration which can be varied by a sudden variation in the gas pressure. This investigation, carried out by Dr. Ward, revealed again the dependence on the Fick diffusion law and the existence of a definite energy of activation for the migration of the hydrogen into the copper.

It is not necessary to point out that for diatomic gases the chemi-adsorbed state may be in the atomic form or even ionic, as is the case of oxygen in copper. In palladium hydrogen is not only dissociated, but under the influence of a potential gradient along a wire saturated with the gas, ionic migration takes place.

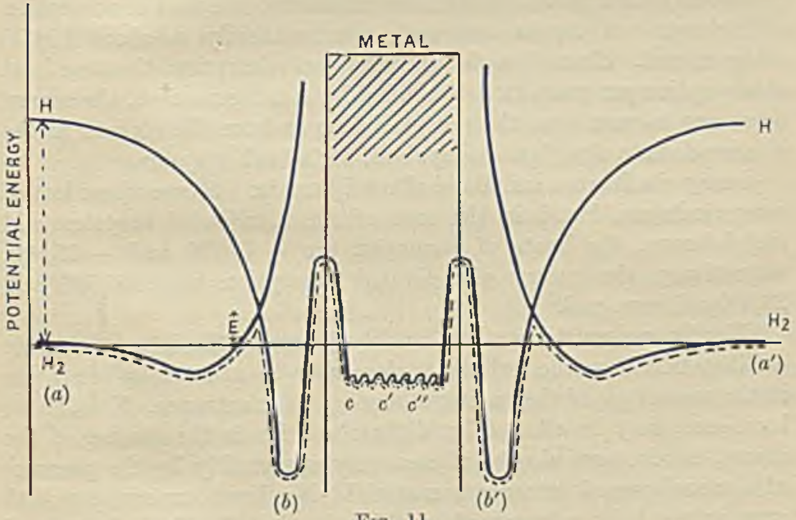


Fig. 11.

We are now in a position to draw diagrams of the changes in potential energy which a simple gas molecule of hydrogen undergoes when it passes through a thin sheet of metal (Fig. 11). In the first case, *e.g.* on palladium, the molecule originally free at *a* becomes chemi-adsorbed as an atom at *b*, passes into the lattice at *c* and through the lattice *c′ c″*, &c., finally re-emerging as an adsorbed molecule at *b′* and being liberated at *a′*. In the second case, *e.g.* on copper, the molecule originally free at *a* becomes chemi-adsorbed at *b*, passes into an intercrystalline crack at *c*, and migrates through the network of cracks, actual penetration of the lattice being small.

It will be noted that each transition involves the passage over a potential barrier. We have seen that in some cases, *e.g.* hydrogen on tungsten the transition $a \longrightarrow b$ may not involve an appreciable energy of activation when the metal is clean and the van der Waals' forces are taken into consideration and that the transition $b \longrightarrow c$ may involve a large one dependent, among other factors, on the lattice constant or size of the crack, as has been shown for gases passing through quartz, whilst the energy involved in the transition c to c' may be very small, as witnessed by the apparently high mobility of hydrogen ions in a palladium lattice, or very large, as is the case in the apparent immobility of oxygen atoms or ions in a copper lattice.

We may attempt to insert numerical values; the heat of adsorption of hydrogen on copper measured calorimetrically is about 10,000 cal./grm.-mol. Since dissociation occurs on adsorption, the true heat of adsorption per gram atom is about 55,000 cal./grm.-mol., the energy necessary to pass over the potential barrier from the surface to the interior down a slip plane being about 16,000 cal./grm.-cm.

I may cite Norton and Marshall's * figures for the case where lattice compounds are found in the case of the nitrides of tungsten and molybdenum, the heats of formation are — 74,700 and — 38,500, respectively, the energy of activated desorption being 50,500 and 26,600 cal./grm.-mol.

Finally, we must note how readily access to the internal surface or liberation from the internal surface may be affected by alteration in the magnitude of the potential barrier at the entrance. This, as we have seen, may be effected by slight alteration in the spacing of the atoms, but it must also be altered very appreciably by the presence of a monolayer of extraneous material. No direct experiments with gases appear to have been made on this point, but the effect of "traces" of poisons on catalytic activity is well known.

In contrasting the entry of oxygen into copper with that of hydrogen, we note that whilst oxygen can migrate through the boundary layers of copper oxide and form a diffusion gradient therein, it penetrates each grain, but with a higher energy of activation; at the same time the energies of migration of oxygen atoms through metallic copper and of cuprous oxide through copper are so great that at least up to the vicinity of the melting point of copper the rate of oxide formation even through a thick layer of oxide greatly exceeds either of these other processes, with the result that the cuprous oxide formation is confined exclusively to a copper/copper oxide interface, and no diffusion of atomic or ionic oxygen nor molecular solution of cuprous oxide in

---

* *Amer. Inst. Min. Met. Eng. Preprint,* 1932, Feb., 1–28.

copper takes place. The same appears to be true in a number of cases, such as platinum and tungsten oxides, investigated by Van Praagh. It is an interesting speculation as to how thick a layer of cuprous oxide on copper is necessary before all the characteristics of a bulk phase of cuprous oxide appear, *e.g.* dissociation pressure, melting point, and the like. Van Praagh showed that a layer of tungsten iodide computed to be less than 100 molecules thick possessed bulk characteristics. It is evident that one has to ensure that no dispersion to form solid solutions takes place during the preparation or examination of the specimen.

In the case of hydrogen, on the other hand, the "lattice solubility," or the amount of hydride held in solid solution at the pressures and temperature of the experiments, is extremely small, whilst the energy of activation for the migration of the hydrogen atom or ion, *i.e.* for the dissociation of the copper hydride on the internal surface and the movement of the resulting atom or ion to the neighbouring copper atom along the grain boundaries, is relatively small, so that at the temperature of investigation a diffusion gradient of hydrogen atoms or ions can be established over the internal surface of the metal, and equilibrium is attained when the internal surface is populated to a definite surface density.

These differences are, I think, important, for they emphasize the contrast between the behaviour of those solid binary mixtures which form solid solutions and those which are completely immiscible; thus in the system calcium oxide/calcium carbonate the relative amounts of each phase present change with the smallest energy of activation by growth and diminution at the interface between each phase, and nucleus formation is an alternative with a large energy of activation to remove metastability. Such a system exhibits a great contrast to that, say, of an amalgam of mercury and thallium.

From these considerations we see that when a gas enters a metal, two distinct processes are at work: the gas travels along the slip planes and in the intercrystalline spaces, and also into the lattice itself. The final distribution of the gas is thus in two phases: one in the lattice, and the other distributed on what I have described as the internal surface of the metal. We are not here concerned with the fate of the gas in the lattice, beyond observing that, as we have shown, the gas must be present in the form of some compound, since the actual solubility of gases in metals is negligibly small. Again, since the majority of compounds, such as the nitrides and hydrides of iron, copper, and nickel, are markedly endothermic in their formation, the "apparent lattice solubility" must increase with elevation of the temperature, an inference in accordance with metallurgical data. On the other hand, the formation of surface hydrides and nitrides are strongly exothermic reactions, and such appears to be the case for compound formation on the internal surface.

It is not improbable that the embrittlement of iron in caustic soda and in sodium nitrate is due to the passage of gas into what I have termed the internal surface of the metal, *i.e.* along the grain boundaries, and weld decay is due to corrosion occurring at the internal surface.

ON THE RELATIONSHIP BETWEEN ADSORPTION AND LATTICE COMPOUNDS.

Gases like nitrogen and hydrogen react with many metals to form nitrides and hydrides, the formation of which are endothermic processes. Our knowledge of these is due chiefly to the investigations of Sieverts,* Hüttig † and Paneth.‡ These compounds we may regard as lattice compounds, as they appear frequently to be in solid solution in the lattice of the metal. We have already advanced arguments as to why the gases must be present in the form of compounds, and this view is confirmed when we consider the large changes which occur in the apparent solubility of a gas in a metal when we traverse the melting point or pass through an allotropic modification, as in the case of nitrogen and iron in the $\alpha \rightleftharpoons \beta$ transition.§

In addition to these lattice compounds, we have seen that chemi-adsorption processes lead to the formation of surface compounds, usually exothermic processes, and that these surface compounds may be either superficial or intercrystalline. Finally, gaseous metallic nitrides and hydrides may be formed either by the interaction of metallic vapours with hydrogen at high temperatures ‖ or by the interaction of atomic hydrogen with metallic foil as carried out by Pietsch.¶ Whilst the experimental data are somewhat uncertain, it is interesting to compute the heats of formation of the compound CuH from copper and molecular hydrogen, the metal atoms concerned being first in a regular lattice, secondly on the surface of the metal, and lastly vaporized in the form of a monatomic vapour.

We obtain the following values :—

$$\underset{\text{Lattice.}}{\mathrm{Cu}} + \tfrac{1}{2}\mathrm{H_2} = \mathrm{CuH} - 10{,}000 \text{ cal.}$$

$$\underset{\text{Surface.}}{\mathrm{Cu}} + \tfrac{1}{2}\mathrm{H_2} = \mathrm{CuH} + 5{,}000 \text{ cal.}$$

$$\underset{\text{Vapour.}}{\mathrm{Cu}} + \tfrac{1}{2}\mathrm{H_2} = \mathrm{CuH} + 19{,}000 \text{ cal.}$$

---

* *Z. Metallkunde*, 1929, **21**, 39.

† *Z. angew. Chem.*, 1926, **39**, 67.

‡ *Ber.*, 1920, **53**, 1710.

§ Sieverts, *Z. physikal. Chem.*, 1931, **155**, 299.

‖ Cf. Farkas, *Z. physikal. Chem.*, 1929, **5**, 467.

¶ *Z. Elektrochem.*, 1933, **39**, 577.

Since the heat of vaporization of copper is some 60,000 cal., the heat of solution of copper hydride must be some 30,000 cal. It is interesting to note that the heat of formation of the surface compounds is a mean value between that for the gaseous and lattice compounds.

It is clear that the strength of union of the CuH bond is dependent on its environment, and in this respect the depth of the potential barrier between the hydrogen atom and a copper atom will be dependent on the proximity of the neighbouring atoms, as was exemplified in the case of the van der Waals' forces operative between a gas atom and the oxygen atoms in a silica skeleton through which the gas is passing. Our potential energy curves will thus form a regular series dependent on the closeness of approach of the neighbouring copper atoms (Fig. 12.) Some semi-quantitative attempts have been made to explore the "rarified" metals by examining the behaviour of condensed atom sponges; thus when metallic wires undergo vaporization in gases at low partial pressures, the phenomenon of "cleaning up" is noted, and provides us with one of the most interesting methods for the control of the state of the metal. Investigations have been carried out by Langmuir,[*]

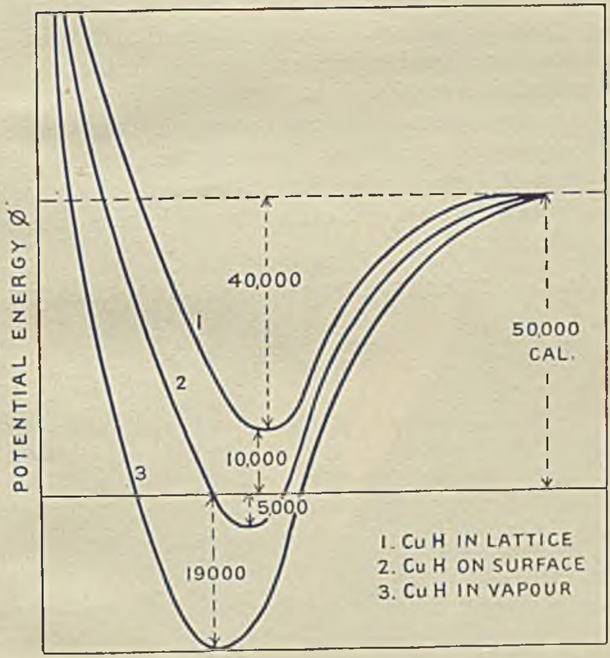


Fig. 12.

[*] *J. Amer. Chem. Soc.*, 1918, 41, 1139, 1918.

Frankenburger,* and by Bastow.† In the case of tungsten, a nitride WN_2 is formed in the gas phase which decomposes thermally only at very high temperatures. With molybdenum two nitrides are formed in the gas-phase; one liberates its nitrogen at room temperatures, but the other is stable up to 360° C. Another type of reaction is noted with iron and platinum, for these metals do not appear to combine with nitrogen or hydrogen in the gaseous state, but do so when they are adsorbed on a cooled surface in an unsintered or partly sintered state. On elevation of the temperature, thus permitting sintering to take place, the gases are evolved. The gases adsorbed by the deposited metallic atoms were found to be chemi-adsorbed in that they behaved chemically as nitrides and hydrides.

Whilst the experimental data are at present in a very unsatisfactory state, we may note a parallelism between these heats of formation and the effect of surface saturation on the heat of desorption of a compound, which I mentioned earlier in my lecture in reference to platinum and iodine.

---

* *Z. Elektrochem.*, 1929, **35**, 359, 591 *et seq.*

† *J. Chem. Soc.*, 1931, 1950.

BIBLIOTEKA POLITECHNIKI ŚLASKIEJ

THE LATE DR. WALTER ROSENHAIN, F.Inst.Met., F.R.S.
President of the Institute, 1928–1930.

OBITUARY.

Walter Rosenhain, Past-President of the Institute, died at his home on March 17, 1934, after a long illness.

He was a son of the late M. Rosenhain of Melbourne, Australia, and received his early education at Wesley College, Melbourne. At an early age he showed definite signs of great intellectual powers, and he proceeded from school to Queen's College, University of Melbourne, from which he graduated in Physics and Engineering in 1897. He obtained one of the research scholarships of the Royal Commission for the Exhibition of 1851, which enabled him to come to Cambridge, where he became a member of St. John's College. He originally intended to adopt a career in Civil Engineering, and his first degree of B.C.E. (Melbourne) was obtained in this subject. Fortunately for the science of metallurgy, he joined Sir Alfred Ewing's laboratory at Cambridge at a time when that distinguished engineer had become interested in the then new experimental method of studying metals by means of the microscope. Ewing was able to interest Walter Rosenhain in studying the phenomena of plastic flow by means of this new technique, and the result was the classical discovery of " slip bands " in metal, leading to the foundation of our present-day knowledge of plastic deformation. About the same time, he made notable contributions to our knowledge of recrystallization, particularly in the softer metals.

These three years at Cambridge determined the future course of Rosenhain's career, for in that time he had discovered his life's work. The time had not arrived, however, when it was possible to earn a living by the practice of physical metallurgy, and he joined the firm of Chance Brothers, glass manufacturers, of Smethwick, Birmingham, as Scientific Adviser, principally in connection with optical glass and lighthouse apparatus. This post he held for six years; his experiences are embodied in his book on Glass Manufacture, published in 1907 and revised in 1920. During the Great War, his knowledge of glass and refractories was of great service to the nation when supplies of German optical glass were cut off.

Although at this time compelled by circumstances to apply most of his energies in other directions, Rosenhain was determined to pursue his studies in physical metallurgy, which he did in a small laboratory of his own, working in the evenings and in his spare time. His wife, whom he married in 1901, shared his work and helped him with the polishing of his specimens. In this way he was able to maintain a succession of scientific papers, and to keep actively in touch with that branch of science which he had grown to love. During this period, he added to his reputation by his forceful and original contributions to metallurgical discussions, and developed that lucidity in writing and speech for which he later became so well known. In 1906, Dr. (now Sir Harold) Carpenter, who had already completed his well-known research on the iron-carbon diagram at the National Physical Laboratory, was called to the newly founded Chair of Metallurgy at Manchester University, and Rosenhain was appointed to succeed him by Sir Richard Glazebrook, the first Director of the Laboratory. In 1908, Glazebrook recognizing the growing importance of metallurgy as a science decided to establish a new department devoted to the subject and invited Rosenhain to become the first Superintendent of the " Department of Metallurgy and

Metallurgical Chemistry." No choice could have been happier, for he quickly developed this department until it became perhaps the foremost and best-known laboratory of its kind in the world. In his new appointment, Rosenhain began that period of intense activity which continued without remission practically to the time of his death. He realized the important part that the science of physical metallurgy was to play in the development of metallurgical and engineering industries, and, above all, he appreciated the need for increased fundamental knowledge in all directions. He carried out or initiated numerous researches into the constitution of alloy systems, using refined methods of investigation, many of which were developed in his own laboratory, and conducted many researches into the physical structure of metallic alloys, particularly in relation to properties and behaviour in service. Throughout this period, his work was governed by a desire to found a fundamental science of metals and alloys, and the immense contribution which he personally made to achieve this end is well seen in his "Introduction to Physical Metallurgy," first published in 1914. He was engaged on a revision of this book at the time of his death; the work is being carried on by Dr. J. L. Haughton, and the new edition should appear during the summer of 1934.

Rosenhain's most outstanding work was perhaps that in support of the so-called amorphous theory, which he developed and defended with his characteristic originality, ingenuity, and skill, both in the laboratory and the debating hall. The original work of Beilby appealed naturally to one who had already made so many investigations into the deformation and cold-working of metals, and he accepted Beilby's conclusions with enthusiasm and extended and amplified them with resource and energy. Even though his views did not find universal acceptance, a glance at the metallurgical literature of the past 25 years shows how profoundly they have influenced metallurgical opinion throughout the world.

Although Rosenhain's work covered the whole field of metallurgy, both ferrous and non-ferrous, his work on aluminium and its alloys was specially noteworthy. Before the Great War, he had already carried out investigations of light alloys for the Alloys Research Committee of the Institution of Mechanical Engineers, and these became greatly intensified owing to the need for studying new materials, particularly in connection with the development of aeronautics. The work done under his direction at the National Physical Laboratory was of the greatest possible value in this connection, and has led to the development of a number of useful new materials, including the now well known "Y"-alloy. Among the many other important investigations carried out, either by himself or under his direction, are those dealing with impurities in copper, the heat-treatment of steel, gas in aluminium alloys, alloys of zinc, dental alloys, beryllium and its alloys, the nature of solid solutions, and the constitution of the alloys of iron. His researches, however, covered a much wider field, and a complete list of his publications would occupy many pages. His research work brought him many honours. He was awarded the D.Sc. degree of his own University, and, in 1913, was elected to a Fellowship of the Royal Society; he was awarded the Carnegie and Bessemer Medals of the Iron and Steel Institute, and the Thomas Turner Gold Medal of the University of Birmingham. In 1932 he was elected an Honorary Member of the Deutsche Gesellschaft für Metallkunde. He was invited to deliver important lectures, not only by many bodies in this country, but also abroad, and for this purpose he paid visits to the U.S.A., Germany, Switzerland, Sweden, India, and Australia.

Dr. Rosenhain's activities were by no means confined to his scientific research, for he engaged in many other forms of metallurgical work. He was an Original Member of the Institute of Metals, and a Member of Council from 1910 onwards. For many years, he was Chairman of the Publication Committee, and his activities and sound judgment in this office had a great influence on the development of the Institute, particularly on its publications. He was May Lecturer in 1923, and President from 1928 to 1930. His valuable services were recognized by his election to a Fellowship of the Institute. He was a Member of Council of the British Non-Ferrous Metals Research Association and of the British Cast-Iron Research Association; he played an active part in the development of both these bodies, and his interest in them was maintained until his death: his services to industry through these connections were undoubtedly very great. He also served on many technical committees of the Department of Scientific and Industrial Research, the Air Ministry, the Dental Board, the British Standards Institution, and other bodies.

One of the major interests of his later years was the promotion of contact and understanding between metallurgists throughout the world, and he was largely responsible for the formation of the New International Association for Testing Materials; in 1927 he was appointed British delegate on the permanent committee of the Association and President in 1931.

Dr. Rosenhain resigned from the National Physical Laboratory in 1931, in order to take up private practice as a consulting metallurgist; in this capacity he was closely connected with the British Aluminium Company, Ltd., the Broughton Copper Company, Ltd., and Messrs. J. Stone & Company, Ltd. The decision to leave the department which he had created was one which he took only after very careful consideration, and the break with the laboratory he loved caused him much grief. The principal reason which influenced him will be recognized by those who knew him as typical of the man; it was that he could not lightly contemplate the possibility of being compelled to retire at the age of 60 or 65 or, indeed, at any age, and wished to establish work of his own to which he could continue to devote his activities.

Rosenhain's death leaves a big gap in the ranks of metallurgists throughout the world. Few men have shown a greater versatility or have been more active either in research or in writing. His views were frequently unorthodox, but always stimulating; it could scarcely be otherwise, for he continually sought to take his subject further; he was never bound by popular opinion, and never hesitated to express and defend his own views, while he welcomed and appreciated a similar frankness in others; he loved a scientific argument, and he was a skilful exponent in debate. His clear diction and extraordinary command of language made him a most attractive speaker, and members of the Institute of Metals will recall the many occasions on which they have listened with admiration to his contributions to their proceedings.

His death at the comparatively early age of 58 takes him from us at the height of his intellectual powers, and leaves us with the full consciousness of the loss our science has suffered.

D. H.

Morris Broad Fowler died on February 8, 1934.

He was born in London on July 19, 1870, his father being a wax refiner and a patentee and manufacturer of nightlights.

He had a varied education, going first to the Brighton School of Science and Art (under South Kensington), where he had as tutors Professor Jago and Professor Young, and later entering London University, where he took his Intermediate B.Sc. Instead, however, of completing the course, he went on to the Royal School of Mines, South Kensington.

On completion of his studies at the latter, he entered his father's business in the early 'nineties. In 1895 he went to Holland to instruct Messrs. Verkade of Zaandam in the manufacture of nightlights. It was on this visit that he met his future wife—Miss Geertruida Verkade—who was the daughter of the head of the firm. They were married in 1898, by which time he had entered the service of Messrs. Chris. Thomas & Brothers, Ltd., soap manufacturers, of Bristol, who were commencing the manufacture of nightlights. In 1900 he joined Messrs. Capper Pass & Son, Ltd., smelters and refiners, of Bristol, of which firm he eventually became a Director and with which he remained until his death. On entering this business he speedily proved his adaptability, and became a first-class metallurgist, and many processes still in use owe their origin or improvement to his skill.

In his early years he was well known as an athelete, taking part successfully in more than one "National" cross-country run, besides winning many cycling races at Herne Hill and the Oval, and holding several cycling records.

To those who knew him well, his passing will leave a gap hard to fill, his affectionate disposition and unfailing courtesy and cheerfulness being his most endearing attributes. Mr. Fowler was elected a member of the Institute of Metals on September 8, 1924.

William Edward Gibbs, Ramsay Professor of Chemical Engineering in the University of London, died on January 18, 1934, at the early age of 44.

After graduating in 1909 with honours in chemistry from Liverpool University, he went to Singapore as assistant chemist to the Straits Trading Company, and his experience with this firm enabled him to develop on his return to England an electrolytic method of extracting tin from fused ores. He was granted his first patent for this process. Subsequently, he was assistant to Dr. G. D. Bengough, and carried on a year's research on the corrosion of brass condenser tubes by sea-water, the results of which were finally embodied in the Third Report to the Corrosion Committee of the Institute of Metals, published in 1916. He was far-sighted enough to realize the part that electrochemical phenomena play in corrosion processes, and included electrode potential measurements in his work. Aeration and temperature of the sea-water were also shown to play an important part. In 1914, he was appointed Special Lecturer in Metallurgy in the University of Liverpool.

After six months with the Aeronautical Inspection Department, Professor Gibbs was appointed Chief Chemist of the Government Rolling Mills at Southampton. The zinc oxide fumes from the brass foundry of these mills were very troublesome, and he found that, if waste steam were injected into this smoke, the steam condensed on the zinc oxide nuclei and caused them to coagulate.

The subject of dusts was enlarged by him in a book, published in 1924, on "Clouds and Smokes," dealing exhaustively with both the theoretical and practical aspects of his subject. Later, he wrote another book—"The Dust Hazard in Industry"—on dust explosions and poisonous or harmful smokes.

During the years 1918–1928, he was Chief Chemist of the Salt Union, Ltd., at Runcorn; and then went to the Department of Chemical Engineering at University College, London, which he developed until he brought it into the position of esteem in the world of applied science which it holds to-day. He found in teaching the vocation for which he was eminently fitted and his kindly personality endeared him to all who came into contact with him.

Professor Gibbs was elected a member of the Institute of Metals on March 21, 1917.

John Bright Hoblyn died very suddenly on December 24, 1933, at the Bute Nursing Home, in his 54th year.

He was born at Dewsbury in 1880, and was educated at Dewsbury Technical College. In 1897, he was awarded a Queen's prize in practical chemistry by the Board of Education, taking third place in England against many thousands of competitors older than himself. In 1898, he obtained Honours

Part I in practical inorganic chemistry in the Board of Education examination, and in 1899 obtained honours in organic chemistry under the same authority.

In 1901, he passed as Hinchcliffe exhibitioner to the Royal College of Science, University of London, and was first in England with First-Class Honours in Part II of the Board of Education examination in practical chemistry in 1903, and was again first with First-Class Honours Part II in theoretical chemistry in 1904, when he was also awarded the Associateship of the Royal College of Science in the first-class division in chemistry. He obtained the Associateship of the Institute of Chemistry in 1905 by examination and the Fellowship in 1912.

Mr. Hoblyn went to Luton in 1904 as Science Master of the Modern School, and after staying there for eleven years, became, at the express wish of the directors, Chief Chemist and Metallurgist of Vauxhall Motors, Ltd. This position he held until his death. In the course of his work, he became an authority on the technology of lubricating oils and perpetuated his name in the Hoblyn oxidation test.

Mr. Hoblyn was largely responsible for the inauguration of the Vauxhall Scientific Society, and was its President from 1918 to 1923. In 1917 he instituted a training scheme for apprentices at Vauxhall Motors, Ltd., the effect of which may be seen in a number of the training schemes of to-day. He also took a keen interest in local affairs, and was a co-opted member of the Public Libraries Committee, a representative of the County Council on the Board of Governors of Luton Modern and High Schools, and until recently he was also a member of the Local Employment Committee, which office, however, he resigned owing to ill health.

He was President of the old Lutonians' Club, and member of the Old Luton Modernians' Club and of the Imperial College of Freemasons, London. At the time of his death he was Chairman of the Committee of the Institution of Automobile Engineers dealing with the rationalization of British steels. He was also keenly interested in sport, and occasionally captained Vauxhall elevens.

Mr. Hoblyn was elected a member of the Institute of Metals on September 11, 1918.

Camille Matignon died suddenly on March 18, 1934, at the Collège de France.

He was born on January 3, 1867, and was educated at the religious houses of Troyes and St. Ouen, and at 19 entered the École Normale Supérieure. He left this after having obtained a science degree in 1889, to become, for four years, assistant to Marcelin Berthelot.

During this period, M. Matignon prepared his thesis for the degree of Doctor of Science, choosing the ureides as his subject. This paper he read in 1892. He also collaborated with Berthelot in thermochemical research, their joint work including the determination of the heats of formation of many fundamental substances such as water, carbon dioxide, methane, &c.

At 26, he became Maître de Conférences at Lille. He was subsequently appointed Maître de Conférences at the Sorbonne and assisted Berthelot with teaching. At 29 he was awarded the Jecker prize by the Académie des Sciences.

He was scarcely forty when he became a Master of Chemistry and was nominated to the chair of mineral chemistry at the Collège de France.

M. Matignon was an officer of the Légion d'Honneur, member of the Chemical Section of the Académie des Sciences in 1926, President of the Société Chimique de France since 1932, President of the Conseil d'Hygiène et de Salubrité Publique de la Seine, President of the Confédération des Sociétés Scientifiques Françaises, Vice-President of the Société de Chimie

Industrielle, and editor of the important industrial periodical *Chimie et Industrie.*

M. Matignon's scientific work is represented by more than 200 original papers, and he contributed more than 300 figures to the science of chemical energy: heat of fusion and of vaporization, direct reaction, specific heat, heats of solution, dilution, and neutralization. As each of his figures is the result of several measurements, the amount of work necessary for this contribution may readily be gauged. He was also responsible for two laws—the law of "Le Chatelier Matignon" dealing with the change in entropy of monovariant systems dissociating into a solid and a gaseous phase, and the "law of volatility," which is an application of the law of Berthollet to a solid system.

With Bourion he studied the rare metals and their compounds, particularly a general method for the preparation of the anhydrous chlorides, which has since become classic and which has been applied with success to the chlorides of the rare earths. An entirely new chemistry was thus created which resulted in the preparation of about 70 new compounds. We also owe to M. Matignon an important series of researches on the fixation of nitrogen and its compounds.

During the War, he was appointed a member of the Commission on Nitrogen, and in this capacity travelled to England, Italy, and Occupied Germany.

His work on nitrogen led to the perfecting of processes for the nitration of aluminium, the catalytic synthesis of ammonia, the preparation of carbamide from ammonia, of ammonium sulphate from gypsum, of the glycols, the action of water on methane, &c. He also made a study of special glass, as this was of interest to the French public health service.

In spite of all the honours bestowed on him, M. Matignon kept throughout his life his liking for simplicity. He was remarkable for his incisive powers of thought, and will always be to those who knew him the model of a noble scientist and a great Frenchman.

M. Matignon was elected a member of the Institute of Metals on February 15, 1934. HENRI MOUREU.

GRAND' UFF. ING. LUIGI ORLANDO, Cavaliere del Lavoro, passed away suddenly in Milan on November 1, 1933. He was born in Genoa in April, 1862, and went to Leghorn at a very early age. For the last fifteen years he lived in the metropolis of Lombardy.

He was the son of Senator Luigi Orlando, whose name is connected with the history of the Resurrection of Italy and who was the founder of the Cantieri Livornesi. A true captain of industry and a tireless worker, a great many of the industries of Tuscany owe to him their existence and their present thriving condition. It was in the field of metallurgy, however, that his work was specially remarkable, and the Società Metallurgica Italiana represents his most outstanding achievement. He became Managing Director of this company in 1902, and overcoming technical, financial, and business difficulties, he succeeded in raising it to the highest level of the industrial life of the country, making of it one of the most solid organizations. Side by side with the Metallurgica Italiana, and always in order to increase its development, Signor Orlando founded in Tuscany the Società Livornese for water conveyance, the Società Ligure-Toscana di Elettricita, the Sindicato di Assicurazione Mutua per gli infortuni sul Lavoro di Firenze; the Società Tubi Mannesmann of Lombardy, with works at Dalmine, the Società Importazione Metalli, the Società Metalli Lavorati e Porcellane, and several other less important companies.

During the War, he placed all the means he had available at the disposal of the National Defence; created fresh works and increased the efficiency of existing ones, in order to provide abundantly the munitions which Italy and the allies required.

At the time of his death he was Chairman of the Società Metallurgica Italiana, of the Società Metallurgica Bresciana già Tempini, Società Elettrica del Valdarno, the Società Litoranea Toscana, the Società Generale Industrie Metallurgiche, the Società G. B. Izar, the Società Metalli Lavorati e Porcellane, the Silurificio Whitehead of Fiume, and of the Ferrovia Alto Pistoiese. He was Managing Director of the Società Telefonica Tirrena, of the Società Romana di Elettricità, the Società Forze Idrauliche dell'Appennino Centrale, the Società Elte, the Società 'Edificio, the Società La Centrale for the financing of electrical undertakings, the Fondiaria Libica, the Colonie Alberto Lodolo, and of other lesser concerns. He was for many years the Managing Director of the Credito Italiano and of the Società del Tirso, of which, indeed, he was one of the founders. He was also Vice-Chairman of the Opera Nazionale Orfano di Guerra Anormali Psichici.

His passing is regretted by all who knew him.

Signor Orlando was elected a member of the Institute of Metals on February 15, 1934.

SUBJECTS INDEX.

Accounts, 20.
Adsorption of gases, 287.
Alloys,
  binary, castability, 48.
  constitution, investigation, appn. of castability test, 54.
  ternary, castability, 45.
Aluminium alloys,
  castability, 56.
  sand-cast bars, transverse tests, 89.
Aluminium–copper alloys,
  inverse segregation, effect of gases, 103.
  segregation, effect of gases, 103.
Annual General Meeting, 13.
Annual May Lecture, 285, 287.
Antimony–cadmium alloys, castability, 49.
Antimony–lead alloys, castability, 49.

Balance sheet, 20.
Beryllium–silver alloys,
  constitution, 161, 180.
  tarnish-resistance, 172, 176.
Bismuth–tin alloys, eutectic, extruded, viscous properties, 111.
Bismuth–tin–lead alloys, castability, 51.

Cadmium–antimony alloys, castability, 49.
Castability, definition, 45.
Castability of—
  Binary alloys, 48.
  Ternary alloys, 45.
Constitution, investigation, use of castability test, 54.
Copper–aluminium alloys,
  inverse segregation, effect of gases, 103.
  segregation, effect of gases, 103.
Copper–iron–silicon alloys, constitution, 229.
Copper–palladium alloys, transformations, 255.
Council,
  corresponding members to, 16.
  election, 22.
  report, 13.

Diffusion of—
  Zinc and iron at temps. below m.p. of zinc, 183.
Ductility of—
  Alloys of low elongation, measurement, 89.

Election of—
  Members, 23, 24, 285, 286.
  Officers, 22.
  Student members, 23, 24, 285, 286.
Eutectics, extruded, viscous properties, 111.
Extrusion of eutectics, 111.

Fatigue, influence of intercrystalline boundary, 193.

Gases and metal surfaces, 287.

Hardness, testing. See *Testing*.
Honorary Treasurer, report, 19.

Inverse segregation of—
  Aluminium–copper alloys, effect of gases, 103.
Iron and Steel Institute, collaboration with, 43.
Iron–copper–silicon alloys, constitution, 229.

Lead–antimony alloys, castability, 49.
Lead–tin alloys,
  eutectic, extruded, viscous properties, 111.
Lead–tin–bismuth alloys, castability, 51.
Library, 15.
Local Sections, programmes, 17.
London Meeting, 13.

Magnesium–nickel alloys, constitution, 275.
Malleability of—
  Monel metal, 145.
  Nickel, 145.
May Lecture, 285, 287.
Members,
  election, 23, 24, 285, 286.
  roll, 13.
Monel metal, malleability, 145.

Nickel, malleability, 145.
Nickel–magnesium alloys, constitution, 275.

Obituary notices, 313.
Officers, election, 22.

Palladium–copper alloys, transformations, 255.
Papers, writing, 31.
Plastic flow of—
  Soft metals, formulæ, 125.

President,
  Address, 26, 29.
  newly-elected, induction, 24.
  retiring, vote of thanks to, 25.

Research organizations, 36.
Roll of Institute, 13.

Scientific papers, writing, 31.
Segregation of—
  Aluminium–copper alloys, effect of gases, 103.
Silicon–copper–iron alloys, constitution, 229.
Silver–beryllium alloys,
  constitution, 161, 180.
  tarnish-resistance, 172, 176.
Silver Jubilee Fund, 14.
Student members, election, 23, 24, 285, 286.
Surfaces, metallic, gases and, 287.

Testing, hardness, Brinell and Diamond Pyramid, minimum dimensions of test-samples, 59.
Tin–lead alloys, eutectic, extruded, viscous properties, 111.
Tin–lead–bismuth alloys, castability, 51.
Treasurer, report, 19.

Viscosity of—
  Extruded eutectics, 111.
  Soft metals, formulæ, 125.

Zinc, diffusion of iron and, at temps. below m.p. of zinc, 183.

NAMES INDEX.

Aldous, C. W. *See* Hankins, G. A.

Allen, Clement Paul. Elected member, 23.

Allen, N. P. *Discussion* on "Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation," 106; *discussion on* "The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin," 138.

Andrew, J. H. Elected Member of Council, 22.

Archbutt, S. L. *Discussion on* "Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation," 109.

Armstrong, Denys George. Elected student member, 286.

Ashby, Cyril Lawrence George. Elected student member, 286.

Ashton, Arnold Broadbent. Elected student member, 24.

Atkinson, R. H. *Discussion on* "Alloys of Silver and Beryllium," 178.

Ayckbourn, Philip John. Elected member, 23.

Badock, Stanley Hugh. Elected member, 24.

Bailey, G. L. *Discussion on* "Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation," 108.

Bain, H. Foster. Elected member, 285.

Ball, Arthur Cyril. Elected member, 23.

Bastien, P. *See* Portevin, A.

Beddows, John Derek. Elected member, 24.

Bermann, Samuel. Elected member, 24.

Bews, William James Linklater. Elected member, 286.

Booth, Leonard Tranter. Elected student member, 23.

Bradley, Alan Ludwig. Elected student member, 286.

Brandt, Alfred. Elected member, 23.

Brown, Bernard. Elected student member, 24.

Brown, H. A. Elected Member of Council, 22.

Brownsdon, H. W. Elected Member of Council, 22; proposes vote of thanks to President for his address, 26.

Buckley, Frank. Elected student member, 285.

Bucknall, E. H. *Discussion on* "The Constitution of Copper–Iron–Silicon Alloys," 249; *discussion on* "The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin," 139.

Burkhardt, Arthur. Elected member, 24.

Burn, Robert Davidson. Elected member, 24.

Cartland, John. Seconds adoption of report of Council, 19.

Chadwick, R. *Discussion on* "The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin," 131

Chard, John Edwin. Elected student member, 285.

Cholewinski, Stanislaw. Elected member, 23.

Colman, Geoffrey William. Elected student member, 23.

Cook, Gilbert. *Discussion on* "A Note on Some Formulæ Concerning Viscous and Plastic Flow in Soft Metals," 134; *discussion on* "The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin," 134.

Cook, Maurice. *Discussion on* "Minimum Dimensions of Test Samples for Brinell and Diamond Pyramid Hardness Tests," 79.

Cowley, Charles Leonard Marshall. Elected student member, 23.

Cox, H. L. *See* Gough, H. J.

D'Auvigny, Henry. Elected member, 286.

Davies, Ernest Allen. Elected member, 286.

Desch, C. H. Moves vote of thanks to retiring President, 25; *discussion on* "A Study of the Influence of the Intercrystalline Boundary on Fatigue Characteristics," 224; *discussion on* "Alloys of Silver and Beryllium," 180; *discussion on* "Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation," 107; *discussion on* "The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin," 140.

Eatwell, Henry Thomas. Elected member, 23.

Elam, C. F. *Discussion on* " A Study of the Influence of the Intercrystalline Boundary on Fatigue Characteristics," 224.

Ellis, Owen W. *Paper :* **" The Malleability of Nickel and of Monel Metal,"** 145.

Ellis, Philip Meredith. Elected member, 23.

Evans, U. R. *Discussion on* " A Study of the Influence of the Intercrystalline Boundary on Fatigue Characteristics," 222.

Fell, E. W. *Paper :* **" A Note on Some Formulæ Concerning Viscous and Plastic Flow in Soft Metals,"** 125.

Forrest, George Kenneth. Elected student member, 286.

Fould, Maurice. Elected member, 23.

Fowler, (Sir) Henry. Induction of Dr. H. Moore as President, 24; reply to vote of thanks as retiring President, 25.

Fowler, Morris Broad. Obituary notice, 315.

Fry, John. Elected Honorary Treasurer, 22; report as Hon. Treasurer, 19.

Gayler, (Miss) Marie L. V. *Discussion on* " Some Alloys of Silver and Beryllium," 180; *discussion on* " The Constitution of Copper–Iron–Silicon Alloys," 251.

Gegg, Christopher Coghlan. Elected student member, 285.

Genders, R. *Discussion on* " Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation," 107.

Gibbs, William Edwards. Obituary notice, 316.

Gough, H. J., Cox, H. L., and Sopwith, D. G. *Paper :* **" A Study of the Influence of the Intercrystalline Boundary on Fatigue Characteristics,"** 193.

Grant, Ivan Stanley. Elected member, 23.

Gray, Kenneth. Elected Member of Council, 22.

Greenwood, Hubert. Elected student member, 24.

Greer, H. H. A. Elected Member of Council, 22.

Grogan, J. D. *See* Phillips, C. E.

Gwyer, A. G. C. Elected Vice-President, 22; *discussion on* " Minimum Dimensions of Test Samples for Brinell and Diamond Pyramid Hardness Tests," 80; *discussion on* "Transverse Tests on Sand-Cast Aluminium Alloy Bars," 99.

Haigh, B. P. *Discussion on* " A Study of the Influence of the Intercrystalline Boundary on Fatigue Characteristics," 223; *discussion on* " The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin," 137.

Hallowes, Arthur Patrick Collis. Elected student member, 285.

Hankins, G. A., and Aldous, C. W. *Paper :* **" Minimum Dimensions of Test Samples for Brinell and Diamond Pyramid Hardness Tests,"** 59.

Hanson, D. Elected Vice-President, 22; *discussion on* " A Study of the Influence of the Intercrystalline Boundary on Fatigue Characteristics," 220; *discussion on* " Minimum Dimensions of Test Samples for Brinell and Diamond Pyramid Hardness Tests," 82; *discussion on* " Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation," 107.

Hanson, D., and West, E. G. *Paper :* **" The Constitution of Copper–Iron–Silicon Alloys,"** 229.

Hargreaves, F. *Discussion on* " A Note on Some Formulæ Concerning Viscous and Plastic Flow in Soft Metals," 136; *discussion on* " A Study of the Influence of the Intercrystalline Boundary on Fatigue Characteristics, 225; *discussion on* " The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin," 136.

Harris, Jacob Henry. Elected student member, 285.

Harrison, Stanley Taylor. Elected student member, 24.

Hartigan, Thomas Joseph. Elected member, 23.

Haughton, John L. Elected Member of Council, 22; seconds vote of thanks to President for his address, 26; *discussion on* " The Constitution of Copper–Iron–Silicon Alloys," 249; *discussion on* " Transformations in the Copper–Palladium Alloys," 272.

Haughton, John L., and Payne, Ronald J. M. *Paper :* **" Alloys of Magnesium Research. Part I.—The Constitution of the Magnesium-Rich Alloys of Magnesium and Nickel,"** 275.

Hauser, Alexander. Elected member, 285.

Hayes, Joseph. Elected member, 285.

Hedges, Ernest Sydney. Elected member, 23.

Hilt, Eugene Henry Hugh. Elected member, 23.

Hoar, Thomas Percy. Elected member, 23.
Hoblyn, Edward Henry Treffry. Elected member, 285.
Hoblyn, John Bright. Obituary notice, 316.
Hoesen, Henry B. Van. Elected member, 285.
Homer, Charles Egbert. Elected student member, 24.
Hopkins, Norman Maynard. Elected student member, 285.
Hora, John Marcel Raymond. Elected student member, 285.
Humphreys, William Gerald. Elected member, 23.
Hutton, R. S. Elected Member of Council, 22; *discussion on* "Alloys of Silver and Beryllium," 176, 179.

Jacques, Arthur. Elected student member, 23.
Jacques, Frank. Elected member, 286.
Jenkins, John Ephraim. Elected student member, 24.
Jones, W. D. *Correspondence on* "The Diffusion of Zinc and Iron at Temperatures below the Melting Point of Zinc," 191.

Kamienski, Erwin. Elected member, 23.
Keeble, Hubert William. Elected student member, 285.
Kerr, Robert. Elected member, 23.
Kirsebom, Gustaf Newton. Elected member, 286.

Lancaster, H. C. Elected Vice-President, 22; seconds vote of thanks to retiring President, 25.
Lewis, Philip Stacey. Elected member, 23.
Lodder, Leslie Arthur John. Elected member, 285.
Louyot, Robert. Elected member, 23.

Mace, Cyril William. Elected student member, 23.
McFarland, David Ford. Elected member, 24.
MacGregor, Ian Kinloch. Elected student member, 285.
McIntosh, Alexander Benjamin. Elected student member, 285.
Matignon, Camille. Elected member, 24; obituary notice, 317.
Mazzola, Mario. Elected member, 24.
Mehl, Robert Franklin. Elected member, 24.
Meikle, G. *Discussion on* "Transverse Tests on Sand-Cast Aluminium Alloy Bars," 99.
Melvin, (Sir) Martin J. Elected member, 23.
Mitchinson, Robert. Elected member, 24.
Moore, Harold. Elected President, 22; moves adoption of report of Council, 19; **Presidential Address**, 29; reply to vote of thanks for Presidential address, 26; *discussion on* "Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation," 109; *discussion on* "Transverse Tests on Sand-Cast Aluminium Alloy Bars," 100.
Morcom, E. L. Elected Vice-President, 22.
Morris, Roland William. Elected member, 24.
Mukumoto, Wasaburow. Elected member, 24.
Mundey, A. H. Seconds adoption of report of Hon. Treasurer, 22.
Murphy, A. J. *Paper:* **"The Constitution of Copper–Iron–Silicon Alloys,"** 250.

Nagao, Takeo. Elected member, 23.
Neave, Digby Percy Cornwall. Elected member, 23.
Nicosia, Beniamino. Elected member, 23.

Orlando, Luigi. Obituary notice, 318.
Orlando, Salvatore. Elected member, 24.
Orr, Hazlett Francis. Elected student member, 23.

Payne, Ronald J. M. *See* Haughton, John L.
Pearce, J. G. *Correspondence on* "Transverse Tests on Sand-Cast Aluminium Alloy Bars," 101.
Pearson, C. E. *Paper:* **"The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin,"** 111.
Phillips, C. E., and Grogan, J. D. *Paper:* **"Transverse Tests on Sand-Cast Aluminium Alloy Bars,"** 89.
Portevin, Albert. *Correspondence on* "Minimum Dimensions of Test Samples for Brinell and Diamond Pyramid Hardness Tests," 85.
Portevin, Albert, and Bastien, P. *Paper:* **"Castability of Ternary Alloys,"** 45.
Priestman, Robert Thomas. Elected member, 23.

Rao, Mannigay Umanath. Elected member, 23.

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

Readman, John Abercromby. Elected student member, 286.
Rice-Oxley, Francis Bowyer. Elected member, 286.
Rideal, E. K. *May Lecture :* **" Gases and Metal Surfaces,"** 287.
Rigg, Gilbert. *Paper :* **" The Diffusion of Zinc and Iron at Temperatures below the Melting Point of Zinc,"** 183.
Robinson, John Herbert. Elected student member, 23.
Rosenhain, Walter. Message of sympathy, 26; obituary notice, 313.
Rouppe van der Voort, Paulus Nicolaas Franciscus Maria. Elected member, 23.

Sallitt, William Baines. Elected student member, 286.
Sanders, Alexander. Elected member, 286.
Savage, Herbert. Elected member, 285.
Schirner, Karl. Elected member, 23.
Schneckenburger, Emil. Elected member, 23.
Schneider, William George. Elected member, 285.
Shao, Chia Chin. Elected member, 24.
Siff, Alfred. Elected member, 24.
Simpson, Joseph Gordon. Elected member, 23.
Slater, Horace. Elected member, 24.
Slater, I. G. *Paper :* **" Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation,"** 103.
Sloman, H. A. *Paper :* **" Alloys of Silver and Beryllium,"** 161.
Smith, Cyril S. *Discussion on* " The Constitution of Copper–Iron–Silicon Alloys," 251.
Smith, R. L. *Discussion on* " Minimum Dimensions of Test Samples for Brinell and Diamond Pyramid Hardness Tests," 81.
Smith, S. W. *Discussion on* " Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation," 108.
Smithells, C. J. *Discussion on* " Alloys of Silver and Beryllium," 178.
Sopwith, D. G. *See* Gough, H. J.
Storke, Arthur Ditchfield. Elected member, 24.
Strauss, Kossy. Elected member, 24.
Stringer, Richard Alfred. Elected member, 24.
Summerhill, Gordon Charles. Elected member 23.
Sutton, H. *Discussion on* " A Study of the Influence of the Intercrystalline Boundary on Fatigue Characteristics," 222; *discussion on* " Transverse Tests on Sand-Cast Aluminium Alloy Bars," 99.

Taylor, R. *Paper :* **" Transformations in the Copper–Palladium Alloys,"** 255.
Thomas, Ivor Henry. Elected student member, 23.
Thomas, Ronald Charles William. Elected student member, 23.
Timms, William. Elected student member, 24.
Tolliday, Joseph Ernest. Elected member, 23.
Turner, T. Moves adoption of report of Hon. Treasurer, 22; *discussion on* " Note on the Influence of Gases in an 8 per Cent. Copper–Aluminium Alloy on Normal and Inverse Segregation," 106; *discussion on* " The Viscous Properties of Extruded Eutectic Alloys of Lead–Tin and Bismuth–Tin," 139.
Turner, T. H. *Discussion on* "Minimum Dimensions of Test Samples for Brinell and Diamond Pyramid Hardness Tests," 82.

Van Hoesen. *See* Hoesen.
Vernon, W. H. J. *Discussion on* " Alloys of Silver and Beryllium," 179.
Voce, E. *Discussion on* " The Constitution of Copper–Iron–Silicon Alloys," 251.
Von Zeerleder. *See* Zeerleder.
Vowles, Charles D. Elected member, 23.

Waddington, John. Elected student member, 24.
Warrington, Harold George. Elected member, 24.
Welsh, William Cameron. Elected member, 286.
West, E. G. *See* Hanson, D.
Whitworth-Jones, Henry Lewis. Elected student member, 286.
Williams, Leslie Ballesat. Elected member, 23.
Williams, Noel Ignace Bond. Elected student member, 23.
Wood, Ernest. Elected member, 285.

Yarrow, Colin Drake. Elected student member, 23.

Zacco, Henrik Yngve. Elected member, 23.
v. Zeerleder, A. *Discussion on* " Castability of Ternary Alloys," 56.
Zwanzig, Walter. Elected member, 286.

Printed in Great Britain by
Richard Clay & Sons, Limited,
BUNGAY, SUFFOLK.

BIBLIOTEKA GŁÓWNA
Politechniki Śląskiej

P 99/34/I