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P.99/LXXXI

The Journal of the

INSTITUTE OF METALS

1952–53, Vol. 81, Prelims, Proceedings, Discussions, and Name Index

Bulletin of the

INSTITUTE OF METALS

1951–53, Vol. 1, Prelims, Name and Subject Indexes

METALLURGICAL ABSTRACTS

1952–53, Vol. 20, Prelims, Abstracts Part 13, and Name and Subject Indexes

THE JOURNAL OF THE INSTITUTE OF METALS

VOLUME LXXXI
1952–53

EDITOR

N. B. VAUGHAN, M.Sc.

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LONDON
PUBLISHED BY THE INSTITUTE OF METALS
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1484.	**Effect of Composition and Heat-Treatment on Yield-Point Phenomena in Aluminium Alloys.** By V. A. Phillips, A.R.S.M., D.Eng., B.Sc., A.I.M.	649	751
1485.	**Growth of Sulphide Films on Copper.** By T. P. Hoar, M.A., Ph.D., F.I.M., and A. J. P. Tucker, M.A., Ph.D.	665	763
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THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS

GENERAL MEETING

8 January 1953

A GENERAL MEETING of the Institute of Metals was held in the University, Edgbaston, Birmingham, on Thursday, 8 January 1953. The Chair was taken by Mr. J. W. THOMAS, Chairman of the Metallurgical Engineering Committee.

Before the meeting members paid a visit to the Aitchison Laboratories, by invitation of Professor A. J. MURPHY.

INFORMAL DISCUSSION ON "ROLLS AND THEIR MAINTENANCE IN THE NON-FERROUS METALS INDUSTRY"

The discussion was opened by Mr. W. H. BOWMAN, Mr. S. G. TEMPLE, and Mr. L. S. D. SMITH. Numerous contributions were made, a summary of which is published in the *Bulletin*, 1951–53, vol. 1, pp. 199–202 (May 1953).

At the conclusion of the meeting, votes of thanks were passed to the University authorities for permission to use the Chemistry Lecture Theatre for the meeting, and to Professor A. J. Murphy for his invitation to members to visit the Aitchison Laboratories.

ANNUAL GENERAL MEETING

THE FORTY-FIFTH ANNUAL GENERAL MEETING of the Institute of Metals was held in London from Monday to Thursday, 23–26 March 1953.

Monday, 23 March

MAY LECTURE

The Forty-Third May Lecture was delivered by Sir CHRISTOPHER HINTON, M.A., M.I.C.E., M.I.Mech.E., Deputy Controller of Atomic Energy (Production), Ministry of Supply, on "The Present and Future Metallurgical Requirements of the Chemical Engineer," in the Lecture Theatre of the Royal Institution, Albemarle Street, London, W.1., at 6.0 p.m. The President, Dr. C. J. SMITHELLS, M.C., occupied the Chair.

At the conclusion, Dr. N. P. INGLIS, M.Eng., Member of Council, proposed a hearty vote of thanks to Sir Christopher Hinton for his lecture, which is printed on pp. 465–470 of this volume of the *Journal*.

In the evening, the Council entertained Sir Christopher Hinton to dinner at the United Service Club, Pall Mall, S.W.1.

Tuesday, 24 March

The meeting was resumed at the Park Lane Hotel, Piccadilly, W.1, at 10.30 a.m. The retiring President, Dr. C. J. SMITHELLS, M.C., occupied the Chair at the opening of the meeting.

The Chairman welcomed members and visitors attending the meeting from overseas.

The minutes of the previous General Meetings, held in London on 19 November 1952 and in Birmingham on 8 January 1953, were taken as read and signed by the Chairman.

ELECTIONS OF ORDINARY MEMBERS, JUNIOR MEMBERS, AND STUDENT MEMBERS

The SECRETARY (Lieut.-Colonel S. C. GUILLAN, T.D.) announced that since the Annual Autumn Meeting held in Oxford in September 1952, a total of 215 Ordinary Members, Junior Members, and Student Members had been elected on 12 October, 19 November, 12 December, and 31 December 1952, and 15 January, 13 February, 25 February, and 23 March 1953, the lists of whose names are printed in the *Bulletin*, 1951–53, vol. 1, pp. 129, 136, 142, 173, 183, 184, and 194.

REPORT OF COUNCIL FOR THE YEAR ENDED 31 DECEMBER 1952

The CHAIRMAN moved, Professor HUGH FORD seconded, and there was carried unanimously, a motion for the adoption of the Report of Council for the Year Ended 31 December 1952, which is printed on pp. 315–324 of this volume of the *Journal*.

REPORT OF THE HONORARY TREASURER FOR THE FINANCIAL YEAR ENDED 30 JUNE 1952

In the absence of the Honorary Treasurer, Mr. E. A. BOLTON, M.Sc. (Member of Council), presented the Report of the Honorary Treasurer and the accounts for the financial year ended 30 June 1952, and moved their adoption. Mr. A. B. GRAHAM (Vice-President) seconded the motion, which was carried unanimously.

The Report and accounts are printed in this volume of the *Journal*, pp. 325–328.

RE-ELECTION OF AUDITORS

It was proposed, seconded, and carried unanimously that Messrs. Poppleton and Appleby be re-elected auditors to the Institute for the year 1953–54.

ELECTION OF OFFICERS FOR 1953–54

The SECRETARY announced that the following officers had been elected to fill vacancies on the Council for the year 1953–54:

President:

Professor F. C. THOMPSON, D.Met., M.Sc.

Vice-Presidents:

Major C. J. P. BALL, D.S.O., M.C.
Professor G. V. RAYNOR, M.A., D.Phil., D.Sc.

Ordinary Members of Council:

W. A. BAKER, B.Sc.
J. C. COLQUHOUN, M.B.E.
E. R. GADD
The Hon. JOHN GRIMSTON, M.P.

SENIOR VICE-PRESIDENT FOR 1953–54

The SECRETARY announced that the Council had elected Dr. S. F. DOREY, C.B.E., F.R.S., to be Senior Vice-President for 1953–54, and that he would be its next nominee for the Presidency.

VOTE OF THANKS TO RETIRING OFFICERS

Professor A. J. MURPHY, M.Sc. (Past-President) proposed, Dr. E. G. WEST seconded, and there was carried with acclamation a hearty vote of thanks to the following retiring officers for their services on the Council: Sir Arthur Smout, J.P.,

Past-President; Professor H. O'Neill, D.Sc., M.Met., Vice-President; and Mr. E. A. Bolton, M.Sc., Mr. C. H. Davy, and Professor A. G. Quarrell, D.Sc., Ph.D., A.R.C.S., D.I.C., Ordinary Members of Council.

Induction of the New President

The Chairman (Dr. C. J. Smithells, M.C.) then introduced the new President, Professor F. C. Thompson, D.Met., M.Sc., and inducted him into the Chair.

Vote of Thanks to the Retiring President

Dr. L. B. Pfeil, F.R.S. (Member of Council) proposed, Professor H. O'Neill, D.Sc., M.Met., seconded, and there was carried with acclamation a hearty vote of thanks to the retiring President, Dr. C. J. Smithells, M.C. Dr. Smithells briefly responded.

Presidential Address

Professor F. C. Thompson, D.Met., M.Sc., then delivered his Presidential Address, which is printed on pp. 401–405 of this volume of the *Journal*.

A vote of thanks to the President for his Address was moved by Dr. J. W. Cuthbertson, seconded by Dr. Ivor Jenkins (Member of Council), and carried with acclamation.

Institute of Metals (Platinum) Medal

The Secretary announced that the Institute of Metals (Platinum) Medal for 1953 had been awarded to Professor Georg Masing, Dr.phil., Dr.Ing.e.h., of the Institut für allgemeine Metallkunde, Universität Göttingen, in recognition of his outstanding contributions in the field of metallography.

Professor Masing was unable to be present at the meeting to receive the medal.

Rosenhain Medal

The Secretary announced that the Rosenhain Medal for 1953 had been awarded to Dr. Charles Eric Ransley, of the Research Laboratories, The British Aluminium Co., Ltd., Gerrards Cross, in recognition of his outstanding experimental and theoretical work on gas–metal equilibria. The President then presented the medal to Dr. Ransley.

W. H. A. Robertson Medal

The Secretary announced that the W. H. A. Robertson Medal for 1952 had been awarded to Mr. John Francis Waight, of the West Midlands Gas Board, for his paper on "Gas Equipment for the Thermal Treatment of Non-Ferrous Metals and Alloys" (*Journal*, 1951–52, vol. 80, pp. 269–285). The President then presented the medal to Mr. Waight.

Students' Essay Prizes

The Secretary announced that as a result of the 1952 Students' Essay Competition, prizes had been awarded to Mr. R. D. Stacey, of the University of Birmingham, for an essay on "Some Experimental Evidence for Dislocations" and to Mr. G. Thomas, B.Sc., of Cambridge University, for an essay on "Martensitic Transformations in Non-Ferrous Metals and Alloys". The President then presented the prizes.

Discussion of Papers

The meeting was resumed in the afternoon at the Park Lane Hotel, when the President, Professor F. C. Thompson, D.Met., M.Sc., occupied the Chair.

A joint discussion was held on the following two papers, which had previously been published in the *Journal*:

"The Effect of Certain Solute Elements on the Recrystallization of Copper," by V. A. Phillips, A.R.S.M., B.Sc., D.Eng., A.I.M., and Arthur Phillips, D.Eng.

"Segregation of Iron and Phosphorus at the Grain Boundaries in 70 : 30 Brass During Grain Growth," by H. M. Miekk-oja, Sc.D.

Young's Modulus of Alloys

A discussion then took place on the theme "Young's Modulus of Alloys", based on the following papers published in the *Journal*:

"A Study of Some Factors Influencing the Young's Modulus of Solid Solutions", by A. D. N. Smith, B.A.

"The Young's Modulus, Poisson's Ratio, and Rigidity Modulus of Some Aluminium Alloys", by N. Dudzinski, Dipl.Ing.

At the conclusion of each discussion a vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

Dinner and Dance

In the evening a dinner and dance was held at the Park Lane Hotel.

Wednesday, 25 March

At the resumed meeting, at 10.30 a.m. at the Park Lane Hotel, Piccadilly, W.1, two concurrent scientific sessions were held: (i) an all-day Symposium on "The Control of Quality in the Production of Wrought Non-Ferrous Metals and Alloys". Part I.: "The Control of Quality in Melting and Casting" and (ii) discussions on other papers previously published in the *Journal*.

Symposium on "The Control of Quality in the Production of Wrought Non-Ferrous Metals and Alloys". Part I.: "The Control of Quality in Melting and Casting".

At the morning session the Chair was taken by the President, Professor F. C. Thompson, D.Met., M.Sc.

Mr. N. I. Bond-Williams, B.Sc. (Member of Council) as rapporteur, introduced the following six papers (see this volume, pp. 329–400) which had been contributed to the Symposium.

In the afternoon, the Chair was taken by Mr. W. J. Thomas, Chairman of the Metallurgical Engineering Committee.

There was an all-day discussion, a report of which is printed on pp. 701–712 of this volume of the *Journal*.

"The Principles of Technical Control in Metallurgical Manufacture", by A. R. E. Singer, B.Sc., Ph.D.

"The Control of Quality in the Production of Brass Ingots and Billets", by Maurice Cook, D.Sc., Ph.D., F.I.M., and C. L. M. Cowley, B.Sc., A.I.M.

"The Control of Quality in Melting and Casting Copper and High-Conductivity Copper-Base Alloys", by J. Sykes, F.I.M.

"The Control of Quality in the Casting of Zinc and Zinc Alloy Rolling Slabs and Extrusion Billets", by C. W. Roberts, B.Sc., A.I.M., and B. Walters, M.A.

"The Control of Quality in the Melting and Casting of Aluminium Alloys for Working", by R. T. Staples and H. J. Hurst.

"The Control of Quality in Melting and Casting Magnesium Alloys for Hot Working", by R. G. Wilkinson, B.Sc., and S. B. Hirst, B.Sc.Tech.

At the conclusion of the Symposium, a vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

Discussion of Other Scientific Papers

At the morning session, the Chair was taken by Dr. L. B. Pfeil, F.R.S. (Member of Council).

Discussions took place based on two groups of papers.

Corrosion of Alloys

"The Effect of Cold Work on the Microstructure and Corrosion-Resistance of Aluminium–5% Magnesium Alloys Containing 0–1% Zinc", by P. Brenner, Dr. Ing., and G. J. Metcalfe, M.Sc.Tech.

"Atmospheric Corrosion and Stress-Corrosion of Aluminium–Copper–Magnesium and Aluminium–Magnesium–Silicon Alloys in the Fully Heat-Treated Condition", by G. J. Metcalfe, M.Sc.Tech.

"Intercrystalline Corrosion in Cast Zinc–Aluminium Alloys", by C. W. Roberts, B.Sc., A.I.M.

High-Temperature Oxidation of Alloys

"The High-Temperature Oxidation of Some Cobalt-Base and Nickel-Base Alloys", by A. Preece, M.Sc., F.I.M., and G. Lucas, Ph.D.

"High-Temperature Oxidation Characteristics of a Group of Oxidation-Resistant Copper-Base Alloys", by J. P. Dennison, Ph.D., B.Sc., and A. Preece, M.Sc., F.I.M.

At the conclusion of each discussion a vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

At the afternoon session, the Chair was taken by Mr. G. L. Bailey, C.B.E., M.Sc. (Vice-President).

Creep and Plastic Deformation

A general discussion took place based on the following 16 papers which had previously been published in the *Journal*:

"The Effect of Grain-Size on the Structural Changes Produced in Aluminium by Slow Deformation", by W. A. Rachinger, M.Sc.

"Stress-Recovery in Aluminium", by W. A. Wood, D.Sc., and J. W. Suiter, B.Sc.

"Creep Processes in Coarse-Grained Aluminium", by D. McLean, B.Sc.

"Electron-Microscopic Studies of Slip in Aluminium During Creep", by J. Trotter.

"Boundary Slip in Bicrystals of Tin", by K. E. Puttick, B.Sc., and R. King, B.Sc.

"X-Ray Diffraction Studies in Relation to Creep", by G. D. Greenough, Ph.D., (Mrs.) Catherine M. Bateman, B.Sc., and (Mrs.) Edna M. Smith, B.A.

"Relative Grain Translations in the Plastic Flow of Aluminium", by W. A. Rachinger, M.Sc.

"The Recovery of Polycrystalline Aluminium", by J. A. Ramsey, M.Sc.

"The Creep/Time Relationship under Constant Tensile Stress", by S. Bhattacharya, B.Sc., Ph.D., W. K. A. Congreve, B.A.Sc., Ph.D., and F. C. Thompson, D.Met., M.Sc.

"The Temperature-Dependence of Transient and Secondary Creep of an Aluminium Alloy to British Standard 2L42 at Temperatures Between 20° and 250° C. and at Constant Stress", by A. E. Johnson, D.Sc., M.Sc.Tech., M.I.Mech.E., and N. E. Frost, B.Sc., A.M.I.Mech.E.

"Crystal Slip in Aluminium During Creep", by D. McLean, B.Sc.

"Plastic Deformation of Coarse-Grained Aluminium", by (Mrs.) V. M. Urie, B.Sc., and H. L. Wain, B.Met.E.

"Deformation of Magnesium at Various Rates and Temperatures", by J. W. Suiter, B.Sc., and W. A. Wood, D.Sc.

"The Sub-Grain Structure in Aluminium Deformed at Elevated Temperatures", by J. A. Ramsey, M.Sc.

"Crystal Fragmentation in Aluminium During Creep", by D. McLean, B.Sc.

"Grain-Boundary Slip During Creep of Aluminium", by D. McLean, B.Sc.

At the conclusion of the discussion, a vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

Conversazione and Exhibition

In the evening a conversazione and exhibition was held at the Institute's Headquarters, 4 Grosvenor Gardens, London, S.W.1.

Thursday, 26 March

Informal Discussion on "Liquid Metals"

The meeting was resumed at 10.0 a.m. at the Park Lane Hotel, Piccadilly, W.1, when the President, Professor F. C. Thompson, D.Met., M.Sc., occupied the Chair.

An Informal discussion took place on "Liquid Metals", introduced by Dr. V. Kondic and Dr. B. R. T. Frost, which concluded at 12.30 p.m.

Visits to Works and Laboratories

Visits were paid to the following works and laboratories:
The British Non-Ferrous Metals Research Association, Euston Street, London, N.W.1.
Hoover, Ltd., Greenford.
The Pyrene Co., Ltd., Brentford.
Vickers-Armstrongs, Ltd., Weybridge.

The meeting then concluded.

ANNUAL AUTUMN MEETING

The Forty-Fifth Annual Autumn Meeting of the Institute of Metals was held in Southport from Monday to Friday, 21–25 September 1953.

Monday, 21 September

A General Meeting was held at the Town Hall, Lord Street, Southport, at 6.30 p.m., the Chair being taken by the President, Professor F. C. Thompson, D.Met., M.Sc.

The Chairman welcomed members, ladies, and delegates attending the meeting from overseas.

The minutes of the previous general Meeting, held in London from 23 to 26 March 1953, were taken as read and signed by the Chairman.

Elections of Ordinary Members, Junior Members, and Student Members

The Secretary (Lieut.-Colonel S. C. Guillan, T.D.) announced that since the last General Meeting held in London in March 1953, a total of 188 Ordinary Members, Junior Members, and Student Members had been elected on 14 April, 30 April, 19 May, 12 June, 30 June, 24 August, and 8 September 1953, lists of whose names are printed in the *Bulletin*, 1951–53, vol. 1, pp. 207, 213, 222, and 223, and 1953–54, vol. 2, pp. 12 and 13.

Election of Officers for 1954–55

The Secretary announced that the following members would retire from the Council at the 1954 Annual General Meeting, as required by the Articles of Association:

President:

Professor F. C. Thompson, D.Met., M.Sc.

Past-President:

H. S. Tasker, B.A.

Vice-Presidents:

A. B. Graham
P. V. Hunter, C.B.E.

Ordinary Member of Council:

L. B. Pfeil, O.B.E., D.Sc., A.R.S.M., F.R.S.

He stated that, in accordance with the Articles of Association, Professor F. C. Thompson, D.Met., M.Sc., would fill the

vacancy as Past-President and that, in accordance with Article 22, the Council had nominated the following members to fill the other vacancies :

As President :

S. F. Dorey, C.B.E., D.Sc., F.R.S.

As Vice-Presidents :

Maurice Cook, D.Sc., Ph.D.
L. B. Pfeil, O.B.E., D.Sc., A.R.S.M., F.R.S.
Major P. Litherland Teed, A.R.S.M.

As Ordinary Members of Council :

R. D. Hamer, B.Sc., Dipl.Ing.
G. P. Tinker, M.Sc.

He reminded members of their rights, under Article 22, to make other nominations, if desired, before the conclusion of the meeting.

Senior Vice-President for 1954–55

The Secretary announced that, in accordance with Article 42, the Council had elected Dr. Maurice Cook as Senior Vice-President for 1954–55, and that he would be their nominee for the Presidency in 1955–56.

Autumn Lecture

The Chairman introduced Dr. Maurice Cook, who delivered the Twenty-Fourth Autumn Lecture on " The New Metal Titanium ". At the conclusion of the lecture, a hearty vote of thanks to Dr. Cook was proposed by Mr. G. L. Bailey, C.B.E., M.Sc. (Vice-President) and carried with acclamation. The lecture was printed in the *Journal*, 1953–54, **82**, 93–106.

Tuesday, 22 September

Welcome to Southport

The meeting was resumed at 9.30 a.m. in the Town Hall, Southport, when the Chair was taken by Lieut.-Commander G. K. Rylands, O.B.E., J.P., R.N. (retd.), Chairman of the Reception Committee.

His Worship the Mayor of Southport (Alderman William Tattersall, J.P.), and Lieut.-Commander Rylands welcomed members and their ladies to Southport on behalf of the Town and the Reception Committee, respectively. Mr. W. B. Wragge, B.Sc. (President of the Manchester Metallurgical Society) also welcomed members and ladies on behalf of the host Societies—the Manchester Metallurgical Society and the Liverpool Metallurgical Society. The President, Professor F. C. Thompson, D.Met., M.Sc., replied.

The meeting was then briefly adjourned until 9.50 a.m. when two concurrent scientific sessions took place.

Discussion of Papers

At Session A, Dr. C. J. Smithells, M.C. (Past-President) occupied the Chair, and a general discussion was held based on the following group of papers published in the *Journal* :

Stretcher-Strain Markings

" Some Observations on the Occurrence of Stretcher-Strain Markings in an Aluminium–Magnesium Alloy ", by R. Chadwick, M.A., F.R.I.C., F.I.M., and W. H. L. Hooper, B.Sc., A.I.M.

" The Influence of Composition on the Incidence of Strain Markings in Aluminium Alloys ", by W. H. L. Hooper, B.Sc., A.I.M.

" The Stepped Stress/Strain Curve of Some Aluminium Alloys ", by N. Krupnik, D.I.C., and H. Ford, D.Sc., Ph.D.

" Discontinuous Flow and Strain-Ageing in a 6% Tin Phosphor-Bronze ", by N. H. Polakowski, Dipl.Ing., Ph.D.

" Yield-Point Phenomena and Stretcher-Strain Markings in Aluminium–Magnesium Alloys ", by V. A. Phillips, A.R.S.M., D.Eng., B.Sc., A.I.M., A. J. Swain, M.A., and R. Eborall, M.A.

" Some Methods of Measuring Surface Topography as Applied to Stretcher-Strain Markings on Metal Sheet ", by W. H. L. Hooper, B.Sc., A.I.M., and J. Holden, Ph.D.

" Effect of Composition and Heat-Treatment on Yield-Point Phenomena in Aluminium Alloys ", by V. A. Phillips, A.R.S.M., D.Eng., B.Sc., A.I.M.

The following paper was then discussed :

" Priming Paints for Light Alloys ", by J. G. Rigg, Ph.D., and E. W. Skerrey, B.Sc., A.I.M.

At the conclusion of each discussion a vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

At Session B, the Chair was taken by Mr. G. L. Bailey, C.B.E., M.Sc. (Vice-President) and two groups of papers were discussed :

Oxidation and Sulphidation of Copper

" The Oxidation of Copper in the Temperature Range 200°–800° C.", by R. F. Tylecote, M.A., M.Sc., Ph.D., F.I.M.

" Growth of Sulphide Films on Copper ", by T. P. Hoar, M.A., Ph.D., F.I.M., and A. J. P. Tucker, M.A., Ph.D.

Diffusion and the Kirkendall Effect

" Micrographic Aspects of the Diffusion of Zinc and Aluminium in Copper ", by H. Bückle, Dr.Ing., and J. Blin.

" The Formation of Intracrystalline Voids in Solution-Treated Magnesium–Aluminium Alloys ", by E. Lardner, B.Sc., A.I.M.

At the conclusion of each discussion a vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

Visits

In the afternoon, visits were paid by members to the works of : Automatic Telephone and Electric Co., Ltd., Liverpool; British Insulated Callender's Cables, Ltd., and British Copper Refiners, Ltd., Prescot; The English Electric Co., Ltd., Liverpool; Fibreglass, Ltd., St. Helens; The Manganese Bronze and Brass Co., Ltd., Birkenhead; D. Napier and Son, Ltd., Liverpool; and Pilkington Brothers, Ltd., St. Helens. Other members and ladies paid visits to the works of Horrockses Crewdson Spinning and Manufacturing Co., Ltd., Preston; Liverpool Cathedral; and Speke Hall, Liverpool.

Civic Reception

In the evening, members and ladies were the guests of the Mayor and Corporation of Southport at a Civic Reception in the Town Hall.

Wednesday, 23 September

Visits

Members and ladies paid all-day visits to places distant from Southport, as follows :

(i) The Lancashire Steel Corporation, Ltd., Irlam, and Rylands Brothers, Ltd., Warrington.

(ii) Ministry of Supply, Division of Atomic Energy (Production), Metallurgical Laboratories, Culcheth, and The British Aluminium Co., Ltd., Warrington.

(iii) John Summers and Sons, Ltd., Shotton.

(iv) Metropolitan-Vickers Electrical Co., Ltd., Trafford Park, and Magnesium Elektron, Ltd., Clifton Junction.

(v) Richard Johnson and Nephew, Ltd., Manchester, and Leyland Motors, Ltd., Leyland.

(vi) Thornton Research Centre, The Shell Petroleum Co., Ltd., Thornton-le-Moors, and the Stanlow Refinery of the Shell Refining and Marketing Co., Ltd.

(vii) The City of Chester and Lever Brothers, Ltd., Port Sunlight.

Banquet

In the evening, members and their ladies were the guests of the Reception Committee at a Banquet and Dance at the Prince of Wales Hotel, Southport.

Thursday, 24 September

The meeting was resumed in the Town Hall, Southport, at 9.45 a.m., when two concurrent scientific sessions were held.

Informal Discussion on "Damping Capacity"

The President, Professor F. C. Thompson, D.Met., M.Sc., took the Chair at Session A. An informal discussion took place on "Damping Capacity", which was opened by Dr. K. M. Entwistle, who gave a survey of the work on the subject.

Discussion of Papers

At Session B the Chair was taken by Dr. L. B. Pfeil, O.B.E., A.R.S.M., F.R.S. (Member of Council), and discussions took place on two groups of papers published in the *Journal*.

Structure of Nickel Alloys

"The Constitution of Nickel-Rich Alloys of the Nickel–Titanium–Aluminium System", by A. Taylor, Ph.D., F.Inst.P., and R. W. Floyd, B.Sc., A.I.M.

"A Study of Order–Disorder and Precipitation Phenomena in Nickel–Chromium Alloys", by A. Taylor, Ph.D., F.Inst.P., and K. G. Hinton, B.Sc.

"The Constitution of Nickel-Rich Alloys of the Nickel–Chromium–Aluminium System", by A. Taylor, Ph.D., F.Inst.P., and R. W. Floyd, B.Sc., A.I.M.

Properties of Chromium and Its Alloys

"The Properties of Cast Chromium Alloys at Elevated Temperatures. I.—The Melting and Casting of Chromium-Rich Alloys. II.—Some Properties of Certain Binary Chromium-Rich Alloys. III.—The Creep Properties of Ternary and More Complex Chromium-Base Alloys", by A. H. Sully, M.Sc., Ph.D., F.Inst.P., F.I.M., E. A. Brandes, B.Sc., A.R.C.S., F.I.M., and A. G. Provan, B.Sc., A.R.T.C., A.R.I.C.

"The Effect of Temperature and Purity on the Ductility and Other Properties of Chromium", by A. H. Sully, M.Sc., Ph.D., F.Inst.P., F.I.M., E. A. Brandes, B.Sc., A.R.C.S., F.I.M., and K. W. Mitchell, B.Sc.(Eng.), Wh.Sch., A.M.I. Mech.E.

In each case a vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

Votes of Thanks

At 12.10 p.m. the President, Professor F. C. Thompson, D.Met., M.Sc., took the Chair at a General Meeting.

Dr. S. F. Dorey, C.B.E., F.R.S., Senior Vice-President, moved:

"That the best thanks of the Institute of Metals be, and are hereby, extended to:

(i) The Presidents and Councils of the Manchester Metallurgical Society and the Liverpool Metallurgical Society for their kind invitation to the Institute to hold this Autumn Meeting in Southport.

(ii) The Chairman, Lieut.-Commander G. K. Rylands, O.B.E., R.N. (Retd.), J.P., the Honorary Secretary, Mr. S. V. Radcliffe, and the members of the Reception Committee, for the excellent arrangements made for this meeting.

(iii) The companies and individuals who so generously subscribed to the Hospitality Fund in connection with this meeting.

(iv) His Worship the Mayor of Southport (Alderman William Tattersall, A.M.I.Mech.E., J.P.) for his welcome and for his hospitality.

(v) The Corporation of Southport for kindly placing accommodation for this meeting at the disposal of the Institute and for their hospitality.

(vi) The Directors of the following establishments and companies for their invitations to members and guests to visit their works and laboratories and for their hospitality: Automatic Telephone and Electric Co., Ltd., Liverpool; The British Aluminium Co., Ltd., Warrington; British Insulated Callender's Cables, Ltd., and British Copper Refiners, Ltd., Prescot; Division of Atomic Energy (Production), Ministry of Supply, Culcheth; The English Electric Co., Ltd., Liverpool; Fibreglass Ltd., St. Helens; Horrockses Crewdson Spinning and Manufacturing Co., Ltd., Preston; W. and R. Jacob and Co. (Liverpool), Ltd., Aintree; Richard Johnson and Newphew, Ltd., Manchester; The Lancashire Steel Corporation, Ltd., Irlam; Arthur H. Lee and Sons, Ltd., Birkenhead; Lever Brothers, Port Sunlight, Ltd., Port Sunlight; Leyland Motors Ltd., Leyland; Magnesium Elektron, Ltd., Clifton Junction; Manganese Bronze and Brass Co., Ltd., Birkenhead; Metropolitan-Vickers Electrical Co., Ltd., Trafford Park; D. Napier and Son, Ltd., Liverpool; Pilkington Brothers, Ltd., St. Helens; Rylands Brothers, Ltd., Warrington; The Shell Petroleum Co., Ltd., Thornton-le-Moors; The Shell Refining and Marketing Co., Ltd., Stanlow; John Summers and Sons, Ltd., Shotton; and Williams, Harvey and Co., Ltd., Bootle.

(vii) All others who have contributed in any way to the success of this meeting."

Dr. L. B. Pfeil, O.B.E., A.R.S.M., F.R.S., Member of Council, seconded the motion, which was put to the meeting by the President and carried with acclamation.

Mr. H. J. Miller, M.Sc. (President of the Liverpool Metallurgical Society) replied on behalf of the hosts.

The business meeting then terminated.

Visits

In the afternoon members visited the works of: British Insulated Callender's Cables, Ltd., and British Copper Refiners, Ltd., Prescot; The Manganese Bronze and Brass Co., Ltd., Birkenhead; and Williams, Harvey and Co., Ltd., Bootle. Other members and ladies visited the tapestry works of Arthur H. Lee and Sons, Ltd., Birkenhead, the biscuit factory of W. and R. Jacob and Co. (Liverpool), Ltd., Aintree, and Knowsley Hall, Prescot.

Friday, 25 September

Tour in North Wales

A party of members and ladies took part in an all-day tour in North Wales.

The meeting then concluded.

Reception Committee

The arrangements for the meeting were made with the assistance and advice of a Reception Committee constituted as follows:

Lieut.-Commander G. K. Rylands, *Chairman* (Rylands Brothers, Ltd., Warrington).
Dr. W. E. Alkins (Thomas Bolton and Sons, Ltd., Stoke-on-Trent).
Mr. H. Allison (Metropolitan-Vickers Electrical Co., Ltd., Manchester; President, Manchester Metallurgical Society, 1952–53).
Dr. S. F. Barclay (Mather and Platt, Ltd., Manchester).
Mr. E. Bowyer (British Insulated Callender's Cables, Ltd., Prescot).
Mr. C. F. Brereton (Richard Johnson and Nephew, Ltd., Manchester).

Mr. R. S. Brown (Rylands Brothers, Ltd., Warrington; President, Liverpool Metallurgical Society, 1952–53).
Mr. G. T. Callis (Manganese Bronze and Brass Co., Ltd., Birkenhead).
Mr. B. G. Churcher (Metropolitan-Vickers Electrical Co., Ltd., Manchester).
Mr. C. F. Davey (Thomas Bolton and Sons, Ltd., Widnes).
Sir Roy H. Dobson (A. V. Roe and Co., Ltd., Middleton).
Mr. I. W. F. Fairholme (Richard Johnson and Nephew, Ltd., Manchester).
Mr. W. L. Govier (Imperial Chemical Industries, Ltd., Metals Division, Kirkby).
Capt. A. C. Jessup (Magnesium Elektron, Ltd., Clifton Junction).
Dr. W. L. Kent (The British Aluminium Co., Ltd., Warrington).
Mr. S. Kerr (The Lancashire Steel Corporation, Ltd., Irlam).
Mr. H. J. Miller (President, Liverpool Metallurgical Society).
Professor E. C. Rollason (University of Liverpool).
Mr. L. Rotherham (Ministry of Supply, Division of Atomic Energy (Production), Risley).
Mr. F. R. Smith (The English Electric Co., Ltd., and D. Napier and Son, Ltd., Liverpool).
Professor F. C. Thompson (University of Manchester).
Mr. W. T. T. Wilcox (The Shell Petroleum Co., Ltd.).
Mr. W. B. Wragge (President, Manchester Metallurgical Society).
Mr. S. V. Radcliffe, *Honorary Secretary* (Rylands Brothers, Ltd., Warrington).

GENERAL MEETING

27 November 1953

A General Meeting of the Institute of Metals was held, jointly with the Institution of Metallurgists, at the Royal Institution, Albemarle Street, London, W.1, on Friday, 27 November 1953, from 10.30 a.m. to 4.30 p.m. The Chair was taken by the President of the Institute of Metals, Professor F. C. Thompson, D.Met., M.Sc.

Informal Discussion on "The Training of Metallurgists for Industry"

An informal discussion was held, which was opened at the morning session by Professor A. G. Quarrell, D.Sc., Ph.D., A.R.C.S., D.I.C., Professor of Metallurgy, University of Sheffield, and at the afternoon session by Mr. James Mitchell, C.B.E., Director of Stewarts and Lloyds, Ltd., Corby, and President of the Iron and Steel Institute. A condensed account of the discussion is printed in the *Bulletin*, 1953–54, vol. **2**, pp. 88–89 (March 1954).

Discussion

Some Friction Effects in Wire Drawing

By G. D. S. MacLellan

(*Journal*, this vol., p. 1.)

Mr. H. G. Baron,* M.Sc., L.I.M. (Member): Dr. MacLellan maintains that the variation of the coefficient of friction with interfacial pressure can be neglected. No doubt this is frequently true, but I feel that it is not a safe generalization. Some recent experiments by Lueg and Treptow † provide further evidence on this point. The graph shown in Fig. A is based on data from their Table III for the drawing of

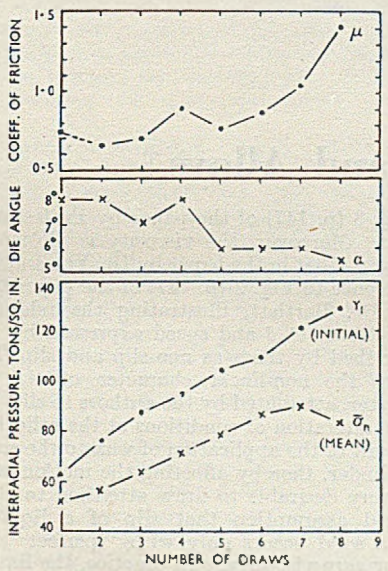

Fig. A.—The Effect of the Interfacial Pressure and Die Angle on the Coefficient of Friction. (Based on data by Lueg and Treptow.)

patented medium-carbon steel wire through tungsten carbide dies, using a soap lubricant and pulverized soap "lubricant-carrier". The wire was drawn down in successive reductions of about 30% until it finally broke. In this graph the coefficient of friction has been calculated from Sachs's equation, and the mean interfacial pressure $\bar{\sigma}_n$ was calculated from Lewis's basic equation as given by MacLellan.‡ The initial pressure Y_1 is the interfacial pressure when plastic flow begins, and is taken to equal the yield stress.

Mr. K. H. Treptow has informed me that the length of the parallel in these dies was one-fifth of the wire diameter or less. The effect of this parallel length has been neglected, but in spite of this and other possible sources of error, certain trends are clear. It will be seen that the coefficient of friction increases with increasing die angle and increasing initial pressure. The effect of pressure is masked in the first five draws by variations in the die angle, and the slight fall in the coefficient of friction between the first and second draw is probably due to an improvement in the surface finish of the wire. It was suggested in the paper by Baron and Thompson § that the initial pressure, rather than the mean pressure, together with other factors govern the depth of the lubricating film, and hence the coefficient of friction, and these curves support this view.

Dr. MacLellan's explanation of the intercept at zero reduction of area in reduction-of-area/drawing-tension curves, is very convincing. Some time ago I was interested in the rather academic question of elastic drawing, as a possible method of measuring the coefficient of friction. This idea was quickly dropped, but some calculations made at the time may be of interest. The drawing force under elastic conditions was estimated by an analysis which followed the usual lines except that the elastic strain condition:

$$\left(1-\frac{D}{D_1}\right)=\sigma_n\left(\frac{m-1}{mE}\right)+\sigma_z\left(\frac{1}{mE}\right)$$

was introduced instead of a plastic stress condition. The reduction and expansion zones of the die may conveniently be neglected, since the work of elastic deformation, some of which can be recovered in the expansion zone, is extremely small. The drawing load is then due to friction in the parallel extension, and is given by:

$$P_{\sigma_1(r=0)}=A_2 mE\left(1-\frac{D_2}{D_1}\right)\left(1-e^{-\frac{4\mu l}{m-1}}\right),$$

where $1/m$ is Poisson's ratio, E is Young's modulus, D_1 is the initial and final diameter of the wire, and D_2 is the diameter in the parallel zone. The other symbols follow the author's notation.

It is evident that the phrase "effective die angle", used by Baron and Thompson, should have been explained more fully. The method of measurement is illustrated in Fig. B,

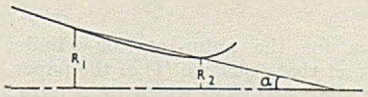

Fig. B.—Illustrating the Method Used to Measure the Effective Die Angle α.

in which R_1 and R_2 are the initial and final radii of the wire and α is the effective die angle. With most of the dies the approximation was appreciably better than that shown in the diagram, and little would have been gained by using the more accurate method suggested by Dr. MacLellan.

He has found that our experimental values § of the additional drag caused by parallel extensions is less than the theoretical value. Consideration of various possible reasons for this difference has led me to the unfortunate conclusion that the operative length of parallel in these experiments may have been somewhat smaller than the apparent lengths shown in our Figs. 8 and 9 (pp. 425 and 427 of our paper). In view of the method of polishing dies, it seems possible that the apparently parallel extensions may in fact have been slightly double-concave in profile. At the exit side, an increase in diameter of the order of 0·00005 in. would allow the wire to break contact with the die. This change in diameter would

* Armament Research Establishment, Woolwich.

† W. Lueg and K. H. Treptow, *Stahl u. Eisen*, 1952, **72**, 399.

‡ G. D. S. MacLellan, *J. Iron Steel Inst.*, 1948, **158**, 347.

§ H. G. Baron and F. C. Thompson, *J. Inst. Metals*, 1950–51, **78**, 415.

be too small to be measured by our impression technique, in fact it is even too small to be measured by the profilometer described by Withers.* After considerable wear one may be certain that the full "parallel" length is operative, but the dies we used were in new condition. This possible source of error in new dies having parallel extensions will not affect our experimental results or have other repercussions, but it is clearly a matter that should be borne in mind in any future work.

In the paper by Baron and Thompson the values of μ for castor oil obtained from back-pull experiments were not given, because of some lack of reproducibility, which perhaps amounts to $\pm 0{\cdot}015$ in the derived coefficient. However, these results acquire an added interest in view of Dr. MacLellan's work with this lubricant. The coefficients of friction which were considered to be the most reliable range from 0·067 to 0·107, the smallest figure being obtained with a 3·0° die angle. The mean value was 0·084, and I prefer this to the value 0·12 given for these experiments in Dr. MacLellan's Table III (p. 11). The other results in which the reduction of area was small or the die angle large gave values of μ between 0·11 and 0·18. It was pointed out that under these conditions the derived coefficients of friction are probably inaccurate owing to the complicating effect of redundant strains. In addition, there was some difficulty in estimating the effective die angle with the smallest reduction of area.

The Author (*in reply*): The recently published data quoted by Mr. Baron provide strong support for the view that in some circumstances interfacial pressure does have a considerable influence on the magnitude of μ, but the fact that the results he quotes lead to values of μ of an order of magnitude larger than those hitherto considered from published work, puts them in a new category.

The value of 0·12 which I gave in my Table III (p. 11) for the coefficient of friction with castor oil was derived from Fig. 16 (p. 443) of Baron and Thompson's paper, and represents a mean value for the three larger reductions, for which the die angle was nearly constant. The corresponding values for μ which I derive from curves 1 and 2 of their Fig. 18 (p. 444) are 0·071 and 0·084, that for curve 3 being somewhat higher and not accurately determinable from the data.

Discussion

The Viscosity of Metals and Alloys †

Dr. E. W. Fell,‡ M.Sc., F.R.I.C., F.I.M. (Member): With regard to the different methods used by the authors of these two papers, the outer-rotating-cylinder method is much to be preferred to the oscillating-pendulum method on theoretical grounds, for the determination of the true viscosity of the liquid metal. In this connection, it is well to recall the definition of the true viscosity of a liquid, which may be expressed in mathematical language approximately as follows: For a liquid in motion, the shear stress S at any point of a plane situated between two layers of liquid moving in the same direction though with different velocities (as in laminar motion), is equal to the product of the viscosity of the liquid η and the velocity gradient at the point taken in a direction normal to the plane, or:

$$S = \eta \cdot \frac{\partial u}{\partial y} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

My preference for the outer-rotating-cylinder method is based on the fact that equation (1) of the paper by Professor Jones and Dr. Bartlett, from which these authors determine the viscosity η, is based on equation (a) above. In the oscillating-pendulum method, on the other hand, there is no such exact mathematical equation representing the flow of the liquid, and containing explicitly its viscosity η, and that is due to the complicated, and mathematically intractable, motion of the liquid resulting from the reversals of the pendulum.

There is a further point of importance in support of the outer-rotating-cylinder method, which becomes evident from a study of the position of the experimental points plotted on the graphs reproduced in the two papers. The values plotted to represent viscosity at specific temperatures, e.g. in Fig. 3 (p. 19) (pure tin), Fig. 4 (p. 20) ("Crown" pure zinc), Fig. 6 (p. 21) (aluminium), of the paper by Dr. Yao and Dr. Kondic, show considerable "scattering", or deviation from the assumed position of the smooth curve. Occasionally, for the zinc and the aluminium, the difference between two points plotted for the same temperature amounts to as much as a third of a centipoise according to the ordinate axis. In comparison, there is very little "scattering" of the values for the viscosity of high-purity aluminium, plotted as a mean value in Fig. 3 (p. 147) of the paper by Professor Jones and Dr. Bartlett. Moreover, the viscosity is plotted to a scale twice as large as that in the paper by Dr. Yao and Dr. Kondic.

With reference to Fig. 2 (p. 147) of the paper by Professor Jones and Dr. Bartlett, illustrating the relation between angular displacement θ and speed expressed by $1/t$ for conditions described by them as non-slip and slip, I am of the opinion that the non-linear character of the broken-line curve for water, attributed by the authors to slip, may be due rather to an alteration of conditions at the solid/liquid interface as a result of the application of wax to the surface of the graphite cylinder, thereby affecting the motion of the water. I think it very desirable to draw attention to the generally acknowledged assumption that slip of a liquid past the surface of a solid occurs only with "perfect" liquids, i.e. those having zero viscosity. In practice, the liquid metal in immediate contact with the surface of the outer rotating solid cylinder would have no velocity relative to the surface of that cylinder (i.e. the liquid metal does not slip) by the boundary-layer theory of fluid dynamics. In consequence, I am unable to accept the authors' conclusion, on p. 147, that the complete form of the curve "can be of use in determining whether or not there is slip between molten aluminium and the graphite-cylinder wall".

Professor Jones and Dr. Bartlett (*in reply*): We agree with Dr. Fell that the non-linear character of the broken-line curve in Fig. 2 (p. 147) of our paper is due to an alteration of the conditions at the solid/liquid interface, such as would establish surface tension or "wettability". If the liquid wets the surface of the solid container, then there will be no motion of the liquid relative to the solid, i.e., a condition of non-slip. However, when the liquid does not wet the surface of the solid, slip between them may occur. It is upon this basis that we carried out the experiment upon a waxed (i.e. non-wetted) surface and, in our opinion, the broken-line curve shows definitely that there was a small amount of slip with the waxed surface. Whichever point of view is accepted, non-slip between the molten aluminium and graphite container prevailed, a condition essential for accurate operation of the viscometer.

* R. M. J. Withers, *J. Iron Steel Inst.*, 1950, **164**, 63.

† Joint discussion on the papers by T. P. Yao and V. Kondic (*J. Inst. Metals*, this vol., p. 17) and W. R. D. Jones and W. L. Bartlett (this vol., p. 145).

‡ Lecturer in Metallurgy, Technical College, Bradford.

Discussion

Creep and Plastic Deformation *

Dr. N. P. Allen,† M.Met., F.I.M. (Member): Several of the papers under discussion originate in the observation made at the National Physical Laboratory, and reported in the names of Wood and Tapsell,‡ that deformation taking place by creep at high temperature results in less general disturbance of the lattice structure than equal deformation taking place rapidly, or at low temperature.

Of the two explanations, that which attributes the final structure to slip by the process of migration of dislocations, followed by polygonization, appears to be gaining ground. The work of Mr. McLean, showing how little of the deformation is to be attributed to grain-boundary movement, and how much may be attributable to very minute slip, is of great importance. Dr. Wood and his collaborators have demonstrated very completely how the sub-grain size is affected by temperature and rate of deformation, and their work is a permanent addition to knowledge of the mechanism of deformation at high temperature, but they have apparently been misled into assuming that where slip cannot be seen it does not exist.

The sub-crystal formation is largely the consequence of the inhomogeneity of the deformation of an aggregate of crystals. Sir Geoffrey Taylor's view that each crystal undergoes the deformation of the mass as a whole by the use of five modes of slip is clearly incorrect.§ The crystals acquire the necessary degree of freedom to accommodate themselves to their neighbours by using different modes of slip in different parts, as Calnan and Burns ‖ showed, and Mrs. Urie and Mr. Wain have now confirmed. It follows that different parts rotate during deformation in different directions, and these varying rotations lead ultimately to the sub-structure. Calnan and Clews ¶ have also shown how these rotations lead to deformation textures.

The stresses are also unevenly distributed about the sample, and must be higher in those parts where complex modes of deformation or excessive local deformation are called for. Slip, grain rotation, and grain-boundary movement all occur, and if the specimen is not to crack, the stresses must be so distributed that the metal can move harmoniously as a whole. One of the interesting aspects of Mr. McLean's papers is the demonstration that each of the processes is dependent upon the rest. A yield in one place is followed by associated movements elsewhere, and it would not be unreasonable to think that the whole pace is set by the rate of stress relaxation in the most highly stressed parts; using dislocation theory, one might say that it is controlled by the rate of diffusion away of dislocations from the points at which they are most closely crowded together.

These considerations are important to investigators who try to derive fundamental laws from the study of creep curves. The division of the creep process into a primary stage (slip), followed by a second stage (grain-boundary movement), obviously has to go overboard and with it such equations as the Andrade equation which assume a sharp distinction between the processes occurring in these stages. The Andrade equation appears just as one of a number of moderately successful equations, and I incline to the view that for the purpose of predicting behaviour the simple equation $\sigma = AS^{\alpha}t^{k}$ is probably as useful, and as full of pitfalls, as any. I have considerable sympathy with the exhaustion theory of the primary stage, inasmuch as there are undoubtedly places in the metal where the activation energy necessary to start plastic deformation is low, and these account for the rapid initial creep, but I prefer it in the form recently advocated by Cottrell,** in which the number of regions having a given activation energy is assumed to rise with the value of the activation energy. We have, however, no idea of the form of the N/E curve, and we might as well admit it.

As regards steady-rate creep, I have some liking for the Kauzmann theory, for we are undoubtedly concerned with the surmounting by thermal fluctuations of an energy barrier to movement, and this barrier is made less by the application of stress; but I look with a jaundiced eye upon any attempt to claim that the equation predicts behaviour over a wide range of stresses and temperature. The stress τ in the equation:

$$V = 2kT/h \exp(\Delta S/R) \exp(-Q/RT) \sinh(Al\tau/kT)$$

refers to stress acting at the point in the metal where the primary-creep process occurs, and this is different at every point of the metal. The activation energy Q is not independent of the temperature. It is primarily dependent on the interatomic forces, and these in most industrial metals are largely made up of ion–ion reactions which are strongly dependent upon the exact distance between the ions, and increase rapidly as the temperature falls. The effect of this is seen in the elastic constants, which fall considerably as the temperature rises, often quite rapidly in the temperature range in which creep begins to be important.

Dr. K. W. Andrews,†† B.Sc., F.I.M. (Member) and Mr. M. G. Gemmill,†† B.Sc., A.I.M.: We shall confine our remarks to the papers by Dr. Bhattacharya, Dr. Congreve, and Professor Thompson, and by Dr. Johnson and Mr. Frost. Although these deal either with pure metals or with non-ferrous alloys, and our own experience has been with ferrous materials, we are gratified to find ourselves in general agreement with the conclusions reached, especially in regard to the best way of representing the creep/time relationship at constant stress.

Some years ago the late Dr. Jay, working in this laboratory, concluded that the most satisfactory relationship for representing the variation of creep strain with time would be given by ϵ (strain) $\propto \sqrt{t}$. Andrade's law was certainly not found to apply in as many cases, whereas the $\sqrt{t}$ relationship applied to a considerable number of creep curves obtained from commercial steels and alloys. It was later decided, however, that a more general power law should be used, and it was shown that this gave a satisfactory creep/time relationship, over at least part of the range for 107 out of 126 creep curves examined. The general power law $\epsilon = at^{m}$, where $m < 1$, does of course correspond to a creep rate which varies as a power of $(1/\epsilon)$

* Joint discussion on the following papers published in the *Journal*: S. Bhattacharya, W. K. A. Congreve, and F. C. Thompson (this vol., p. 83); G. B. Greenough, C. M. Bateman, and E. M. Smith (1951–52, **80**, 545); A. E. Johnson and N. E. Frost (this vol., p. 93); D. McLean (1951–52, **80**, 507; this vol., pp. 133, 287, 293); K. E. Puttick and R. King (1951–52, **80**, 537); W. A. Rachinger (1951–52, **80**, 415; this vol., p. 33); J. A. Ramsey (this vol., pp. 61, 215); J. Trotter (1951–52, **80**, 521); V. M. Urie and H. L. Wain (this vol., p. 153); W. A. Wood and J. Suiter (1951–52, **80**, 501; this vol., p. 181).

† Superintendent, Metallurgy Division, National Physical Laboratory, Teddington, Middlesex.

‡ W. A. Wood and H. J. Tapsell, *Nature*, 1946, **158**, 415.

§ (Sir) G. I. Taylor, *J. Inst. Metals*, 1938, **62**, 307.

‖ E. A. Calnan and B. D. Burns, *ibid.*, 1950, **77**, 445.

¶ E. A. Calnan and C. J. B. Clews, *Phil. Mag.*, 1950, [vii], **41**, 1085.

** A. H. Cottrell, *J. Mechanics Physics Solids*, 1952, **1**, 53.

†† Research and Development Department, The United Steel Companies, Ltd., Rotherham, Yorks.

and which is thus infinite initially, when $\epsilon = 0$ and $t = 0$. We have found this law to be quite generally applicable.

Several attempts have been made to represent the second and third stages of creep, and our attention was given for some time to a formula discussed by de Lacombe*:

$$\epsilon = \epsilon_0 + at^m + bt^n$$

where ϵ_0 = instantaneous extension on loading, a and b are constants, and $1 > m > 0$ and $n > 1$. This empirical formula has the advantage that it can be fitted to technical creep curves, which it can represent to a sufficient degree of accuracy. By means of the methods described by de Lacombe, it is possible to apply it to find, from the actual experimental results:

(1) An exact value of ϵ_0.
(2) The four constants, a, b, m, and n.
(3) The time to minimum creep rate (i.e. where the deceleration due to the second term is exactly balanced by the acceleration due to the third term)—a function of a, b, m, and n only.
(4) The minimum creep rate itself.

If, however, the test has not been carried on for a sufficient length of time, the possible errors in b and m are likely to be uncertain. Thus, we have recently obtained some accurate data from a series of tests on a widely used commercial steel. This gives exceedingly good plots on the simple power law for the greater part of the creep curve at lower stresses and temperatures, but at higher stresses and temperatures the second term becomes appreciable within the range of testing time.

These later results have enabled us to consider the effect of stress and temperature. The constants a and b can both be represented in terms of fractional powers of the stress, so that we support the views of Dr. Bhattacharya, Dr. Congreve, and Professor Thompson, that the stress is involved in a manner similar to that suggested by the Nutting and Scott-Blair relationship. The variation of the constant a, with temperature at constant stress appears to be adequately represented by an expression of the form:

$$a = \text{const.} \times \exp(-Q/RT)$$

Q, the activation energy, has values between 21,200 and 34,000 cal./g.-atom., varying somewhat with the stress. The values obtained appear to be of the right order. A similar variation has been described by Hazlett and Parker.†

We should like to emphasize the importance of these attempts to represent the creep curves analytically, from the point of view of the manufacturer and user of commercial alloys, since it would be most valuable if some reliable formula were available for interpolation between stresses and temperatures for which creep curves had actually been determined. In certain cases extrapolation to longer times and/or lower stresses, could also be safely carried out.

We should also like to comment briefly on the suggestion by Dr. Bhattacharya, Dr. Congreve, and Professor Thompson on p. 89, that the mechanism of creep is not dissimilar in the primary and secondary stages. This may be true, particularly with the materials, stresses, and temperatures they employed, and perhaps generally with many other materials. Our experience would, however, lead us to support the view that if the total creep strain is separated into two parts by the use of some such formula as that given above, certain characteristic properties can sometimes be associated with one or other of these fractions of the total creep strain. Thus, in certain cases, if the terms ϵ_0 and at^m are subtracted from the total creep strain, there remains a residual creep strain which we call "quasi-viscous creep", the term at^m representing "transient creep". It is not necessary to postulate that either of these parts of the creep strain is definitely associated with a single type of slip process or movement along inter-crystalline boundaries. It has, however, been found that either of these components derived in this way may show its own peculiar dependence upon, say, a particular alloying element or some other variable. Thus, it was noted in a study of the effect of phosphorus in a series of ½% molybdenum steels under low deformation conditions, that the transient creep, but not the quasi-viscous creep, was directly influenced by the phosphorus content. In other types of steel both transient and quasi-viscous creep may depend on the relative proportions of transformed austenite and primary ferrite present in the specimen, after heat-treatment before testing.

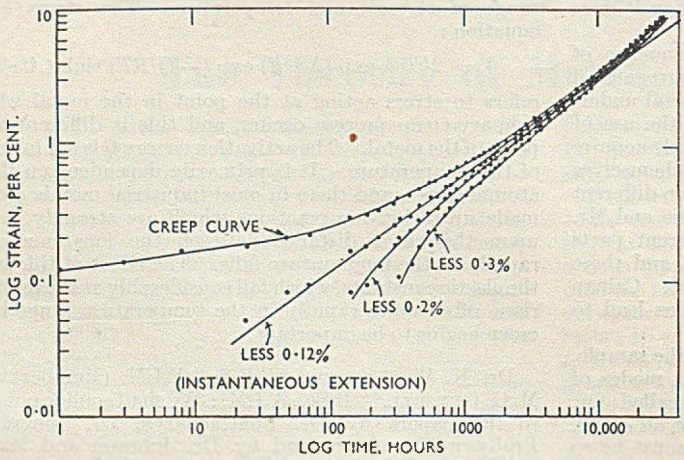

FIG. A.—Results for a Lead–1% Tin Alloy Extruded at 200° C. and Tested under Constant Stress Conditions at 300 lb./in.².

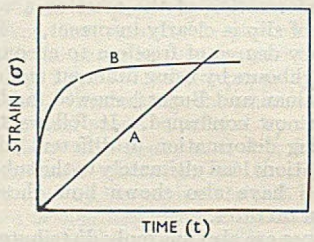

FIG. B.—Extreme Types of Creep Curve.

Dr. L. M. T. HOPKIN,‡ B.Sc., A.R.S.M., A.I.M. (Member): Dr. Bhattacharya, Dr. Congreve, and Professor Thompson express the belief that the power equation is universally a good representation of experimentally determined creep curves. However, it can be seen in Fig. A that the power equation does not provide a good fit of creep curves for long periods of time. The results shown were obtained from a lead–1% tin alloy extruded at 200° C. and tested under constant stress conditions at 300 lb./in.². Tertiary creep was not reached at the longest time of test. The upper curve shows the creep curve plotted directly, which is far from a straight line. The

* J. de Lacombe, *Rev. Mét.*, 1939, **36**, 178; 1942, **39**, 105, 152, 171.

† T. H. Hazlett and E. R. Parker, *Trans. Amer. Inst. Min. Met. Eng.* (in *J. Metals*), 1953, **197**, 318.

‡ Metallurgy Division, National Physical Laboratory, Teddington, Middlesex.

next curve shows the plot of the creep strains only, as suggested by Bhattacharya *et al.*, i.e. total strain minus instantaneous extension. A straight line is obtained for short times, but the creep strains for long times are greater than those predicted by the power equation. Subtracting from the total extension values greater than that of the instantaneous extension actually observed, does not produce better straight lines. The lower portions of the lines now curve downwards, while for long times they still curve upwards. Thus, even before tertiary creep begins, it would be dangerous to use the power equation for extrapolation purposes.

In many tests the period of secondary creep extends over a major portion of the creep curve. Two extreme types of creep curve fall within this category, as shown in Fig. B. Considering secondary creep as represented by the straight-line equation $\sigma = mt + c$, we have:

$$\log \sigma = \log \left(t + \frac{c}{m}\right) + \log m$$

In the curve of type *A*, c is small or zero and m is large, so that the logarithmic equation becomes a straight line of slope 45°. In a curve of type *B*, c is large and m is small, so that $\log \sigma$ is constant for small values of t, i.e. the plot is a horizontal line. As t increases, the horizontal line bends upwards and eventually approaches the straight line of slope 45°. Thus, although the usual creep curve lies somewhere between these two extremes it would seem that there is no modified relationship between strain and time for short times, as claimed by the authors in their Fig. 13 (p. 89). It seems more likely that the two intersecting straight lines in Fig. 13 are parts of smooth curves and in fact the figure could easily be so drawn.

Bhattacharya *et al.* consider that the parallelism of their plots of $\log \sigma$ and $\log \dot{\sigma}t$ against $\log t$ shows that the power equation is a true representation of creep curves. However, during secondary creep, these lines can be parallel only in special cases. During secondary creep the rate of creep is constant, so that a straight line of slope 45° is obtained, for all values of t, when $\log \dot{\sigma}t$ is plotted against $\log t$. This straight line can be parallel with the plot of $\log \sigma$ against $\log t$ only when t is large compared with c/m, as explained earlier. In the paper none of the plots of $\log \dot{\sigma}t$ against $\log t$ has a slope of 45°, showing that secondary creep was not reached in the authors' longest times of test. Thus, their straight lines must either abruptly change their slope when secondary creep begins, which is unlikely, or the lines are not straight but gentle curves.

Mr. R. C. Gifkins,* B.Sc., A.I.M. (Member), and Mr. J. W. Kelly,* B.Sc.: We consider Mr. McLean's paper on "Creep Processes in Coarse-Grained Aluminium" (Vol. **80**, p. 507) a significant contribution to knowledge of creep. The discussion of some of the points raised is perhaps best postponed until our own work on this subject is completed. However, there are a few comments we should like to make now.

The white-line patterns brought out by stopping-down the illumination and de-focusing have interested us, since it was by this technique that Wilms † first obtained metallographic evidence of the cell sub-structure. We find that several distinct patterns may be obtained corresponding to focus above or below the Gaussian plane.

From multiple-beam interference fringes obtained with specimens showing the various patterns, we find that:

(i) Most white-line patterns obtained inside focus correspond to ridges of up to 2 μ height and of about 0·05 mm. lateral extension.

(ii) White lines outside focus often correspond to comparable troughs.

(iii) Patterns white outside focus and black inside or vice versa occur; these correspond to ridges or troughs of about 0·15 μ vertical extension or to the line of intersection of slightly inclined areas.

(iv) Sometimes black and white lines, similar to diffraction fringes, are seen; again black and white interchange on moving through focus. These correspond to a sinusoida topography similar in size to (iii).

Patterns (iii) and (iv) show a greater degree of correspondence to cell boundaries revealed by deep etching or anodic filming than do (i) and (ii). The change in focus necessary to observe all the patterns is about ± 6–$8\,\mu$, and they have been observed at as little as 2% extension.

The types of pattern are illustrated by Figs. C, E, and F (Plate XCVII). Figs. C and E show an area on a specimen deformed 14% at 200° C., inside and outside focus, respectively; white lines of types (i) and (ii) and reversible lines of type (iii) can be seen. Fig. D (Plate XCVII) is the multiple-beam interferogram from the same area, and illustrates the surface features associated with the patterns. Fig. F shows examples of types (iii) and (iv) on a specimen deformed 12% at 325° C., repolished and extended a further 3%.

We had ascribed all these patterns to diffraction effects similar to those observed by Griffin,‡ using the same microscopical technique, on beryl crystals, although his suggestion of systematic irregularities along the edges of small steps did not seem likely with aluminium. Recently our attention was drawn to work by Berek,§ who used diffraction theory to calculate the intensity distribution of the image of a line discontinuity adjacent to the true image plane, and it appears to us that at least some of the patterns observed with aluminium may be due to similar diffraction effects at changes in curvature. Although the patterns listed under (i) and (ii) above may be due to the geometrical effect suggested by Mr. Lomer (p. 511 of Mr. McLean's paper), this explanation is not so convincing when such large radii of curvature are involved.

The diffraction origin of the patterns is strongly indicated also by evidence obtained with zinc deformed at elevated temperature. The cell boundaries under narrow-pencil illumination and out-of-focus conditions are always of types (iii) or (iv); examples of these have been published.‖ Usually at a given focal setting all those boundaries at the bottoms of valleys formed by cells appear white, whilst those at the crests appear black.

The fact that the out-of-focus markings can indicate either ridges or troughs would appear to strengthen the polygonization hypothesis of cell formation. This is also supported by further evidence of the banded nature of cells like those Mr. McLean noted, which we have found, using the anodic-film technique, on specimens deformed at various rates and temperatures up to 300° C. At 300° C. the banded nature of the cells is not apparent on deep etching, probably because of the rapid migration of cell boundaries which we find often occurs under stress. Our observations on cell boundaries suggest that they do not differ greatly from ordinary grain boundaries between grains of similar orientation.

Finally, we have been unable, using the phase-contrast microscope, to detect fine slip in specimens deformed 1·0% or more at 300° C. This confirms and extends to lower strains the electron-microscope observations of Garrod, Suiter, and Wood.¶ We have confirmed its presence, however, on a specimen deformed 2·7% at 200° C., but find that soaking the specimen, unstressed, at 200° C. for 48 hr. causes a distinct diminution of the fine slip. It may be that this thermal polishing (or oxide film formation), explains, at least in part, Mr. McLean's failure to detect fine slip at later stages of the test and its apparent absence in tests at higher temperatures.

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* Baillieu Laboratory, University of Melbourne, Australia.

† G. R. Wilms and W. A. Wood, *J. Inst. Metals*, 1949, **75**, 693.

‡ L. J. Griffin, *Phil. Mag.*, 1951, [vii], **42**, 775.

§ M. Berek, *Optik*, 1949, **5**, 1, 144, and 329.

‖ J. A. Ramsey, *J. Inst. Metals*, 1951–52, **80**, 167.
R. C. Gifkins, *Australasian Eng.*, 1952, (May), 63.

¶ R. I. Garrod, J. W. Suiter, and W. A. Wood, *Phil. Mag.*, 1952, [vii], **43**, 677.

Mr. A. P. Miodownik,* B.Sc., L.I.M. (Student Member): The wealth of experimental data now available on creep marks a stage in the study of this subject which has already been passed in that of age-hardening. Bearing in mind the conflicting arguments which have raged and are still raging on the ultimate mechanism of age-hardening, it is instructive to compare certain aspects of the two fields of research, in order that unnecessary conflict as regards creep may be avoided.

Although at first sight not closely related, the two subjects exhibit several basic similarities. Changes on ageing consist essentially of the constraint of excess solute ions in enforced solid solution being relieved by clustering, rearrangement, and lattice change. The final equilibrium condition is not attained until a series of interdependent processes have taken place, there being a wide variation in the rates of reaction for the various stages, particularly in relation to temperature. It is generally admitted that precipitation of any kind, even under equilibrium conditions, is preceded by pre-precipitation phenomena, which become, however, progressively more transient as the conditions of precipitation approach equilibrium. The processes occurring during the creep of aluminium, as envisaged by Mr. McLean, show a striking resemblance to those occurring during ageing, if the term " solute atoms " is replaced by " dislocations ". Thus, the restraint in the initial condition is thought to be due to an enforced excess of dislocations in the lattice, and relief is obtained by clustering of dislocations (the polygonization process), followed by a gradual rearrangement of the dislocation boundaries which leads to a type of boundary with the properties and characteristics of a conventional grain boundary.

The value of the comparison lies in the acceptance in the field of creep of the concept already enunciated for precipitates, namely that the equilibrium condition is always preceded by some transient stages, and that the temperature will largely control the rate of reaction of each stage. The controversy between the school of thought which adheres to direct fragmentation of grains into cells, and that which upholds the alternative theory of polygonization, can then be resolved simply into a question of the rate of polygonization.

While this concept is admittedly an oversimplification of the problem, it would be interesting and instructive to obtain some values of the rate of polygonization, although owing to the marked heterogeneity of such a process, the experimental difficulties are very great and, to the best of my knowledge, no such values are available at present in the literature.

Mr. E. C. W. Perryman,† M.A., A.I.M. (Member): During a study of the recrystallization characteristics of super-purity aluminium and super-purity-base aluminium–magnesium alloys, I have also investigated the recovery process and found similar sub-grain structures to those shown by Mr. Ramsey in connection with his first paper. I have not observed any sub-structure in the as-cold-worked material, but find that there is a tendency for the sub-structure after annealing to become finer as the amount of cold work increases from 20 to 80%. For example, after annealing at 375° C. super-purity aluminium cold worked 20% gave sub-grains approximately 30 μ in size, whereas after 60% cold work the grains measured about 10 μ. Like the author, I found that these sub-structures, once formed, did not change in size or shape with longer annealing times, and, moreover, formed in certain grains and certain regions of grains more readily than in others (see Fig. G, Plate XCVII).

The equi-axed type of sub-structure, similar to that illustrated in Fig. 8 (Plate VIII) of the paper, forms in very short times; for example, with 50% cold work such sub-structures were observed in specimens annealed for only 10 sec. at 375° C. X-ray examination of these equi-axed sub-structures by an oscillating-beam method similar to that used by Mr. Ramsey showed that after short annealing times discrete spots from the sub-grains are obtained, superimposed on an intense diffuse background. With longer annealing times the intensity of the background decreases. It would thus seem that the polygonized areas become more strain-free as the annealing time increases. Further support for this was obtained by carrying out micro-hardness tests on the polygonized areas. The hardness of areas showing an equi-axed sub-structure decreased slightly with annealing time, but they were always much harder (approx. 25 D.P.N.) than the fully recrystallized areas (18 D.P.N.). It thus appears that these sub-structures are not completely strain-free; further evidence for this is found in the observation that slip proceeds far more readily in the fully recrystallized grains than in the polygonized areas (see Fig. H, Plate XCVII).

Growth of new grains takes place within the recovered areas and, in view of the observations mentioned above, it appears that the driving force for this growth is the remaining strain energy. It is not necessary to assume, as Beck ‡ has recently done, that the driving force for growth is the increased surface energy due to the small size of the sub-grains.

It has often been suggested that these sub-grains or polygons may act as the nuclei for recrystallization. In the specimens examined, I never observed recrystallization nuclei within these polygonized areas, but observed them within the unrecovered areas. Fig. G shows recrystallization nuclei within a grain which showed no signs of recovery, while the neighbouring grain had started to recover. Has Mr. Ramsey been able to identify recrystallization nuclei with the sub-grains in the recovered areas?

Is he convinced that the recovered structures of the equi-axed type are formed by a diffusion of dislocations such as that described by Cahn? It is possible that the much smaller sub-grains, approximately 2 μ in size, which have been observed in cold-worked materials by Heidenreich § and by Hirsch and Kellar,‖ are unstable at higher temperatures and thus grow until an equilibrium size is reached? In view of this suggestion it would be instructive to investigate the recovery of material which had been cold worked at very low temperature.

Dr. W. A. Rachinger,¶ M.Sc. (Junior Member): Dr. Greenough, Mrs. Bateman, and Mrs. Smith have shown that a solid-solution aluminium–silver alloy breaks down, during slow deformation at an elevated temperature, into a sub-structure of small, relatively perfect crystal blocks. This they attribute to a polygonization process activated by both stress and temperature, dislocation movement being unimpaired by the presence of the silver atoms, which are of approximately the same size as the aluminium atom. On the other hand, a two-phase alloy did not exhibit a sub-structure after deformation, the interpretation being that the dislocation movements necessary for polygonization are inhibited by the presence of precipitate particles.

It is of interest to compare these results with the findings of a similar investigation on aluminium–magnesium alloys carried out at the Baillieu Laboratory, University of Melbourne. The results and their interpretation followed the same general trends as those described by the authors, although some minor differences existed.

Solid-solution alloys (1% magnesium), deformed slowly at various temperatures, developed a sub-structure whose size was the same as that observed in high-purity aluminium deformed under similar conditions. The cells formed in the alloy had, however, not achieved the same degree of internal perfection as those formed in pure aluminium. This was evidenced by a slight blurring of the X-ray reflections from an internal section of the alloy test-piece. Apparently many

* Research Demonstrator, Battersea College of Technology, London.

† Aluminium Laboratories, Ltd., Kingston, Ont., Canada.

‡ P. A. Beck, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 979.

§ R. D. Heidenreich, *Bell System Tech. J.*, 1951, **30**, (4), 867.

‖ P. B. Hirsch and J. N. Kellar, *Acta Cryst.*, 1952, **5**, 162.

¶ Aeronautical Research Laboratories, Melbourne, Australia.

of the dislocations were unable to take part in the polygonization process and remained in the interior of the cells, thus causing minor disorientations. It seems likely that the large magnesium solute atoms inhibited dislocation movement.

The structure of the deformed two-phase alloys (10% magnesium) is also of interest. It was found that, for a given strain, the internal disorientations suffered by the grains decreased with increasing temperature of deformation. Cell formation was not observed, provided that the alloys were strain-free before the high-temperature deformation. Here the interpretation was the same as that of the authors, namely that the precipitate particles act as effective dislocation traps. If, however, the alloy was deformed at room temperature (~5% elongation), a cell structure was developed during subsequent creep at an elevated temperature, and the size of these cells was found to be much smaller than those formed in pure aluminium deformed under the same conditions. It would appear that, of the large number of dislocations produced by the initial cold working, some are able to take part in a polygonization process whose extent is limited by the presence of precipitate particles.

Dr. Greenough and his collaborators also found that the deformation sub-structure of high-purity aluminium, as revealed by X-ray-diffraction methods, was the same at the surface as in the interior of test specimens. These results presumably apply to specimens whose final elongation was of the order of 10%. With heavier deformations (~50% elongation) slight structural differences can be observed. The cells in the surface grains were found to be less perfect than those in the interior, as demonstrated by a slight blurring of their X-ray reflections. It is not surprising that such an effect exists, since recent work * has shown that during the slow deformation of aluminium at elevated temperatures the surface grains deform to a much greater extent than those in the interior.

The cells formed in the surface grains of aluminium–magnesium solid-solution alloys were found to be less perfect than those in the interior. Here the effect was more marked, being readily observable at 10% elongation. If more dislocations are produced in the surface grains and consequently more are trapped by the solute atoms, this feature may readily be explained.

In his paper on "Grain-Boundary Slip During Creep of Aluminium" (p. 293) Mr. McLean has shown that, during creep, the strain due to grain-boundary slip bears a linear relation to that due to crystal slip. He has furthermore derived a theoretical relationship between these two quantities (equation (3), p. 298) and has shown that this is numerically in agreement with his experimental results. However, in view of the assumptions made and the mode of derivation of equation (3), this agreement might appear fortuitous.

Briefly the assumptions are:

(*a*) Grain-boundary slip is due entirely to polygonization, i.e. lattice rotation in the neighbourhood of the grain boundary, as indicated in Fig. 9 (p. 298).

(*b*) The extension of the individual crystals arises wholly from polygonization movements. This means: (i) that all the dislocations remain within the crystal, ultimately forming a polygonized array and giving rise to the observed tilts between sub-crystals, and (ii) that the dislocations move only through distances of the order of d, the sub-grain size.

It is to be noted that in an earlier paper,† it was not the total extension due to crystal slip, but only the "missing creep" which was identified with polygonization. Mr. McLean found that this "missing creep" accounted for approximately one-half of the total extension. If this is the case for the present experiments, whose conditions were not widely different from the earlier ones, the values of $\bar{p}/E$ shown in the last column of Table I (p. 299) should be increased by a factor of about two.

If, moreover, two slip directions are considered, as in Mr. McLean's earlier papers,‡ equation (2) (p. 298) would read $E \approx \theta_f$ whilst the mean value of p, as given by equation (1) (p. 298), would remain unchanged. Equation (3) would then be replaced by $d = 2\bar{p}/E$. Thus, for purposes of comparison with the values of d, the quantities in the last column of Table I should be increased by a factor of 3 or 4. The comparison still shows the quantities involved to be of the same order of magnitude, but their agreement can hardly be considered as evidence of the correctness of assumption (*a*).

Thus, although the linear relationship between the total elongation and the elongation due to grain-boundary slip is well founded, it is uncertain whether this feature is due to the physical processes which Mr. McLean envisages.

A further objection to the proposed mechanism of grain-boundary slip is that it does not necessarily imply a wholesale movement of one grain past another, but requires only localized movements at the boundary to accommodate shears in the neighbouring deformation band. Thus, marker lines drawn on the surface would be expected to show deflections near a grain boundary even in the absence of boundary migration. This is not generally the case.§

An obvious difficulty arises on consideration of the case in which no deformation banding occurs,‖ the grains retaining their internal perfection throughout the deformation. On Mr. McLean's hypothesis, grain-boundary slip would necessitate large grain rotations of approximately 1° for each 1% elongation. X-ray diffraction evidence shows that the rotations are much smaller than this. It seems more likely that the grain-boundary slip arises from translatory movements. Systematic movements of this type are necessary if boundary slip is to contribute to the deformation. Observed differences in the lateral displacement of the longitudinal and transverse marker lines * would tend to suggest that this is the case.

The existence of a linear relationship between the grain-boundary displacements, as measured on the surface, and the total elongation, is said to suggest that "the surface measurements do not seriously misrepresent the grain-boundary movements throughout the metal" (p. 298). In view of the recent work on this subject * I feel that, although the amount of grain-boundary slip is linearly related to the total elongation, the factor of proportionality will be dependent on the distance below the surface. Considerations such as this suggest the vital need for new experimental techniques which will allow investigations of the interior of a plastically deforming metal.

Dr. Johnson and Mr. Frost (*in reply*): We entirely agree with Dr. Allen's remark that the division of the creep process into primary and secondary stages has to be abandoned, and with it any equation which assumes a sharp distinction between processes occurring in these stages. On the other hand, equations which indicate the simultaneous progress of a number of processes throughout the whole creep test are certainly rational in form. The writers and Mr. A. Graham, of the National Gas-Turbine Establishment, among others, are attempting to develop this type of equation on a sound experimental basis.

With regard to the view expressed by Dr. Allen that equations of the type $\sigma = AS^{\alpha}t^{k}$ are as likely as any reasonably to predict behaviour, we would point to the suggestion made on p. 106 of our paper that such an equation is valid for a limited temperature range. Further data in our possession indicate that at a specific temperature the creep strain may be well represented over considerable periods of time by a generalized version of the above equation, viz. $\sigma = \Sigma AS^{\alpha}t^{k}$. This equation, of course, fulfils the condition mentioned above of representing several co-existing processes throughout the whole creep period concerned. The constants in such an

* W. A. Rachinger, *J. Inst. Metals*, this vol., p. 33.

† *J. Inst. Metals*, 1951–52, **80**, 507.

‡ *ibid.*, 1951–52, **80**, 507; this vol., p. 287.

§ See e.g. W. A. Rachinger, *ibid.*, this vol., Plate V, Fig. 2.

‖ W. A. Wood, G. R. Wilms, and W. A. Rachinger, *ibid.*, 1951, **79**, 159.

equation can be determined from moderately short tests over a reasonably wide stress range.

However, the use of such equations must obviously be restricted on two counts. They give no information concerning actual fracture, and for very long life periods they give no account of thermal deterioration of the material. Nevertheless, as Dr. Andrews has emphasized, their usefulness in restricted fields should not be under-estimated.

In view of the remarks of Dr. Allen quoted above, we were somewhat surprised that he should express sympathy with the exhaustion theory of creep, although he does express a preference for it in the form advocated by Cottrell. Our paper has shown that, for the particular material tested, the exhaustion theory as expressed by Mott and Nabarro is very inadequate to represent the results obtained. Admittedly, as Dr. Allen points out, there are places in the metal where the activation energy is low, and accordingly some mechanism of the exhaustion type is likely to be operative, but it appears that this must be allied in the theory with some other co-existing mechanism. The modification of the Mott and Nabarro equation given by Cottrell involves the Orowan assumption of a work-hardening relation, the shortcomings of which were discussed in our paper (p. 97). We do not, therefore, regard it as a satisfactory means of relating the exhaustion theory to our experimental results.

Dr. Allen's preference for the Kauzmann theory of secondary flow, as against the Nowick and Feltham theories, is in a sense somewhat invidious, since all three theories are based on the Eyring rate-process theory, used in conjunction with an expression of statistical probability of occurrence of the basic-flow operation, and they virtually say the same thing in different words (whether the units of operation are termed units of flow or dislocations), and yield similar numerical results in any specific case.

Dr. Allen may be perfectly correct in his remark that the activation energy would be expected to vary in a manner not dissimilar from that of the elastic moduli with temperature. However, this consideration does not affect the validity of our interpretation of Fig. 6 (p. 100) of our paper. At 20°, 100°, 150°, 200°, and 250° C., 2L42 alloy has the approximate moduli 10·5, 10·1, 9·8, 9·4, and 8·9 $\times$ 10^6 lb./in.^{2}, respectively. Obviously in the range up to 200° C. these values cannot be said to be dropping at all rapidly, and accordingly, as indicated in Fig. 6, the Kauzmann equation (other things being equal) would, on Dr. Allen's criterion, be expected to apply reasonably within this range. This is not, however, to say that causes other than the deviation of the value of Q do not contribute to the failure of the equation to represent the results beyond 200° C.

With regard to the stress τ, it seems possible that while, as Dr. Allen suggests, τ varies from point to point in the metal, the Kauzmann relation might reasonably hold with an effective statistically averaged value of τ.

However, the above remarks should not be taken as advocacy on our part of the Kauzmann theory of secondary creep. Our general view is precisely that expressed in the opening paragraph of our reply.

Finally, we wish to emphasize a point which appears to have been largely overlooked by contributors to the discussion, i.e. the existence and quite appreciable magnitude of purely anelastic and recoverable creep strain. In the tests described in the paper, this anelastic strain represented the whole of the creep at 20° C. and was still of the order of 20–30% at 150° C. Accordingly, such anelastic strain cannot be neglected in framing any theoretically based equation to represent the creep field. Any such equations to be truly general must apply both to the loaded and unloaded state and must accordingly treat anelastic strain as a separate entity. In this connection the efforts of Yu. N. Rabotnov * are to be applauded.

In the majority of practical cases of creep, where strains are of a relatively low order and primary creep persists for long periods, the recoverable portion may remain a comparatively large proportion of the total creep. The reason why this aspect of creep has been largely overlooked by physicists in framing their equations is probably that the majority of their tests have used stresses and temperatures giving large strains in short times (i.e. the opposite to practical requirements) and under these conditions the recoverable creep is relatively unimportant.

Dr. Bhattacharya, Dr. Congreve, and Professor Thompson (*in reply*): It is gratifying to find that Dr. Andrews and Mr. Gemmill are in general agreement with the conclusions which we have reached. It is implicit in our paper, however, that the power-law equation has been shown to apply specifically only to cases where phase changes are excluded. In the case of the steels, and in certain non-ferrous alloys as well, structural changes may go on simultaneously, and as a result creep relationships distinctly more complicated than that which we have proposed are required to express the results with any degree of exactitude. In the steels, for instance, spheroidization of the carbide and, not impossibly, even changes in the ferritic matrix may complicate matters considerably. It is possibly for this reason that Dr. Andrews and Mr. Gemmill prefer equations containing more terms than are required by the simple power law, and why in certain cases they find residual strains. We would emphasize that no equation can be other than merely empirical which does not satisfy ordinary dimensional requirements. On this ground, therefore, we should regard both the equation of de Lacombe, for instance, and their own equation for secondary creep as being merely empirical in nature and possessing no real physical meaning. As to Dr. Hopkin's remarks concerning the parallelism of the plots of log σ and log δt against log t, we must point out that he has suggested an equation for secondary creep which we should not accept in the case of a pure metal. It is not surprising, therefore, that he reaches conclusions not altogether consistent with our own.

Mr. D. McLean (*in reply*): My experience with the white-line patterns is similar to that of Mr. Gifkins and Mr. Kelly, except that I have ascribed those listed under (i) and (ii) to the occurrence of large slip bands. Some examples in their Figs. C and E (Plate XCVII) seem to be due to this; certain of the white lines bordering the "prominent" slip bands running from bottom left to top right change from one side of the slip band to the other as the specimen is moved through focus. This is the effect that optical theory predicts at a step in the surface.

Another factor may affect the image of a stepped surface. I understand that all objectives give a small phase-contrast effect, at least when stopped-down, since the optical path along the axis may differ in length from one near the perimeter. This might sometimes complicate the interpretation of appearances such as are shown in Figs. C and E.

In reply to Dr. Rachinger, the extension associated with polygonization was not intended to be identified only with the "missing creep" in my earlier paper,† although this impression may have been given in the short résumé in the Introduction. According to a later definition ‡ the extension associated with polygonization is correctly explained as being the whole of that part of the extension due to deformation of the crystals, as distinct from that part due to sliding of the crystals over each other. If this is accepted, it eliminates Dr. Rachinger's first factor of 2.

Dr. Rachinger suggests that a second factor of 2 should be included when two slip directions operate, since the relation derived between extension and angle of disorientation is $E = \theta/2$ for one slip direction and $E = \theta$ for two directions, i.e. the extension is twice as large for the same disorientation in the latter case. The inclusion of this second factor leads, as Dr. Rachinger points out, to the relation between grain-boundary

* Yu. N. Rabotnov, *Vestn. Moskov. Univ.*, **1948**, (10), 81.

† D. McLean, *J. Inst. Metals*, 1951–52, **80**, 507.

‡ D. McLean, *ibid.*, this vol., p. 291 (1st column).

displacement and extension $\bar{p} = dE$ (d is the sub-crystal diameter) for one slip direction and $\bar{p} = dE/2$ for two slip directions, i.e. for a given extension the grain-boundary displacement is halved if there are two slip directions. This, however, seems a little questionable. Consider the two slip directions to operate, not simultaneously, but consecutively. Dr. Rachinger's formula then becomes equivalent to assuming that slip in a second direction produces an increment of extension but not of grain-boundary displacement. According to the model I depicted,* that is so only in the special case where the second slip direction is parallel to the grain boundary. In other cases Dr. Rachinger's factor will be less than 2. My formula makes the alternative assumption that slip in a second direction produces an increment of extension and a proportionate increment of grain-boundary displacement, thus maintaining the relation $\bar{p} = dE$. This in turn is true only when the two slip directions make the same angle with the boundary. The correct conclusion to be drawn from the model in Fig. 9 * appears to be as stated in the same page, namely that a multiplying factor should be introduced to take into account the fact that slip bands are not necessarily normal to grain boundaries (consequently, that polygonization bands are not necessarily parallel to grain boundaries). In Dr. Rachinger's argument this factor is 2, in mine 1, but as its average value is in the region of unity, is it worth considering in detail before the $\bar{p} = dE$ relation has been tested much more widely?

I agree with Dr. Rachinger that, in so far as the results and the model in Fig. 9 of my paper imply that grain-boundary displacement other than that associated with polygonization does not occur, both are unexpected and difficult to account for. I also agree that in the case where the grains do not break down into sub-crystals this model predicts that relative grain rotation takes place. If the amount predicted is consistently greater than that found, this would be evidence that the model does not apply under such conditions.

Dr. Rachinger's last point about the degree to which the surface movements are typical of those occurring in the interior is a most important but difficult one. The difficulty lies in establishing a reliable standard. On the one hand, surface measurements are open to the objection that the surface may deform differently from the interior; while on the other hand the alternative procedure of deducing the amount of grain deformation from measurements of grain shapes as they appear on sections is open to the objection that grain-boundary migration occurs during creep and will produce some modification of shape apart from, or in addition to, that due to grain deformation. However, at 200° C., the temperature at which some of Dr. Rachinger's † and all my tests were made, there is good agreement between our results where the other conditions were similar. For an aluminium specimen containing 10 grains/mm. strained at a rate of 0·1%/hr., Dr. Rachinger found from measurements on a section that grain deformation contributed 88/100ths of the total extension, while under virtually identical conditions my result from surface measurements was that 86/100ths was contributed by grain deformation. Since under these conditions the two different methods of measurement agree, they probably measure the same thing. At higher temperatures and a similar rate of strain and grain-size, Dr. Rachinger found that the surface and interior appeared to behave differently. Possibly under these and other different conditions one or both of the tendencies referred to above become significant.

In connection with the discussion on finding formulæ to fit creep curves, two types of formulæ are involved. The controversy in some of the papers and contributions to the discussion is concerned with the type of formulæ produced by fitting curves to experimental data. Such formulæ cannot safely be extrapolated but enable interpolations to be made between experimental results. To be useful in this way they must be accurate, and making them accurate will probably limit their field of application. Consequently, to prove or disprove the applicability of such formulæ to conditions other than those to which they were originally fitted is to assess their value for something which they were not designed to do. There is also the type of formula deduced by supposing a particular mechanism of creep. From such formulæ one cannot as yet reasonably demand great accuracy, but one is entitled to expect them to be approximately substantiated whenever, or if ever, the supposed mechanism is dominant.

Mr. J. A. Ramsey (*in reply*): As regards Mr. Perryman's first question, my own work on the subject began as an attempt to discover possible structural changes during recovery, and, if any such changes occurred, to determine whether they could be related to the predisposition of the deformed structure, at least in parts, to form recrystallization nuclei. Therefore, when the existence of the recovery effect was established, I went to some trouble to find out, both by X-ray diffraction and microscopically, whether individual sub-grains became active and grew rapidly at the expense of their neighbours, i.e. acted as recrystallization nuclei. As far as I could discover, this did not occur; generally the nucleus developed with an orientation quite different from the range of orientation occurring in the grains under observation.

The second question is rather more difficult to answer. Deformation occurs by slip on a variety of systems of planes, though a single system evidently predominates in a number of grains. One would not expect, therefore, to find the same straight boundaries, and the simple dislocation movements suggested, as are obtained with annealed bent single crystals. Further, I feel that the boundaries observed in deformed polycrystals after heating are, at least in part, delineated during the deformation at room temperature as more or less sharp curvatures in the lattice, similar to the main boundaries of deformation bands. It would certainly be of great interest, as Mr. Perryman suggests, to study the deformation structure produced at very low temperatures, in order to eliminate thermal effects as far as possible, and the subsequent recovery of such structures.

Lastly, I would like to comment on Mr. Perryman's interpretation of the results of his microhardness measurements and the effect of straining after recovery. It would seem that the higher hardness of the recovered zone might be due to the impression covering a number of sub-grains tilted with respect to each other.

It has been suggested ‡ that the absence of slip in the substructure might be due to the fact that the small diameter of the sub-grains forces the dislocations to behave non-dynamically,§ thus producing widespread slip which may not be visible even with phase-contrast illumination at a magnification of 200 times.

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* D. McLean, *J. Inst. Metals*, this vol., p. 298 (Fig. 9).

† W. A. Rachinger, *ibid.*, this vol., p. 33.

‡ R. C. Gifkins, private communication.

§ N. F. Mott, *Phil. Mag.*, 1953, [vii], 44, 742.

Discussion

Young's Modulus of Alloys *

Professor G. V. Raynor,† M.A., D.Sc. (Vice-President): It is perhaps appropriate that I should consider the paper by Mr. Dudzinski first, because I was to a slight extent associated with this investigation in its early days, and because of the interesting way in which the results can be related to the constitution of the alloys. When I first became aware of the work, the effects on Young's modulus of silicon, beryllium, cobalt, manganese, and nickel had been examined, and the question arose as to what further solute metals to try. It seemed, on the basis of results then available, that the effect of a given solute metal on the Young's modulus of aluminium could be interpreted in terms of two main factors: firstly, the magnitude of the modulus of the intermetallic compound or other hard particles in the alloy, and secondly, the percentage of aluminium in the compound. Thus, in comparing two alloys with the same amount of intermetallic compound present, the one with the higher modulus will be that for which the compound has the higher modulus. It is also fairly clear that if we are dealing with the effect of a compound *A* which contains a high proportion of aluminium, a given solute percentage will provide more intermetallic compound, and hence a higher Young's modulus, than in the case of a compound *B*, of equal Young's modulus to *A*, but of lower aluminium content. We know so little of the Young's modulus of compounds that it was necessary to consider the magnitude of the heat of formation of a compound as a rough indication of the magnitude of its modulus, on the general grounds that the stronger the bonding, the stiffer would be the structure. This takes no account of structure, and that of course, is the weakness of the concept. These general considerations were dealt with during the discussion of Mr. Dudzinski's earlier paper,‡ so I will not dwell on them here.

One of the most interesting features of the present paper is the work on the aluminium–manganese–chromium alloys. I believe that I am right in saying that this was undertaken as a result of my suggestion some years ago that if aluminium–manganese–chromium alloys containing a ratio of 4 manganese atoms to 1 chromium atom were to be annealed below 590° C., the increase in Young's modulus would exceed that expected from the additive effects of manganese and chromium, because of the precipitation of a phase of composition approximating to $(CrMn)Al_{13}$. Table II (p. 52) shows that this increase does in fact occur, under precisely the conditions laid down, and this is quite gratifying. I also committed myself to saying that no improvement over the additive effects of manganese and nickel was to be expected in the aluminium–manganese–nickel system, since the ternary compound formed, $Ni_4Mn_{11}Al_{60}$, contained a smaller proportion of aluminium than $MnAl_6$. Table IV (p. 53) confirms this in the main; the relatively low values of the modulus in alloys rich in manganese but poor in nickel may be due essentially to this reduction in the aluminium content of the compound. I think we can also give a reason for the relatively high values obtained at low manganese and high nickel, because it is just in this composition region that a metastable ternary phase appears, the aluminium content of which is unknown but probably relatively high. This phase does not belong to the equilibrium diagram, but is of remarkable persistence, and disappears only after very long annealing. It would almost certainly be present under the conditions employed. With regard to the aluminium–chromium–silicon alloys, no predictions were made, but I think it is possible to understand the effects referred to on p. 52. In this ternary system, according to the composition, there may be deposited as primary crystals either α(AlCrSi), which has a ratio of aluminium atoms to solute atoms of approximately 3 : 2, or β(AlCrSi) which is very poor in aluminium. In either case the ternary compound contains much less aluminium than $CrAl_7$, and the decrease below the calculated additive value is to be expected.

Turning to the binary alloys, the observation that chromium is more effective than manganese, while copper is much less effective than nickel, again confirms earlier predictions, which were, however, incorrect with regard to iron. This is much more effective than it should be according to the composition and heat of formation of $FeAl_3$. I am afraid that I mistrust Mr. Dudzinski's explanation of this. The reported breakdown of $FeAl_3$ into Fe_2Al_7 and Fe_2Al_5 takes place below 600° C., so that I do not see how secondary crystals of Fe_2Al_7 can exist in the microstructure of Fig. 5 (Plate VII). I should add here that at Birmingham we have recently obtained diffraction patterns from crystals of $FeAl_3$ extracted from slowly cooled alloys, from alloys chill cast and annealed for long times above the suspected transformation, and from alloys chill cast and annealed for long times below the suspected transformation. These were all identical, and we doubt very much whether the reported decomposition does indeed take place under either our conditions or those of Mr. Dudzinski.

As the author states, the results for titanium, vanadium, molybdenum, and silver are relatively easy to understand in terms of the compounds formed, but it must be admitted that the low value of the increment for tungsten is a little surprising, in view of the high proportion of aluminium in WAl_{12}. This fact, and the fact that $CaAl_4$, in spite of its high heat of formation, depresses the Young's modulus of aluminium, definitely show that the early interpretation was seriously incomplete.

Where one general type of intermetallic compound of relatively complex crystal structure is under consideration, the correlation with heat of formation and alloy constitution is not unsatisfactory, but it is apparent that we cannot carry these considerations over to include all cases. What is now required, as a complementary research to this very valuable piece of work, is a full-scale investigation of the relationship of Young's modulus to heat of formation and to crystal structure for a wide range of intermediate phases. It might then be possible to develop a real theory, but in the meantime one must congratulate Mr. Dudzinski on having, as he says, provided enough information on which to base the development of a commercial alloy of considerably enhanced elastic properties.

The work described by Mr. Smith is of great interest in quite another way. Here we are concerned with the effect on Young's modulus of a foreign atom in solid solution, and Mr. Smith has set out clearly the factors which are likely to prove important, and proceeds to make a check by calculating the part of the variation which may be expected to be due to atomic-size differences, the remaining part being regarded as due to electronic factors. It appears to be a little indefinite as to whether the effect due to electronic factors is proportional to (solute valency)^2, or to the electron concentration. It is a pity that the accuracy attainable does not permit a choice between these alternatives; I do not criticize the author on this point, because he has probably squeezed the last ounce of accuracy out of this method. What I must criticize, however, is his choice of the apparent atomic diameters as a basis for the calculation of the atomic size effect. It is well known that the lattice distortion produced by metals of the B sub-groups

* Joint discussion on the papers by A. D. N. Smith (*J. Inst. Metals*, 1951–52, **80**, 477), and N. Dudzinski (this vol., p. 49).

† Professor of Metal Physics, Birmingham University.

‡ *J. Inst. Metals*, 1948, **74**, pp. 686, 697 (discussion).

in copper and silver depends intimately on the valency of the solute. An analysis of lattice spacings indicates very strongly that the distortion produced is the resultant of the atomic size-effect, which may lead to expansion or contraction according to whether the introduced atom is larger or smaller than that of the solvent, and a valency effect such that an expansion is produced if the solute has a valency higher than that of the solvent. It is for this reason that germanium expands the lattice of copper, in spite of its much smaller atomic size. Now, the apparent atomic diameter which Mr. Smith has used is obtained, essentially, by extrapolating the lattice-spacing/composition curve to 100% of solute, and therefore includes the whole of the distortion due to valency, and it may well be that part of the effect of valency on the Young's modulus has therefore been included in trying to make allowance for the size-effect. I feel that it would have been far better to take the closest distances of approach in the crystals of the elements for assessing the size-effect. Let us see what happens if we do this. If we consider the atomic diameters of zinc and cadmium to be the closest distances of approach in the respective crystals, and take, for the complex gallium structure and the partially ionized indium structure, the atomic diameters of 2·595 and 2·926 Å. deduced from other work, we find that Z in Table II (p. 480 of the paper) works out as follows (assuming the same proportionality factor in equation (3) as the author):

In Cu		In Ag	
Zn	Ga	Cd	In
10	1	6	1

Hence the quantity $X-Z$ becomes:

In Cu		In Ag	
Zn	Ga	Cd	In
27	81	21	64
or a ratio of 1 : 3		or again a ratio of 1 : 3	

This means that, when plotted in terms of electron : atom ratio, the curves of the valency contribution to the decrease in Young's modulus against electron concentration do not superimpose, as in Fig. 5 (p. 481), but lie apart, the curve for gallium in copper having twice the slope of that for zinc in copper, and that for indium in silver having twice the slope of that for cadmium in silver. This is a relationship of exactly the same type as that shown by the lattice distortion due to valency. I make no claim that this is a correct interpretation, but it indicates that there may be alternative interpretations. In particular, the use of apparent atomic diameters may be misleading. I must admit that tin and germanium do not work out nicely on the analysis I have suggested, and this may be connected with the marked shrinkage of the ion as we pass along each period from copper to germanium, or from silver to tin. This is a factor which has not been taken into account explicitly in the present paper, but which should be considered. We know that the elastic constants are intimately connected with the degree to which the ions overlap, and this factor may be important. In spite of the difficulties of interpretation, this paper has made a very useful contribution; and in view of these difficulties, I would heartily support the author's suggestion that further work should be carried out on single crystals, rather than on polycrystalline aggregates.

Mr. G. Bradfield*: At the National Physical Laboratory much information has been collected on elastic constants of alloys. The effect of preferred orientation, which is liable to cause serious errors in elasticity measurement, has been studied and details of means of correcting for or avoiding these errors by measuring three elastic constants instead of one, have been published.†

I shall confine my remarks on the paper by Mr. Smith to comments concerning the techniques employed and the author's recommendation for future work of high accuracy.

The accuracy of the bending-mode-vibration method used in the above investigation is low. The longitudinal and torsional vibration methods which we employ can give errors five to ten times smaller, but it is the errors arising from the effect of preferred orientation which are most serious, since they can frequently amount to several per cent. for degrees of preferred orientation which are difficult to assess by X-rays.

It is to be noted that the values of dE/dC deduced for the Cu–Zn system from Fig. 1 (p. 479 of the paper) and given in Table II (p. 480) as 37 units, would be 55 units if the first four alloy points were used and the final one ignored. 55 units is much nearer to the Köster and Rauscher figure and much nearer the value measured at the N.P.L. Such a slope may therefore be in error by 50%, when obtained by these means.

It should be pointed out that the value of the modulus shown for silver is high by well over 1½%.

Finally, I feel that the statement (p. 481) that "the most profitable line of attack for work of high accuracy would seem to be to use single crystals" needs some qualification. A standard deviation of $\pm 1/5\%$, i.e. 0·2%, for a straight line representing a plot of $\Delta E/\Delta C$ for an alloy series can be achieved on polycrystalline materials carefully made and measured by existing techniques. Thus, although the single-crystal method is highly desirable for other reasons, e.g. because it gives all the elastic constants, it is not essential for reasons of accuracy, and it is dangerous to assume that the available techniques for making alloy single crystals will at present produce what is required.

Mr. J. Lumsden,‡ B.Sc., A.R.I.C. (Member): Mr. Smith has discussed the relation between the Young's modulus of alloys and their electron : atom ratio. I should like to make a plea for an alternative approach, through proximate rather than ultimate causes.

As has been shown by Druyvesteyn and Meijering,§ the entropy of an alloy can be calculated from its elastic constants. For solid solutions of zinc in copper they found poor agreement with the entropy calculated from other thermodynamic data then available. From later vapour-pressure measurements,‖ I have calculated the partial molal entropy of the zinc,¶ and find it to be in excellent agreement with Mr. Smith's figures for Young's modulus. On many alloys it is difficult to measure the free energy over a sufficiently large temperature range to give an accurate value of the entropy; a knowledge of elastic constants should be useful for deriving the complete thermodynamic properties.

A free-energy equation contains two terms, heat content and entropy, which can be related, respectively, to the interatomic energies and the rates at which the interatomic forces vary with distance. I suggest that atomistic explanations should be directed at these interatomic energies and forces, rather than at particular equilibrium properties such as phase boundaries. For instance, from the thermodynamic viewpoint, the course of a solidus line has significance only in conjunction with the course of the corresponding liquidus. These two boundaries are determined by the condition that the thermodynamic potential of each component is the same in both phases; their initial courses are determined by the heat of fusion of the solvent and the ratio between the activity coefficients of the solute in the liquid and solid alloys. It is difficult to see how the slope of a solidus line, by itself, can have any fundamental theoretical significance.

In general, the variation with composition of thermodynamic

* Physics Division, National Physical Laboratory, Teddington, Middlesex.

† G. Bradfield and H. Pursey, *Phil. Mag.*, 1953, [vii], **44**, 437.

‡ Research Department, Imperial Smelting Corporation, Ltd., Avonmouth.

§ M. J. Druyvesteyn and J. L. Meijering, *Physica*, 1941, **8**, 1059.

‖ A. W. Herbenar, C. A. Siebert, and O. S. Duffendack, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 323.

¶ J. Lumsden, "Thermodynamics of Alloys" (*Inst. Metals Monograph and Rep. Series*, No. 11), 1952, p. 257.

properties can be deduced only for dilute solutions. If, however, the atoms are of equal size and no directional forces are operative, simple statistical mechanics predicts that the deviation from linearity of the energy and compressibility should be represented by a symmetrical function, which, to a first approximation, is proportional to the product of the atomic fractions. This theoretical prediction is fulfilled for alloys of gold and silver, which have practically equal atomic volumes and also the same valency. The measurements on the gold–silver system prove it unjustifiable to assume that the variation with composition of the energy or elastic constants of alloys can be completely accounted for as the sum of effects attributable to differences between the atomic volumes and valencies of the components.

In liquids, the atomic arrangement is already so irregular that no special difficulty arises in accommodating an atom of different size. When the interatomic energies and forces are intrinsically the same in the solid and liquid states, the effect of relative atomic sizes should be represented by the extent to which the heat or entropy of formation of a solid alloy from its solid components exceeds that of the corresponding liquid alloy from its liquid components.*

The terminology customarily used in discussing the electron : atom ratio of alloys rather glosses over the fact that the solute is a different metal from the solvent. A satisfactory formulation for solid solutions of zinc in copper would include the properties of face-centred cubic zinc. It may be pointed out that the aluminium–zinc phase diagram clearly suggests a melting point for face-centred cubic zinc not much below 350° C.; analogy with the gold–platinum system supports this extrapolation. The molal free energy of transformation of the stable hexagonal zinc to the face-centred cubic form is therefore probably about 200 cal.

Dr. F. R. Morral,† B.Sc. (Member): The data presented by Mr. Dudzinski should make it possible to design new and useful aluminium alloys.

Table A.

Alloying Element					Second Phase	
Position in Table I (p. 51)	Symbol	Crystal Structure	Lattice Constant, Å.	Solid Solubility, %, at 20° C.	Crysta Structure	Formula
1	Cr	Body-centred cubic	2·88	0·01	Monoclinic *	$CrAl_7$
3	Mn	Complex (?)	...	0·05	Orthorhombic	$MnAl_4$
4	V	Body-centred cubic	3·01	0·37	,,	VAl_7
5	Mo	,, ,,	3·14	0·2	?	$MoAl_5$
6	Fe	,, ,,	2·86	0·03	Orthorhombic	$FeAl_3$
10	W	,, ,,	3·16	1·7	?	WAl_{12}
2	Ti	Close-packed hexagonal	...	0·03	Tetragonal	$TiAl_3$
7	Be	,, ,,	...	0·05	Close-packed hexagonal	Be
8	Co	,, ,,	...	0·02	Monoclinic	Co_2Al_9
14	Mg	,, ,,	...	1·1	Face-centred cubic (?)	Mg_2Al_3
9	Ni	Face-centred cubic	3·51	0·05	Orthorhombic	$NiAl_3$
12	Cu	,, ,,	3·61	0·1	Tetragonal	$CuAl_2$
13	Ag	,, ,,	4·08	0·5	Hexagonal	Ag_2Al
15	Sr	,, ,,	5·66	0·3	Body-centred tetragonal	$SrAl_4$
16	Ca	,, ,,	6·07	0·7	,, ,,	$CaAl_4$

* Some authors consider this phase to be orthorhombic.

The high elastic properties are explained in one case as being due to the presence of $CrAl_7$, which contains a large proportion of aluminium atoms. The effect of titanium is attributed to the high elastic modulus of $TiAl_3$, and the limited effect of $CaAl_4$ to the low modulus value of calcium itself.

The effect of the addition elements seems to show fairly good correlation when other factors listed in Table A, are taken into consideration. The basic data, the order of effect of the alloying elements, are taken from Table I (p. 51) of the paper.

This correlation seems to indicate that the solid solubility of the alloying elements for a given crystal structure, as well as the crystal structure of the second phase, may be significant.

Mr. J. T. Richards,‡ B.S. (Member): We have conducted tensile tests on aluminium–beryllium alloys containing 35–40% beryllium and have obtained E-modulus values ranging from 20 to 23 × 10^6 lb./in.^{2}. These values compare favourably with a calculated value of 22 × 10^6 lb./in.^{2} for an alloy containing 37·5% beryllium, based upon E-moduli of 10 × 10^6 lb./in.^{2} for aluminium and 42 × 10^6 lb./in.^{2} for beryllium.

As a result, the increment in E-modulus for 1 wt.-% of added element becomes approximately 0·307 × 10^6 lb./in.^{2}. Comparison of this value with the figures of 0·188 × 10^6 lb./in.^{2}, listed by Mr. Dudzinski in Table I (p. 51), suggests either a non-linear relationship or a broken modulus/composition curve in the case of beryllium additions.

Dr. A. N. Turner,§ B.Sc., A.R.S.M., A.I.M. (Member): I should like to discuss the practical utilization of the information contained in Mr. Dudzinski's paper. Mr. Dudzinski believes that it should be possible to develop an alloy having elastic properties approximately 20% higher than those aluminium alloys at present in use. We have, in fact, carried out work on the production by conventional means of alloys of high Young's modulus on a pilot-plant scale and have succeeded in producing 36-in.-wide sheet, 0·080 and 0·036 in. thick, which goes some way towards fulfilling this promise. I would like, however, to make a few observations on the difficulties encountered.

First, it may be said that, in general, the type of alloy suggested as a result of Mr. Dudzinski's work suffers from two disadvantages during casting by the semi-continuous process. These are segregation and axial cracking. Segregation is most pronounced and difficult to control in those alloys containing hypereutectic silicon. Primary silicon is lighter than the material from which it crystallizes, and consequently rises to the surface of the molten pool during casting, leading to the build-up of a silicon-rich semi-solid crust, which periodically breaks away, leading to gross inhomogeneity in the ingot. Other elements, e.g. manganese, may also segregate as primaries, but so long as they are more dense than the melt, they tend to sink and cause less difficulty during casting or subsequent working. Axial cracking tends to increase with the brittleness of the as-cast alloy, and it is necessary to balance carefully the operating conditions and the composition, in order to cast an alloy successfully at all.

The alloys are not easy to roll, hot rolling in particular causing some difficulty. Ingots must be scalped before breaking down and again after breaking down, before hot rolling is continued. The greatest difficulty is surface crazing, which may lead to the general break-up of the ingot. There are indications that this phenomenon is connected with the presence of coarse primary intermetallic constituents at the surface, and that a great improvement in rolling characteristics may be obtained by cladding the ingot with a thin layer of commercial-purity aluminium before rolling.

Another difficulty in the fabrication of these materials is that even if the alloy has been successfully cast and rolled, it does not follow that the properties obtained are those expected. For example, an alloy prepared to contain approximately silicon 10, manganese 2·4, nickel 2·35, cobalt 0·18, and copper 2·0%, which according to the results given in Mr. Dudzinski's paper should have given a modulus of a little over 12 × 10^6 lb./in.^{2}, actually gave a value in the sheet form of about 10·6 × 10^6 lb./in.^{2}, notwithstanding the fact that in the as-cast condition the modulus was very much that calculated. The reason for this discrepancy is not difficult to see when the microstructure of the alloy is examined. Fig. A (Plate XCVIII)

* J. Lumsden, *loc. cit.*, p. 343.

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for example, illustrates the presence of a large manganese-bearing primary particle in the rolled sheet. It may be seen that the particle has not been deformed nor reduced appreciably in size, but is surrounded by a series of cracks separating it completely from the matrix. The volume occupied by this constituent, therefore, acts as a void, and the modulus of the material, far from being increased by the presence of manganese, is actually decreased in proportion to the cross-sectional area of the constituent involved. This separation of the primary constituents from the matrix occurs during hot rolling. There appear to be two possible solutions to this difficulty; either to produce alloys in which the constituents do not appear as large brittle primaries, or alternatively to devise methods of deformation which do not lead to the separation of the constituent from the matrix. How practicable these two methods may be is largely a matter for conjecture. However, we have distinct hopes that it may be possible to evolve a method of producing an alloy with a Young's modulus of elasticity of at least 12×10^6 lb./in.^{2} with acceptable other mechanical properties, by the normal methods of fabrication in general use today.

Mr. Dudzinski (*in reply*): Professor Raynor has discussed the effect of the heat of formation of intermetallic compounds on the elastic properties of alloys. It may be useful to say a few words about the detrimental effect of calcium. Expressing the heat of formation of the compound in cal./g. of the alloying element, it is found that the values increase in the following order: $CuAl_2 < Co_2Al_9 < FeAl_3 < NiAl_3 < CaAl_4$, and the corresponding increments of E referred to 1 wt.% of the alloying element are: Cu 0·08, Co 0·185, Fe 0·23, Ni 0·165, Ca 0·3 lb./in.$^2 \times 10^6$. The reason for the low value of E in aluminium–calcium alloys is obvious. $CaAl_4$ has a typical layer structure in which the elastic modulus along one crystallographic axis is relatively high, but in the plane perpendicular to it is low. As reported by the German workers, the compounds of magnesium with bismuth or antimony, which also have a layer structure, show a similar behaviour in spite of their heteropolar type of bonding.

It is also possible that the structure of the two outermost electron shells of the atom of the alloying element have an effect upon the elastic modulus of the alloy. If the increments in E are expressed per 1 at.-%, and the elements are arranged according to their groups in the Periodic Table, the result is as follows:

Group	IIA	IVA	VA	VIA	VIIA	VIIIA	VIIIB	VIIIC	IB
	Ca	Ti	V	Cr	Mn	Fe	Co	Fe	Cu
ΔE	−0·4	0·6	0·55	0·82	0·62	0·44	0·37	0·32	0·18
				Mo					
				0·97					
				W					
				0·75					

In solid calcium the forces of cohesion are small. Its high compressibility and high atomic volume (26) indicate a weak atomic bonding. Metals of this type show a low value of E. Titanium, the next element after scandium (not investigated) in the First Long Period, has a strong cohesive force because, according to Pauling, the electrons derived from the (4*s*) and (3*d*) energy states of the free atoms are hybridized in the solid, giving a strong bond. Accordingly, the increment in E for aluminium–titanium alloys is large. This process develops further in Groups VA and VIA. The atomic diameters of vanadium and chromium, as defined by the closest approach of atoms in the crystals, decrease. The melting point of vanadium, however, decreases a little, and the increment in E for aluminium–vanadium alloys is of the order of 0·55. The elements of Group VI show the highest increase in E, and it is interesting to note that in this group the number of electrons taking part in the bond formation is, according to Pauling, 5·78 electrons/atom. Molybdenum, the element lying below chromium, shows the highest effect on E of the alloying additions, and its melting point is higher than that of chromium. One would expect, therefore, that ΔE for aluminium–tungsten alloys would be still higher, but or some unknown reason the increment is lower than for molybdenum-bearing alloys. In the elements beyond Group VIA the Pauling theory does not hold; there is a decrease in the cohesive forces, and the beneficial effects of manganese, iron, cobalt, and nickel also decrease in the order named. This may perhaps explain why the values of E for aluminium–nickel alloys are lower than expected from the heat of formation of the compound. In copper the strength of bonding is further lowered by the fact that the third quantum shell has been completely filled and only the valency electrons of the (4*s*) shell take part in bonding, assisted by van der Waals forces; the value of ΔE for aluminium–copper alloys is therefore low.

I am grateful to Professor Raynor for clarifying the position regarding the transformation $FeAl_3 \longrightarrow Fe_2Al_7$. The results given in Fig. 2 (p. 51) are correct, but it is apparent that their interpretation is wrong. The paragraph on p. 52 dealing with aluminium–iron alloys should therefore read: "Annealing at 530° C. below the temperature for the hypothetical transformation $FeAl_3 \longrightarrow Fe_2Al_7$ and also, for comparison, just below the eutectic temperature, resulted, however, in only a slight improvement in E." As there is no direct evidence that the above transformation occurs, it is possible that the recorded variation in E should be ascribed to some other unknown reasons. The Young's modulus of these alloys, when annealed and slowly cooled, returned to its previous values for the as-chill-cast condition.

Dr. Turner describes the difficulties encountered in connection with the development of an alloy of high elastic modulus for commercial application, and shows a photomicrograph in which a large constituent has separated from the matrix, resulting in the reduction of E. This is rather a gloomy picture. The composition of the alloy in which these "voids", as defined by Dr. Turner, occurred, was approximately silicon 10, copper 2, nickel 2, manganese 2·4, cobalt 0·2%. The manganese content in alloys of this type is critical, i.e. the $MnAl_6$ constituent separates in very large formations above certain concentrations of manganese. I have suggested a composition: silicon ~11, copper 4, nickel 2, manganese 0·5, magnesium 0·3, cobalt 0·2, titanium 0·1%. This alloy is very complex, and its microstructure is not very well known. It probably contains $CuAl_2$, ternary Al–Cu–Ni complex, $NiAl_3$, Mg_2Si, ternary Al–Co–Fe complex and quaternary Al–Fe–Si–Mn complex. I was aware that this type of alloy would not be easy to cast by a continuous process or to roll, and I am therefore grateful to the Aluminium Laboratories for their excellent work in overcoming the difficulties. An alloy of composition very similar to that given above was rolled to 14 and 20 S.W.G. sheet, and when examined by Mr. Meikle and his associates gave the following properties:

Table B.

Condition	20 S.W.G.			14 S.W.G.			Elongation, %
	0·1% P.S., tons/in.^{2}	U.T.S., tons/in.^{2}	E, lb./in.^{2} $\times 10^6$	0·1% P.S., tons/in.^{2}	U.T.S., tons/in.^{2}	E, lb./in.^{2} $\times 10^6$	
A	14·5	26·0	11·8	14·5	26·2	12·0	10
B	22·0	28·7	11·8	21·4	28·7	11·9	5½
,,	21·3	27·9	11·8	21·6	28·4	11·9	5½

A = Solution-treated and aged at room temperature. B = Fully heat-treated

The results shown in the table are very close to the predicted values. One could increase the manganese content to about 1% by reducing the copper content to about 2% and keeping the other alloying additions at the same concentration, or even increase it to 2% by leaving the nickel out.

Returning to the photomicrograph (Fig. A, Plate XCVIII), I am not sure that the large manganese-bearing constituent has dissociated itself from the matrix, although it exhibits cracks which are detrimental to the properties. It looks rather as though some parts of it had been crushed out in the polishing operation. In some other regions one can distinguish small black areas associated with the silicon particles; these also may be considered as holes. I have encountered a similar tearing out of brittle constituents in polishing, as shown in Figs.

B and C (Plate XCVIII). These represent the structure of cast binary aluminium alloys containing, respectively, 6·37% chromium and 2·4% vanadium. The Young's modulus of these alloys was 11·9 and 10·4 lb./in.^{2} × 10^6, the values agreeing with calculation. To eliminate such large formations, I would suggest pre-forging or pre-extrusion, so that the constituent might be broken up before the rolling process, or a slight reduction of temperature in the first stage of rolling to facilitate the breaking up of the manganese-bearing phase.

With regard to Dr. Morral's contribution, various workers have shown the detrimental effect of elements which form solid solutions with copper or silver, and a similar effect might be anticipated with aluminium. The few experiments which I have carried out indicate that this is the case, but the fact that the solid solubility of other elements in aluminium is very low, limits its extent.

The crystal structure of the second phase is undoubtedly important, but unfortunately little is known about the structure of the intermetallic compounds formed in equilibrium with the aluminium solid solution. The $CaAl_4$ and $SrAl_4$ compounds display a typical layer structure similar to that of Mg_3Sb_2 or Mg_3Bi_2. In this type of structure the binding in one crystallographic axis is smaller than in the plane perpendicular to it, and as mentioned above, the forces of cohesion in metallic calcium are low, with a corresponding reduction of the Young's modulus of aluminium–calcium and aluminium–strontium alloys. At a higher concentration of calcium the compound $CaAl_2$ makes its appearance. This belongs to the group of Laves phases characterized by a very high co-ordination number; this favourable condition to some extent offsets the effect of weak bonding, and the Young's modulus for $CaAl_2$ is accordingly higher than for $CaAl_4$.

Mg_2Si is a typical valency compound, anti-isomorphic with CaF_2. The elastic modulus of Mg_2Si is higher than that of magnesium, and therefore the detrimental effect of magnesium in aluminium alloys is counteracted by the addition of silicon.

The structure of the $CuAl_2$ compound may be regarded as being derived from two face-centred cubic copper units stacked vertically, in which the atoms at the centre of the vertical faces are each replaced by a pair of aluminium atoms; in addition such a structure has been elongated horizontally. Here, the size-factor is important and is reinforced by strong bonding. As a result the values of E for aluminium–copper alloys are above the line connecting the values for the two elements.

It is interesting to note that high values of E are shown by certain electron compounds, such as the Hume-Rothery phases (e.g. Cu_9Al_4, Cu_5Zn_8, $Cu_{31}Sn_8$) with a constant electron : atom ratio of 21 : 13, and possessing a complex structure.

The binary compounds formed by aluminium with the transition metals in equilibrium with the primary solid solution are $CrAl_7$, $MnAl_6$, $FeAl_3$, Co_2Al_9, and $NiAl_3$. According to Raynor,* an approximately constant electron : atom ratio of about 2·1 is maintained in these compounds, with the exception of $FeAl_3$. They crystallize in a complex structure of low symmetry and having rather large unit cells. They are all effective in raising the value of E, their effect diminishing in the order named. It is interesting to note that Co_2Al_9 is isomorphic with the ternary $FeNiAl_9$ compound. In an examination of the elastic properties of aluminium–iron–nickel alloys, I found a marked improvement in E when the ratio of iron to nickel was about 1 : 1.

Mg_2Al_3 has a cubic structure, and the values of E for aluminium–magnesium alloys follows the rule of mixtures.

Mr. Richards suggests a non-linear relationship or a broken modulus/composition curve in the case of beryllium additions. It is difficult to comment on this suggestion, as we examined the elastic moduli of binary aluminium alloys only up to 5·6 wt.-% beryllium, very remote from the range of compositions studied by Mr. Richards. In correspondence previously published,† it was shown by a mathematical calculation that the values of Young's modulus of the alloys assume a linear relationship with the vol.-% of the beryllium content.

The increment in the values of Young's modulus for binary alloys given in the present paper persisted also in ternary aluminium–cobalt–beryllium and aluminium–copper–beryllium alloys; in aluminium–silicon–beryllium alloys, however, an increment of 0·32 lb./in.^{2} × 10^6 was observed, which approaches the figure given by Mr. Richards.

Mr. Smith (*in reply*) : I am grateful to Professor Raynor for pointing out the error in my use of the "apparent atomic radii" as a measure of the atomic sizes of the solutes. He is quite correct in saying that by this means the effect of valency may twice be taken into account. In point of fact it is doubtful whether any useful result is to be obtained by separating out the contribution from the size-effect to the overall measured effect, since neither quantity is known with sufficient accuracy. On the other hand, if no account at all is taken of the size-effect, the measured values of dE/dC obtained in the paper for the B sub-group alloys vary quite closely as the square of the valency of the solutes. This is shown in Table C.

Table C

Element	In Copper				In Silver		
	Zn	Ga	Ge	As	Cd	In	Sn
Measured $(-dE/dC)$ = X, kg./mm.^{2}/at.-%	37	82	150	240	27	65	92
X (valency of solute)$^{-2}$	9·2	9·1	9·4	9·6	6·7	7·2	5·7

This result may well be fortuitous, and no particular significance should be attached to it at this stage.

I fully agree with Mr. Bradfield's point that accurate measurements may be made of the elastic constants of polycrystalline aggregates, using the technique developed at the National Physical Laboratory to which he refers. It is certainly to be preferred to measurements on single crystals, having regard to the difficulties of their production.

With regard to the slope of the line for the copper–zinc system, I agree that if the last point is ignored the value increases from 37 to 55 units. The fact that the latter figure is in agreement with measurements at the National Physical Laboratory argues that this should be done. On the other hand, one expects that the lines for different copper alloys should intersect the pure copper axis at the same point. On this basis it is difficult to draw any other line for the copper–zinc system than that shown in Fig. 1 (p. 479) of the paper, whether the last point is ignored or not.

In reply to Mr. Lumsden, my object in comparing the slopes of the modulus and solidus lines was to demonstrate that both appear to vary together. Hence, factors which influence one probably also influence the other, and Jones' theory ‡ indicates that the atomic size and valency are the most important factors in determining the solidus line. I agree that other factors also affect the modulus, as pointed out by both Professor Raynor and Mr. Lumsden, but for the particular alloys considered here it seems likely that the valency effect is the most important. Although it appears probable that the relationship between the slopes of the solidus and modulus lines, shown in Figs. 2 and 3 (p. 479) of the paper, is largely coincidental, it is of interest to see what happens when the points are plotted non-dimensionally. This is done by dividing the abscissæ by the modulus, and the ordinates by the absolute melting temperature, of the pure metal. The slopes of the lines (shown dotted in the figures) then become nearly equal for the copper and silver alloys, having values of 1·38 and 1·31, respectively. This fact suggests that there may be some rational basis for the comparison.

* G. V. Raynor, "Progress in Metal Physics", Vol. I, p. 49. 1949 : London (Butterworths Scientific Publications).

† *J. Inst. Metals*, 1948, **74**, 706 (correspondence).

‡ H. Jones, *Proc. Phys. Soc.*, 1937, **49**, 243.

Discussion

High-Temperature Oxidation of Alloys *

Dr. O. Kubaschewski,† (Member): The oxidation of copper alloys has been widely studied, but very little information has been available on alloys of cobalt, and this part of the present work is therefore particularly welcome.

There are two ways of approaching the problem of finding oxidation-resistant alloys: one may either explore systematically simple gas–metal systems and try to determine the fundamental mechanisms, or one may work empirically and copy exactly the conditions that occur in practice. Professor Preece and his co-workers have chosen a middle way, and the research worker interested in the fundamental side of the problem would have liked to see parallel experiments carried out in pure dry oxygen, not only with pure cobalt and pure nickel, and also further experiments with much smaller percentages of the alloying elements, which might have included monovalent metals. On the other hand, engineers might ask for some sodium sulphate and vanadium pentoxide to be present in the fuel gas. In view of the formation of generally badly adhering oxidation layers, they might also ask for parallel oxidation tests under temperature changes.

I am more interested in the conclusions of a general nature that can be drawn from the present results. I note that the oxidation rates found for pure nickel agree with those observed by Pilling and Bedworth. As nickel of "commercial purity" was used, it is not surprising to find that the authors' oxidation rates are somewhat higher than the bulk of the data obtained with high-purity nickel.‡§ This is in agreement with the diffusion mechanism in NiO, as I have described elsewhere.‡‖

The peak in the oxidation/temperature curve for cobalt is somewhat puzzling. It was not observed by Johns and Baldwin,¶ and I wonder whether the authors have any explanation for this discrepancy. True, thermochemical data show that Co_3O_4 decomposes in air at about 950° C., as was confirmed by the authors experimentally, but this does not explain the peak unless mechanical imperfections are developed in the layers. The formation of two distinct layers of CoO structure is interesting. The authors' interpretation of this implies that CoO is an amphoteric conductor, i.e. stable with an excess as well as with a deficit of metal. One could imagine the inner layer to possess vacant anion sites, the outer layer vacant cation sites. This would account for the diffusion mechanism propounded by the authors. The difficulty that such a mechanism would create a space between the two CoO layers could be overcome by the assumption that the interface energy pulls the two surfaces continuously together as the vacancies are formed. The interface thus does not correspond to a change in phase, but is simply a mechanical boundary. I doubt whether this interpretation is correct, but it may be that the authors have hit upon an important idea in interpreting certain oxidation phenomena. Previous interpretations of the diffusion mechanism in CoO have been divided, some workers favouring the mechanism of an oxygen diffusion inwards, others that of a diffusion of Co^{++} ions outward. It would be welcome if the present authors could strengthen their point by oxidizing cobalt in the presence of inert markers, which should be found after oxidation at the mechanical interface within the CoO layer. The platinum wires used for suspending the specimens may have provided this information, as they did in the case of the oxidation of titanium.**

There is no reason why a true diffusion of oxygen should not frequently occur in oxide layers. When Pfeil's now well-known experiments with inert markers on iron surfaces showed for the first time that the cations, rather than oxygen, provide the exchange of matter in oxidation layers, this came as such a surprise that public opinion accepted this mechanism as being of quite a general nature. Another authority in this field, C. Wagner, also favoured the idea of cationic diffusion in oxides, on the basis of considerations of ion sizes. This should be no deterrent, however, to assuming a diffusion of oxygen ions, for instance over vacant anion sites, whenever justified by experimental evidence. The conclusions concerning the oxidation of iron at low temperatures drawn by Vernon, Calnan, Clews, and Nurse †† may be mentioned as an example. Dr. Dennison and Professor Preece have assumed oxygen diffusion also in cupric oxide and, since this is a transition conductor,‡‡ I should say that such a mechanism is possibly applicable. I should like to ask them, however, how they explain the difference between their curve for the composition of the oxide layer on copper (Fig. 4, p. 231) and the corresponding one determined by Valensi,§§ which does not show the inflection that they found. Is it attributable to the difference in the gaseous atmosphere, which was dry oxygen in Valensi's experiments? Or is it somehow due to the change in the oxidation mechanism of copper generally assumed to occur between 500° and 600° C.? An explanation of this point would be quite important, as Valensi has based his theory of multilayer formation on his experimental results.

With regard to the oxidation of alloys, I have already mentioned that it would be useful to know the effects of small percentages of the additions on the oxidation rate, as this would help to elucidate the mechanism of diffusion.‖ As long as no second oxide layer is formed, one would expect, on the basis of the Wagner mechanism of oxidation, that high-valency metals should increase, monovalent metals decrease, the oxidation rates of copper, nickel, and possibly cobalt. This applies, for instance, to the copper–chromium alloys. The authors explain why there is not sufficient chromium to produce a protective Cr_2O_3 layer; they do not explain the increase in oxidation actually observed. This, I suggest, is due to the creation of additional cation holes in Cu_2O, which is a cation-deficit conductor, by replacement of monovalent Cu^+ by trivalent Cr^{+++}. It is also possible that the relatively high oxidation rates of the cobalt–10% chromium alloy observed by the authors are due to an increase of the number of vacant lattice sites in the CoO lattice, corresponding to similar observations with nickel–chromium alloys discussed by Wagner and Zimens ‖‖ and by ourselves.‖ This would require, however, that

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* Joint discussion on the papers by A. Preece and G. Lucas (*J. Inst. Metals*, this vol., p. 219) and J. P. Dennison and A. Preece (this vol., p. 229).

† Metallurgy Division, National Physical Laboratory, Teddington.

‡ O. Kubaschewski and O. v. Goldbeck, *Z. Metallkunde*, 1948, **39**, 158.

§ W. J. Moore and J. K. Lee, *Trans. Faraday Soc.*, 1952, **48**, 916.

‖ O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys". **1953**: London (Butterworths Scientific Publications).

¶ C. R. Johns and W. M. Baldwin, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **185**, 720.

** M. H. Davies and C. E. Birchenall, *ibid.*, 1951, **191**, 877.

†† W. H. J. Vernon, E. A. Calnan, C. J. B. Clews, and T. J. Nurse, *Proc. Roy. Soc.*, 1953, [A], **216**, 375.

‡‡ K. Hauffe and H. Grunewald, *Z. physikal. Chem.*, 1951, **198**, 248.

§§ See O. Kubaschewski and B. E. Hopkins, *loc. cit.*, p. 139.

‖‖ C. Wagner and K. E. Zimens, *Acta Chem. Scand.*, 1947, **1**, 547.

CoO, like NiO, be a cation-hole conductor, contrary to the suggestions made earlier. At least, I feel, one should be very careful in generalizing from a few empirical observations. The authors hold the view that the formation of spinel structures on alloys is undesirable for oxidation-resistance. Arkharov* has expressed just the opposite view. The obvious answer to this difference of opinion is that the spinel structure, as such is neither a typical inhibitor nor accelerator of oxidation, any more than any other structure, for instance the NaCl-type. The diffusion mechanism in an oxidation layer depends on the concentration and type of defects in the lattice, and the spinels must be treated individually from this point of view. With this in mind, Hauffe and Pschera† have investigated the diffusion rates in the $NiO.Cr_2O_3$ spinel. The results indicate that this particular spinel should, in fact, offer quite a good protection to oxidation. Since pure chromium oxide is not particularly protective, the high oxidation-resistance of 80 : 20 nickel–chromium must be due either to the spinel or to a chromium oxide that contains nickel ions in solid solution. Corresponding considerations may apply to cobalt–chromium alloys.

The results obtained with the copper–aluminium alloys are interesting. If diffusion in the alloys were infinitely rapid, only alumina should be formed on oxidation, owing to its high free energy of formation. Diffusion rates are, however, not infinite, and the effect that this would have on the type of oxidation layers formed was recently discussed by Wagner.‡ From the work of da Silva and Mehl§ it follows that the individual diffusion rate of aluminium in aluminium–copper alloys increases with temperature, relative to that of copper. This is in qualitative agreement with the authors' observation that coherent, protective Al_2O_3 layers are formed only at high temperatures, while at low temperatures insufficient aluminium diffuses to the surface to form more than clusters of alumina in the Cu_2O. It follows that selective oxidation at very low oxygen pressures (i.e. in H_2O/H_2 mixtures) should produce protective films on alloys of, for instance, aluminium with copper or cobalt.

Finally, I should like to ask Professor Preece and Dr. Lucas to state the time of oxidation in Tables I–VI (pp. 221–223); and, although there appears to be little difference in the rates of attack by air and air/fuel gas mixtures, it would be useful to know which of the atmospheres had actually been used to obtain the figures in the tables.

Mr. E. Ll. Evans,‖ B.Sc. (Member): Dr. Kubaschewski has mentioned the care needed in drawing general conclusions on the protective or non-protective properties of a group of oxides such as the spinels. I wish to underline this point, because these substances have often been the subject of broad generalizations based on observations on one or two particular spinels. Quarrell in 1940 ¶ identified the protective oxide on a 13% Cr, 13% Ni steel as a spinel, and suggested that spinels in general should afford good protection against continued oxidation owing to their flexibility in composition and their stability. (The exceptional behaviour of magnetite was related to the ease with which it would break down to form ferrous oxide.) In an electron-diffraction study of oxide films on alloys of iron, cobalt, nickel, and chromium, Hickman and Gulbransen ** identified spinels in a number of films, both protective and non-protective. In the summarized conclusions at the end of their paper, they remarked only upon those spinels which appeared protective, and a number of superficial readers have been led to believe that this work confirms the view once advanced by Quarrell. The converse may easily happen as a result of a hurried perusal of the paper by Professor Preece and Dr. Lucas. Of the four spinels encountered, two are detrimental (Co_3O_4 and $CoO.Cr_2O_3$), one seems not particularly detrimental ($CoO.Al_2O_3$), and the fourth is described by the authors as not appearing to have any serious effect on the rate of oxidation ($NiO.Al_2O_3$). Despite these mixed observations, the authors state without qualification in their conclusions (p. 227) that " this type of structure greatly accelerated the oxidation process ", and in their synopsis (p. 219) that " spinel formation is shown to be detrimental to the formation of a protective oxide layer ". This kind of statement is to be regretted, if only because abstractors, particularly those reading a foreign language, may tend to be guided to some extent by authors' own summaries.

The spinel structure is very stable, and can accommodate a number of species of metallic ions. There has appeared no reason *inherent in the structure*, however, why any particular spinel should not form a protective or a non-protective oxide layer in any given circumstances. Rather, it might even prove possible, as a result of this flexibility in composition, and in view of the variety of oxidation-resistant properties so far observed, to produce spinels of any desired resistance to continued oxidation. It is certainly undesirable and unnecessary to speak in this connection of the properties of spinels as a class.

I should have welcomed the inclusion of fuller details of experimental methods, in both papers, if only by suitable references where the methods have been described previously. For many years Professor Preece has been associated with work on scaling, and he and his various colleagues have given us a series of excellent and valuable papers. It is just possible that, the various techniques they have developed and applied having become so familiar and commonplace to them, they may overlook the fact that the methods may be of great interest to other people. I refer particularly to methods of mounting and polishing samples for the microscopical examination of scale and adjacent metal. There are very few accounts of such methods in metallurgical literature, and it is evident from the photomicrographs in the present papers that Professor Preece and his collaborators have much to teach us.

Mr. M. H. Davies,†† B.Sc. (Junior Member): These papers form a useful addition to the literature on the practical aspect of the oxidation-resistance of materials for possible use at high temperatures. The underlying fundamental reasons for the oxidation behaviour should, however, not be neglected, since only a full understanding of the oxidation process in both pure metals and alloys will lead ultimately to the best practical solution of the problems associated with high-temperature service.

During protective scale formation, and in the absence of transformations occurring in the metal or major changes in the nature of the products of oxidation, it is to be expected that the rate of oxidation will be a smooth function of temperature. That is, the standard Arrhenius plot of the logarithm of k, the rate constant, against the reciprocal of the absolute temperature will yield : (1) a straight line, or (2) a smooth curve. The smooth curve will be produced if the composition limits of the phase, diffusion in which is the rate-controlling step, alter with temperature so that there will be an additional change in concentration gradient and thus an added contribution to the rate of growth of the phase. This is implied in the formal diffusion equations.

The discontinuity in the rate of oxidation/temperature curve plotted for cobalt in Fig. 2 (p. 220) is attributed by Professor Preece and Dr. Lucas to the disappearance from the reaction products of the thin outermost layer of Co_3O_4. From the general oxidation behaviour of cobalt it appears more likely that cobalt-ion diffusion through the principal oxide CoO will be the rate-determining step, and thus the presence or absence of a small amount of Co_3O_4 should not

* V. I. Arkharov, *Izvest. Akad. Nauk. S.S.S.R.*, **1946**, [Khim.], 127.

† K. Hauffe and K. Pschera, *Z. anorg. Chem.*, 1951, **264**, 217.

‡ C. Wagner, *J. Electrochem. Soc.*, 1952, **99**, 369.

§ L. C. C. da Silva and R. F. Mehl, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 155.

‖ Chemical Research Laboratory, D.S.I.R., Teddington.

¶ A. G. Quarrell, *Nature*, 1940, **145**, 821.

** J. W. Hickman and E. A. Gulbransen, *Trans. Amer. Inst. Min. Met. Eng.*, 1947, **171**, 344.

†† Fulmer Research Institute, Ltd., Stoge Poges, Bucks.

markedly affect the oxidation rate. It is suggested in the paper that the presence of this oxide at the outer surface of the scale increases the rate of oxygen transfer to the underlying CoO. This contention implies strong oxygen-pressure-dependence of the rate of scaling, and it would be of value to know whether or not a variation of scaling rate with partial oxygen pressure has been found.

In most other cases of protective scale formation where a parabolic rate law is obeyed, the rate-controlling step is the diffusion of ions (or vacancies which result in a net ion transfer) through the scale. On considering the oxidation of iron * under conditions which allow formation of Fe_2O_3 in one case (oxidation in O_2) and which prevent it in another (oxidation in water vapour), one finds no material difference in the overall scaling rate. Diffusion through "FeO" is the rate-determining step, and different rates of oxidation are obtained at the same temperature only by controlling the atmosphere to such an extent that the composition gradient in "FeO" is limited (no Fe_2O_3 or Fe_3O_4 is formed) and considerably less than the maximum allowed by the width of the equilibrium phase field.† Thus, it is hard to ascribe the vast change in oxidation behaviour of cobalt at 950° C. merely to the disappearance of a scale constituent which occupies only a small volume fraction of the total scale, unless there is an extremely strong oxygen-pressure dependence.

The figures for the oxidation of cobalt for 50 hr. at temperatures between 800° and 1200° C. (taken from Tables I–IV, pp. 221–222) show that the temperature increment of the rate constant decreases in the region 900°–1000° C., but the sharp inflection of Fig. 2 (p. 220) (for 24-hr. oxidation times) is not indicated. Although only a few results are given, it appears that the plots for the oxidation of cobalt for varying times do not conform to the parabolic relationships found by other workers.‡§ Additional results in the range 900°–1000° C. would assist in showing whether there is a marked difference in the *shape* of the rate/temperature curves obtained for different times of oxidation. Such a difference should not exist, and reasons for any apparent difference must be sought in the experimental methods.

Fischbeck and Salzer‖ observed discontinuities in the rate/temperature plot for the oxidation of iron in various atmospheres, and attributed it to the transformation in the metal. Later work,* however, showed that such apparent discontinuities were due to the experimental conditions, i.e. to the non-isothermal oxidation in the initial stages. Fischbeck and Salzer allowed their specimens to heat from room temperature to the operating temperature in the oxidizing atmosphere. An oxide film was formed during the initial heating, and on passing through the ferrite/austenite transformation the volume change occurring led to partial rupture at the oxide/metal interface. This resulted in a lower *apparent* oxidation rate referred to the original surface area, due to the decreased supply of iron ions across the reduced coherent interfacial area. It also resulted in an alteration of the proportions of higher oxides found.¶ Strict isothermal oxidation of iron results in a smooth variation of the oxidation rate with temperature.

Other investigations on the oxidation of cobalt have not indicated any inflection in the rate/temperature plot. Thus it may be pertinent to ask: (1) whether the present experiments were carried out isothermally, (2) whether oxygen in solution in the metal could raise the transformation temperature, thus producing the mechanical effect which might manifest itself in an apparent reduction of oxidation rate. This transformation might be restricted to a very thin zone in the neighbourhood of the metal/oxide interface since there will be an oxygen-concentration gradient in the metal.

Mechanical effects such as that described, or the development of "diffusion holes", or the stresses associated with the mass/volume relationships of oxide and metal, are frequently responsible for inconsistency in the results of oxidation experiments. Experimental conditions should therefore be held under the strictest possible control, if the maximum benefit and accuracy of information is to be obtained.

Dr. U. R. Evans,** M.A., Sc.D., F.I.M., F.R.S. (Member): The paper by Dr. Dennison and Professor Preece is most interesting, and its interest is increased if the results are considered in connection with other work not mentioned by the authors. It is perhaps a pity that they confine themselves so closely to the contents of Dr. Tylecote's admirable review, which of necessity contains no references to work published since it was written and no reference to metals other than copper, although progress in our understanding of the oxidation of one metal must help us to understand the behaviour of another. The recent tendency to confine literature surveys up to the date of publication of some text-book or review is a disquieting feature of the times, which deserves the attention of the Publication Committee.

An interesting question discussed in the paper is whether oxide scale grows by outward passage of metal or by inward passage of oxygen. It is of great practical importance to settle this matter in any particular case, for outward passage results in holes below the scale which, being left unsupported, can break down even though the scale material is intrinsically protective. This is well illustrated in the recent work on iron at 1090° C. of Dunnington, Beck, and Fontana,†† who showed, how, by diffusion of vacancies in the metal, the numerous holes of atomic size left below the scale can combine to give a few large holes; then the scale covering the holes becomes leaky, a new scale forms at the bottom of each hole, and the process repeats itself, leading to the formation of a number of scales separated by cavities. Caplan and Cohen ‡‡ studying high-chromium steel, showed that these break-downs are accompanied by sudden rises in oxidation rates; in favourable cases, they found a relation between the number of scales and the number of sudden rises in the oxidation/time curves.

Applying these ideas to copper alloys, it is helpful to study the three papers by de Brouckère and Hubrecht §§ on copper–beryllium alloys; their results agree broadly with those recorded by Dr. Dennison and Professor Preece but, since they concentrated on one class of alloys, they naturally provide greater detail. It appears that once a layer of beryllia has appeared between the cuprous oxide film and the metal, it prevents passage of either copper or oxygen through it, and the only change which can then occur is the conversion of the cuprous oxide to cupric oxide; in some cases this conversion becomes complete. Does it occur by passage of copper cations outwards (as in the formation of cuprous oxide films on metallic copper) or by the passage of oxygen inwards? If the latter, how does oxygen move inwards? It should be noted that the driving force is the same in both cases; adsorbed oxygen atoms attract electrons, becoming oxygen ions, and the electric field thus set up can either draw cations outwards or force anions inwards; the decision between the two

* M. H. Davies, M. T. Simnad, and C. E. Birchenall, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 889.

† L. Himmel, unpublished work, Metals Research Laboratory, Carnegie Institute of Technology.

‡ C. R. Johns and W. M. Baldwin, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **185**, 720.

§ J. S. Dunn, quoted by J. S. Dunn and F. J. Wilkins in "Review of Oxidation and Scaling of Heated Solid Metals" (Department of Scientific and Industrial Research). **1935**: London (H.M. Stationery Office).

‖ K. Fischbeck and F. Salzer, *Metallwirtschaft*, 1935, **14**, 733, 753.

¶ J. Bénard and O. Coquelle, *Rev. Mét.*, 1946, **43**, 113.

** Reader in the Science of Metallic Corrosion, Cambridge University.

†† B. W. Dunnington, F. H. Beck, and M. G. Fontana, *Corrosion*, 1952, **8**, 2.

‡‡ D. Caplan and M. Cohen, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 1057.

§§ L. Hubrecht, *Bull. Soc. Chim. Belges*, 1951, **60**, 311; **61**, 205.

L. de Brouckère and L. Hubrecht, *ibid.*, 1951, **61**, 101.

alternatives is likely to be determined by the presence of holes which will permit the movement of ions or other particles, and also facilitate the atomic rearrangement involved when cuprous oxide disappears and cupric oxide is formed.

At the outset, there is little doubt that cuprous ions move outwards through the cuprous oxide, taking up positions between the adsorbed oxygen ions and starting to build up cupric oxide at certain favoured points; for vacant cation sites exist in cuprous oxide, whilst, so far as is known, there are no vacant anion sites. When once cupric oxide has formed at a point on the outer surface, it can still spread sideways, but the mechanism of growth in depth requires consideration. Cupric oxide (unlike cuprous oxide, which contains less metal than the formula Cu_2O would suggest, and thus possesses vacant cation sites) is believed to possess a composition represented fairly accurately by CuO, and to be almost free from vacant ionic sites. The electronic conductivity is due to electrons being out of place; cupric oxide is an *Eigenhalbleiter*, as the Germans call it; its electrical behaviour is discussed by Hauffe and Grunewald.* It is difficult to see how either ion can pass readily through cupric oxide, which should theoretically be protective, although most investigators, from Pilling and Bedworth† onwards, seem to regard it as being, in practice, non-protective. A possible reason may be the fact (for which evidence has long existed) that the nucleation rate of cupric oxide is low, so that it is formed at a limited number of points, growing sideways and outwards; this doubtless accounts for the somewhat columnar structure of the cupric oxide seen in the authors' photomicrographs (Plate XXXII) which is very different from that of the cuprous oxide layer below it. Until the cupric oxide crystals starting at different points have grown laterally into contact, some outward passage of cuprous ions to join the adsorbed oxygen is still possible; but if the crystals meet one another, sealing the whole surface, the outward movement must cease, and it might be thought that conversion would be at an end. It seems likely that the crystals do not grow into contact at all points, and that pores remain, perhaps along the lines where three crystals approach one another; such a pore would permit oxygen to pass inwards as molecules (not ions) and to convert cuprous oxide to cupric oxide at the base of the pore. In some circumstances, it might be expected that the pores would become blocked, and possibly the Pilling–Bedworth ratio may be determinative in deciding whether blockage occurs, although there is in recent years a tendency to regard lattice parameters as the determining factor. This matter cannot be discussed here, but it is significant that 1 g.-mol. of Cu_2O occupies 23·86 c.c., whereas 2 g.-mol. of CuO (containing the same amount of copper) occupy 24·87 c.c.—perhaps an insufficient volume increase to press the crystals into lateral contact at all points. Such an explanation, however, is put forward tentatively; the argument has several doubtful features.

"Outward movement" does not involve the dissociation of cuprous oxide into cupric oxide and metallic copper, but the dissociation of two Cu^+ ions into two Cu^{++} ions and two electrons; an oxygen atom adsorbed at the outer face of the cupric oxide layer will take up two electrons, becoming an ion, and the electric field set up will cause a Cu^{++} ion to move into place alongside it at the outer surface of the cupric oxide layer. In effect, two new molecules of CuO are formed, one at each interface. The e.m.f. available for the outward movement of Cu^{++} ions is the same as that available for inward passage of O^{--} ions. The question will be decided by the resistance to the two forms of motion. It seems, however, a little doubtful whether either Cu^{++} or O^{--} could readily move through a cupric oxide film, if it is true that there is no deviation from the composition CuO. Thus, the possibility of O_2 molecules moving inwards along pores between the crystals at least deserves consideration.

Dr. K. Sachs,‡ M.Sc., A.I.M. (Junior Member): It is known that the presence of molybdenum in heat-resistant alloys containing chromium may cause a very rapid type of oxidation which has been dramatized by the adjective "catastrophic". It is attributed to the accumulation of volatile MoO_3 near the surface, and is closely related to the accelerated scaling produced by the presence of vanadium pentoxide, which Professor Preece and Dr. Lucas observed in the oxidation of the cobalt–32% chromium alloy with 0·64% vanadium.

It is surprising, therefore, that in binary cobalt–molybdenum and nickel–molybdenum alloys the formation of a molybdate was capable of suppressing the liberation of free MoO_3. The fact that MoO_3 was found above 1200° C., and that oxidation became very rapid at that temperature, suggests that MoO_3 vapour is in equilibrium with the molybdate and that the rate of flow of the gases past the specimens, reported to have been "well above the critical speed", was sufficient to sweep away the MoO_3 volatilized at lower temperatures, but could not cope with the quantity of vapour present at 1200° C. To explore the effect of varying molybdenum contents on the oxidation of the cobalt–32% chromium alloy would have been of great interest because a number of creep-resistant alloys, particularly those of American manufacture, are based on cobalt and contain both molybdenum and chromium, though usually rather less than 30% of the latter; it would have been helpful to know to what extent the higher chromium content protects this type of alloy against the influence of volatile MoO_3 derived from the molybdenum content.

Professor Preece and Dr. Lucas express disappointment that none of the elements added to the cobalt–32% chromium alloy increased the adhesion of the scale. One factor which favours the adhesion of oxide layers is the presence of metallic particles in the scale, which help to key the brittle oxide to the surface; such metallic particles tend to make their appearance in the presence of an element less readily oxidized than the base metal. In the case of a cobalt alloy, one would suggest copper or the precious metals. However, experiment may show that the additions required to give the effect are higher than the alloy can support, either from an economic point of view or because other properties will be affected.

In the paper by Dr. Dennison and Professor Preece on the oxidation of copper alloys, information is given regarding the peculiar behaviour of silicon. Apparently, no silica is found in scales formed above about 850° C., contrary to thermodynamic requirements, which insist that silicon oxidizes more readily than copper at all temperatures. It requires little ingenuity to devise a mechanism to account for the observation, but in the absence of any experimental evidence this is perhaps a more suitable place than the paper itself to discuss the matter.

It is possible that silicon goes into solution in the scale at the lower temperatures and, as it diffuses outwards, is oxidized to silica; at the higher temperatures silicon is prevented from entering the scale and is completely protected against oxidation because it cannot diffuse through the oxide layer. The main effect of the temperature on the scale appears to be to determine the proportion of cupric oxide present. Cupric oxide and silica both disappear from the scale at temperatures above 850° C.

It cannot be said that silicon is capable of dissolving in cupric oxide but not in cuprous oxide, because even when the former is present it is on the outside of the scale layer, so that silicon would have to enter the Cu_2O lattice. The latter is known to contain bivalent copper ions, balanced by lattice vacancies, and it is possible that temperatures which make cupric oxide unstable may have the same effect on cupric ions in the CuO lattice. It may be this effect of rising temperature which accounts for the failure of silicon to enter the lattice.

Whatever the mechanism, the results indicate that silicon

* K. Hauffe and H. Grunewald, *Z. physikal. Chem.*, 1951, 198, 248.

† N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, 1923, 29, 529.

‡ G.K.N. Research Laboratory, Wolverhampton.

accumulates at the metal surface, so that in effect an alloy of higher silicon content is being oxidized. Increase in silicon content from 2 to 3·5% increases the rate of oxidation above 800° C. (Figs. 8 and 9, p. 233). However, since silicon does not enter the oxide, oxidation depends on the rapid diffusion of copper through the silicon-enriched layer at the surface.

When the silicon-rich phase covers most of the surface, it may form a barrier to the entry of copper into the scale, and one can perhaps predict that a further rise in the silicon content beyond 3·5% would have the effect of decreasing oxidation, provided that melting is avoided. The increase in silicon content of the surface layer should have a similar effect in all copper–silicon alloys oxidized. At 850° C. oxidation will be very rapid at first, but will slow down when a continuous silicon-rich phase has been built up on the surface of the metal; this will occur earlier, the higher the silicon content of the alloy. Above 850° C. a liquid phase will be present as soon as about 5% silicon has accumulated in the surface layer.

Mr. J. Cantrell* (Member): The results presented by Professor Preece and Dr. Lucas are of great interest. One point, however, causes some uncertainty, since some of the alloys tested were prepared by sintering, followed by working.

We have observed a tendency, particularly in mixtures containing two metals of widely differing melting points, for the sintered body to retain a very fine, continuous porosity, even when high density values are obtained. Although cold working may remove all evidence of this porosity and yield theoretical densities, a subsequent heat-treatment may cause certain of the original discontinuities to reappear. This effect can be seen in worked compacts of certain iron powders which, after heating in a protective atmosphere, are left in moist conditions. A network of internal corrosion can often be detected.

In the processing of molybdenum, heavy drafting of the sintered ingot during swaging may cause "lap-over" of the square section. This fin will apparently become a part of the body of the material and cannot be detected after a little further reduction in diameter. Often, however, the weakness will reveal itself during the annealing of the finished wire, even at diameters as small as 0·002 in., the reheating apparently causing "springing out" of the sealed fin.

We can visualize the possibility of such a mechanism in the experiments covered by the paper. Is it possible that the heating during oxidation testing may have caused partial reopening of the pores from the initial porosity of the sintered material? If, in Fig. 9 (Plate XXXI), the microsection has been cut at right angles to the direction of rolling, the nature of the internal oxidation may be a result of the mechanism which we have suggested. Difficulties experienced with residual porosity in our own work have been eliminated by hot pressing the powder mixtures to 100% density before working.

I should like to ask the authors if any tests were made on the sintered alloys, before working, to ensure that there was no trace of continuous porosity networks.

Professor Preece and Dr. Lucas (*in reply*): We must first apologize for the omission of the time factor from the Tables. This should be 50 hr.

With regard to the point raised by Dr. Kubaschewski concerning the two types of CoO layer, there is little doubt that the junction is coincident with the original metal surface. This was shown both by measurements and by markers in the form of the platinum supporting wires.

The pronounced peak in the oxidation/temperature curve for pure cobalt certainly raises several interesting questions and appears to have been missed by other investigators. We first noticed that the results obtained in the 60 : 1 turbine atmosphere at 900° and 1000° C. were almost identical. This suggested some alteration in the mechanism of oxidation in the region of the $Co_3O_4 \rightarrow CoO$ transformation, and it was decided to investigate this point by further tests, using pure dry oxygen at much closer temperature intervals. The furnace was purged with nitrogen during the heating period. The reproducibility of the results is indicated in Fig. 2 (p. 220) either by the size of the point on the graph, or, at temperatures close to the peak where greater scatter occurred, by the small arrows.

In considering this temperature range, it seems relevant to mention Mme. Chaunevet's work† on the $Co_3O_4 \rightarrow CoO$ transformation, in which it is shown that the oxygen content of Co_3O_4 falls below stoicheiometric requirements at approximately 800° C., gradually changing to CoO with an increased oxygen content before finally reaching the stoicheiometric composition of CoO at about 1075° C. This result strongly suggests that, in our experiments, the complex transition was greatly influencing the mechanism of oxidation.

With regard to Mr. Davies' remarks on the oxidation curve for cobalt, we did find a difference between the results obtained in air and in oxygen, the former being much lower at 900° and 1000° C., but approximately the same at 800° or 1100° C. The results obtained after 24 hr. in the 60 : 1 atmosphere were:

°C.	Wt. increase g./cm.²	°C.	Wt. increase g./cm.²
800	0·013	900	0·029
1000	0·031	1100	0·103

and these may be compared with the values shown in Fig. 2.

His further statement that the sharp inflection in Fig. 2 is not indicated in the results obtained in the 60 : 1 atmosphere is surprising in view of the fact that the values at 900° C. (0·042 g./cm.²) and 1000° C. (0·045 g./cm.²) are almost identical, as is also the case in Fig. 2. Results in the intervening temperature range were not included in the Tables, since the peak had already been indicated in a detailed manner in Fig. 2. The oxidation of cobalt obeys the parabolic law irrespective of temperature, and Mr. Davies is incorrect in comparing results for 24 hr. in oxygen with those for 50 hr. in the 60 : 1 atmosphere. The experimental method used in this work has been shown to be satisfactory, since the shape of the rate/temperature curve in the 60 : 1 atmosphere was the same for times ranging from 24 to 120 hr. The fact that the layer of Co_3O_4 occupies only a small volume fraction of the total scale does not necessarily imply that this constituent may be ignored, since the rate of oxidation is controlled by the properties of the oxide rather than by its relative thickness.

It does not appear that the diffusion of cobalt ions through CoO is the rate-determining factor, as suggested by Mr. Davies, since, if this were true, one would not expect the oxidation rate at 1000° C. to be much lower than at 950° C., as is found to be the case, since at that temperature the scale also consists very largely of CoO.

Consequently, it seems feasible to us that of all the factors involved the most influential is that governing the transfer of oxygen into the CoO lattice. In the presence of a Co_3O_4 layer, the energy barrier for this movement might be replaced by a combination of a low barrier between the gas and the Co_3O_4 and a low transfer barrier between Co_3O_4 and CoO.

The question of the effect of spinel formation on the oxidation process is discussed by Mr. E. Ll. Evans. We would point out that the influence of a spinel is certain to be governed by the presence of other oxide layers. In the cobalt–chromium alloys, it is found in direct contact with the metal surface in association with CoO, whereas in the nickel–aluminium system a layer of aluminium oxide is interposed between the spinel and the metal, and this would be expected to provide a strong rate-influencing effect, as indeed is the case. The same reasoning may be appropriate to the cobalt–aluminium alloys, although no alumina layer was actually detected.

We would further draw Mr. Evans' attention to the fact that the paper by Hickman and Gulbransen to which he refers was published in 1947, whereas the statement of these authors that: "Our results do not indicate that the marked non-

* The Carborundum Co., Ltd., Trafford Park, Manchester.

† G. Valensi, *Métaux et Corrosion*, 1950, **25**, 283 (reporting results obtained by Mme. G. Chaunevet, *Dr. Thesis, Université de Caen*).

oxidizing property of the 80 : 20 nickel–chromium series of alloys may be explained on the basis of the formation of $NiO.Cr_2O_3$, as postulated by Iitaka and Myake, but rather that long lifetime may be associated with the occurrence of Cr_2O_3 and the absence of $NiO.Cr_2O_3$", was made by them in 1949.* In the best nickel–chromium–iron alloys, although Hickman and Gulbransen observed the presence of a small amount of spinel, the alloys formed Cr_2O_3 primarily.

While we would hesitate to make a general statement on the protective properties of spinels, no spinel has ever been shown to be more protective than a pure oxide film; furthermore, their flexibility in composition should not be quoted as a favourable property for confirming oxidation-resistance, since this may actually promote diffusion rather than prevent it.

With reference to Mr. Evans' request for further experimental details concerning the procedure for mounting sealed specimens, this is as follows : A metal cylinder, approximately 1 in. in dia. × 1 in. high, is glued to a glass plate and the specimen placed inside in the required position. The cylinder is filled with N.P.A. Bakelite Cement, a thermosetting liquid. The mount is treated for about 1 hr. in a vacuum desiccator attached to a water-suction pump. This removes the occluded air in the scale and, on releasing the vacuum, the cement is forced into the pores of the scale. Heating to 80° C. overnight, followed by a final hardening at 120° C. for 1 hr., completes the mounting process. The specimen is then carefully polished by the usual methods.

Dr. Sachs' remarks on the cobalt–molybdenum and nickel–molybdenum alloys may be supplemented by noting that the molybdate is surrounded by an excess of cobalt oxide which may suppress the action of any free MoO_3. As the temperature is increased, the molybdate will undoubtedly become more unstable, and the amount of free MoO_3 formed is such that coherent scale formation is impossible. We do not think that free MoO_3 was swept away by the air stream at the lower temperatures, since, had this been the case, it would have been found on the cooler parts of the apparatus, as at the higher temperatures.

Mr. Cantrell's contribution is very interesting. However, we feel certain that the relatively shallow zone of internal oxidation which we observed was not due to an effect similar to that which he mentions; the particles of oxide did not constitute a network at grain boundaries, nor was any weakness noticed in the remaining section of the alloy. The variation of the thickness of the internal oxide region was in accordance with theoretical considerations.

Dr. Dennison and Professor Preece (*in reply*): Dr. Kubaschewski points out that Valensi † has stated that in the reaction between copper and pure oxygen to form Cu_2O and CuO the relative thickness of the two oxide layers is independent of time. This observation is not in agreement with our experimental results. In either ordinary air or the simulated gas-turbine atmosphere, the percentage of cupric oxide in the scale increased with time, as shown in Fig. 4 (p. 231) of the paper under discussion. Moreover, during oxidation of copper in air at 650° C., the proportion of cupric oxide in the scale formed increased with time, as indicated in Fig. A.

In our opinion it is necessary to assume a change in the oxidation mechanism with temperature to account for the variation in the proportions of Cu_2O and CuO after different periods of oxidation. We found that from 850° to 600° C. an outer layer of CuO formed an increasing percentage of the scale with decrease in temperature. Consideration of the results obtained on the 2% aluminium and 2% silicon alloys (pp. 232 and 234) shows that oxygen must in some way diffuse inwards to cause an originally Cu_2O layer to be converted to CuO. The mechanism for this inward diffusion may be either the existence of anion vacancies in the CuO lattice or, as Dr. U. R. Evans suggests, by way of gaps in the crystal structure of the CuO layer formed under these conditions.

Fig. B shows a distinct change in the relationship between rate constant and temperature for the high-conductivity copper oxidized in air. As a straight-line relationship exists from 1000° C. to between 550° and 600° C., presumably the mechanism of oxidation remains the same within this range. Above 900° C. no CuO exists in the scales, and therefore the

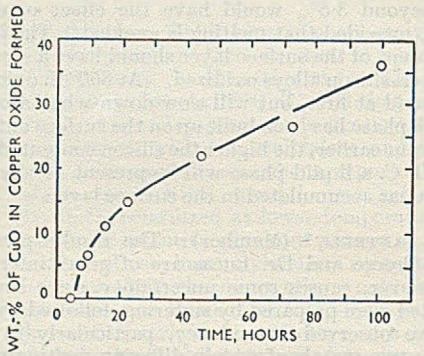

Fig. A

ruling factor will be the rate of outward diffusion of copper through Cu_2O. This mechanism presumably controls the overall rate of oxidation down to 500°–600° C. As shown in Fig. A., for a temperature within this range, the percentage of CuO in the scale increases with time. This may perhaps be explained by a dual process of film growth comprising outward diffusion of copper through Cu_2O and inward diffusion of oxygen through CuO. The relative rates of growth of

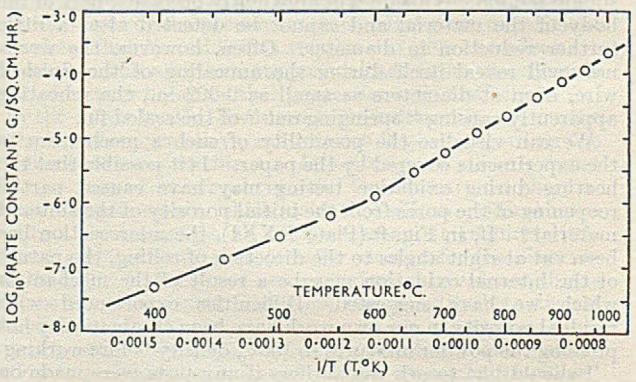

Fig. B

the films may be determined by the concentrations of copper and oxygen at the interface between the two oxide layers. Cu_2O alone will be formed until the concentration of copper at the scale surface falls below a limiting value, when the higher oxide will begin to form.

At 550°–600° C. there is a sudden decrease in the percentage of CuO formed in a given time, corresponding with the break in the relationship between oxidation rate constant and temperature. Zhuze and Kurchatov ‡ suggest that there is a corresponding increase in the conductivity of the scale formed on copper at temperatures below 600° C.

This may be taken to indicate that below this temperature range the relative diffusion rates of copper through Cu_2O and of oxygen through CuO will be affected, with the result that

* J. W. Hickman and E. A. Gulbransen, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **180**, 519.

† G. Valensi, [*Proc.*] *Pittsburgh Internat. Conf. on Surface Reactions*, **1948**, 156

‡ V. P. Zhuze and B. V. Kurchatov, *J. Eksper. Teoret. Fiziki*, 1932, **2**, 309; also *Physikal. Z. Sowjetunion*, 1933, **2**, 453.

greater proportions of Cu_2O will be found in the scales at temperatures immediately below this break than at those just above it. It may be that at these lower temperatures the rate of diffusion of oxygen inwards through the CuO layer is the controlling factor in overall oxidation rate, once the latter oxide has begun to form. Analysis of the scales formed after various periods of oxidation at 400° and 500° C. seems to suggest that a CuO outer layer is formed almost immediately on entering this temperature range, an observation which is supported by the work of Cruzan and Miley,* who detected CuO in films of the order of 100° A. thick at temperatures within this lower range.

It is obvious that further work is necessary on the composition of oxides formed on copper, particularly with regard to the effect of varying atmospheres.

In reply to Dr. U. R. Evans, we would point out that the investigations recorded in the paper were carried out in the period 1947–49 and have been available as a report of the British Non-Ferrous Metals Research Association since early in 1950. In this report a more detailed review of the literature was given. We believe that to enter upon a comprehensive review of the oxidation of metals for each new publication is impossible in view of the ground to be covered and the space available. A great many comparisons from previous work could have been quoted with equal, if not greater, justification than those which Dr. Evans has brought forward.

Dr. Evans does not appear to have noticed that the ideas involved in the work of Hubrecht and de Brouckère on copper–beryllium alloys are very similar to those outlined in the present paper for the behaviour of the copper–aluminium series of alloys, but not repeated in detail for the copper–beryllium alloys. He does, however, provide an interesting alternative for the diffusion of oxygen inwards through CuO, but at first sight this does not appear to account for the conversion of a layer initially consisting of Cu_2O to one entirely of CuO.

The explanation offered by Dr. Sachs for the behaviour of the copper–silicon series unfortunately does not take into account all the experimental evidence. His assumption of solution of silicon in the scale in the lower temperature ranges is incompatible with the formation of pronounced subscale layers consisting of precipitated SiO_2 at temperatures below 750° C. (p. 233 of the paper). In addition, scale analysis shows that the silicon, when present in the scale, invariably exists as SiO_2.

It appears that, contrary to Dr. Sachs' opinion, an explanation taking into account all the experimental evidence available will require some considerable degree of ingenuity.

Discussion

A Method of Determining Orientations in Aluminium Single Crystals and Polycrystalline Aggregates

By G. E. G. Tucker and P. C. Murphy

(*Journal*, this vol., p. 235.)

Dr. J. Hérenguel† (Member) and M. P. Lelong‡: We consider this method of determining orientations in aluminium and certain of its alloys very interesting, and to demonstrate its value would recall the applications of the etch-pit technique made by one of us (J. H.) with various co-workers during the last ten years.

As the authors point out, it is necessary to take into consideration the complications that may arise through simple or multiple truncations of the pits caused by impurities or deliberate additions to the aluminium. We have studied these etch-pits extensively on high-purity and commercial-purity aluminium (containing iron and silicon)§ and have identified the fundamental forms shown in Fig. A. We have

Fig. A.—Possible Truncations of an Etch-Pit.

confirmed, by taking sections perpendicular to the etched surface, that the centre of the elementary cube forming the hollow depression is always considerably above the surface being examined. Therefore, observation of the three edges of the basic trihedron is easy and accurate, thus removing all uncertainty arising from the use of truncated pits. Such observation is facilitated by utilizing certain special characteristics of the microscope, e.g. a variable angle of incidence of the beam and a revolving stage.

The nature of the etching reagent and the conditions of attack also have a marked effect on the degree of complexity of the pits. Moreover, the treatment undergone by the specimen before etching plays a part in modifying the number, size, and form of the pits. We are thus led to believe, in agreement with Mahl and Stranski, that the surface oxide layer plays a part in the attack. In particular, we have observed that washing in 10% caustic soda at 50° C. for several seconds after electrolytic polishing and before etching proper, generally has a beneficial effect. Of course, it cannot be considered valid to study crystal orientations by means of etch-pits on a sample polished only mechanically, as the cold-worked surface layer introduces a very considerable disturbing effect.

It is essential to use a microscope with a graduated rotating stage and a vernier. Precision is unlikely to be better than ½°. Most metallurgical microscopes, because of their construction, give with direct examination, with projection on a ground-glass screen, or with photography, a "left" image symmetrical with the object actually seen "right". It is essential to take this into consideration in the interpretation in order to obtain the correct orientation.

Use may be made of the measurement of the angles of the basic triangle in several ways:

(*a*) It is possible, as shown by Tucker and Murphy and by Kostron, to pass directly by calculation, by diagrams, or by tables, to the conventional Miller indices.

(*b*) The pole of the observed plane may be plotted on a stereographic projection. This is accomplished either by calculation of the angles made by the plane being studied

* C. G. Cruzan and H. A. Miley, *J. Appl. Physics*, 1940, **11**, 631.

† Director of Research to the Société des Tréfileries et Laminoirs du Havre and to the Compagnie Française des Métaux, Centre de Recherches d'Antony (Seine), France.

‡ Research Assistant, Centre de Recherches d'Antony (Seine), France.

§ J. Hérenguel, *Rev. Mét.*, 1949, **46**, 309.

with the three {100} planes, or by direct construction. Mr. Tucker and Mr. Murphy have established a particularly convenient double-entry table for such calculations.

(*c*) Simple models allow a rapid appreciation of the orientation being studied; we have used for this purpose a cut-out triangle (identical with the etch-pit), which is fitted into a hollow trihedron of Plexiglas.* It is even easier to construct the measured angles using a jointed triangle, in which is placed a trirectangular trihedron or a cube; this indicates immediately the required orientation (Fig. D, Plate XCIX). These methods are particularly useful for the study of progressive disorientations of a lattice. The law which this disorientation obeys is found unambiguously; this, as is well known, is not always the case with X-ray diagrams or stereographic representations.

We give below some examples of investigations which it has been possible to carry out satisfactorily by the use of etch-pits, and for which the classical methods employing X-rays could be used only with difficulty. The reagent was, basically, that of Lacombe, mentioned by the authors, modified only in respect of the concentrations of HCl and HNO_3. The temperature of etching was kept between 0° and 10° C., depending on the purity of the metal or the composition of the alloy.

(1) *Twinned Structures Obtained in Semi-Continuous Casting.*†

By this casting process a crystalline structure with a very high degree of order throughout the entire ingot is usually obtained in aluminium of about 99·5% purity. This is made up as follows:

(*a*) An outer zone, e.g. 5–15 mm. in thickness, with the ordinary columnar structure having a [100] fibre axis.

(*b*) The interior, which has a texture in which the basic unit is a flat plate composed of twin elements in contact on a (111) plane. A large number of plates are associated with one another, the twin plane of each being almost vertical, the [112] axis frequently containing the principal vector of the heat flow. In these units a progressive disorientation from

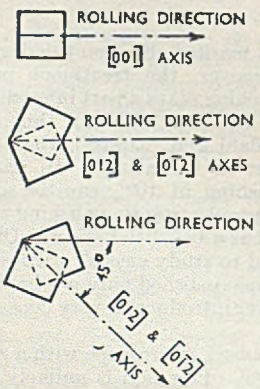

Fig. B.—Principal Orientations Shown by a Sheet of 99·5% Aluminium with a Very Strong Cube Texture.

plate to plate is often seen. At the junction of two such units, which are fairly strongly disorientated relative to one another, interpenetration of the type known as "felting" can be seen (Fig. H, Plate C). The constituents forming a separate phase are regularly distributed either at the junction of the plates (never on the twinning plane or in its immediate vicinity), or regularly spaced on the {100} planes. In section this structure has the appearance of a fish-bone, each bone being attached to a plate boundary. Fig. E (Plate C) shows a typical example.

Since the time of this investigation, a twin texture has been found in aluminium ingots solidified in a permanent mould (Fig. F, Plate XCIX) and in ingots of very complex alloys (e.g. Al–Zn–Mg–Cu).

(2) *Preferred Orientation After Annealing.*

Products rolled from semi-continuously cast ingots tend to exhibit, on annealing, textures with a high proportion of

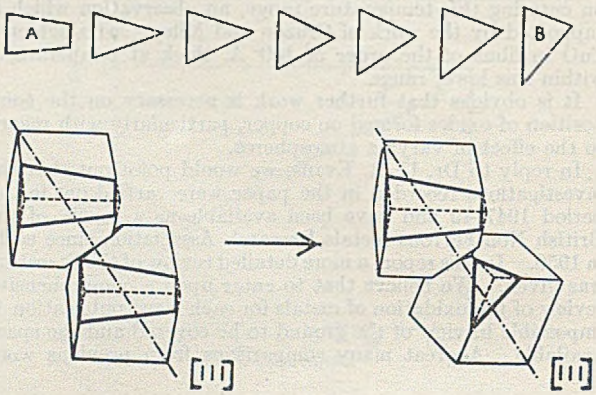

Fig. C.—Diagram of the Etch-Pits Shown on the Test-Piece Illustrated in Fig. K (Plate C).
A. Initial position in single crystal.
B. Final position, perceptibly twinned.

the cube texture. This has been studied in aluminium of 99·5% purity by means of etch-pits;* the orientations illustrated diagrammatically in Fig. B are based on statistical considerations. By this method it is also easy to estimate quantitatively the amount of cube texture and to determine its distribution on various scales (Fig. J, Plate C). This identification of the units on a large scale (whether in the cube texture or other relationship) is significant in connection with the surface markings which develop after deformation of the test-piece (orange-peel effect).‡

(3) *Internal Disorientation of Grains Produced by Plastic Deformation.*

Anomalies observed in the anodic oxidation of homogenized and cold-worked high-purity aluminium–magnesium alloys led to a study of the effects of plastic deformation on a single crystal.§ The disorientations were determined and measured by various micrographic methods used in combination: etch-pits, examination of oxide films in normal and polarized light, chemical "engraving", and observation of slip lines after deformation. The growth of deformation bands by progressive curvature has been clearly revealed, measurements of the relative orientations and dimensions of the bands and of the zones of curvature being carried out without difficulty. We have observed, as a result of increasing cold work, the appearance of multiple systems of alternating bands made up of short, strictly regular units, finally affecting the whole of the initial lattice. Fig. K (Plate C) shows a zone of curvature revealed by etch-pits. Fig. C illustrates diagrammatically, by means of some of the etch-pits observed, the transition from the initial orientation of the lattice to that of the band itself, by a plane curvature having a [111] axis of rotation common to the whole structure. The (110) plane containing this [111] axis forms the interface between the band and the initial lattice.

(4) *Rate of Anodic Oxidation as a Function of Orientation.*

In this investigation the orientations were again established rapidly and accurately by means of etch-pits.‖ A marked

* J. Hérenguel, *Rev. Mét.*, 1948, **45**, 505.
† J. Hérenguel, *ibid.*, 1949, **46**, 309.
‡ J. Hérenguel and G. Scheidecker, *ibid.*, 1949, **46**, 537.
§ J. Hérenguel and P. Lelong, *ibid.*, 1951, **48**, 875; 1952, **49**, 374.
‖ J. Hérenguel and P. Lelong, *ibid.*, 1952, **49**, 374.

anisotropy has been established and measured. For the aluminium–3% magnesium alloy studied, the planes of maximum oxidation were around [111], those of minimum oxidation around [100]. For a c.d. of 27 amp./dm.^{2} the relative difference was about 33%. More recent determinations have shown that this figure varies with current density. Fig. G (Plate XCIX) shows two neighbouring grains of different orientation carrying etch-pits and having, respectively, oxide films 50 μ and 57 μ thick. A transition zone can be seen extending over about 180 μ. Finally, etch-pits can be equally useful for indicating the variations in composition of a solid solution, for instance in the region of phases which have separated out in the cast structure.* By precipitation, or conversely, by homogenization, the distribution and density of the etch-pits can be changed, making it possible to follow the evolution of the structure. It may be noted that, in a cast alloy, the groupings of the pits follow, and thus delineate, preferred crystallographic directions which are traces of the {100} planes on which the phases precipitate, there being a composition gradient around each. These traces of the {100} planes, after etching, can be examined at low magnification in order to determine the grain orientation. Fig. L (Plate C) provides a good illustration of this in 99·5% aluminium.

These examples show the use which can be made of the etch-pit technique in the study of aluminium alloys in general. It would be valuable to extend its applications by finding etching reagents suitable for ferrous metals and alloys based on copper, &c.

The Authors (*in reply*): The examples of possible applications of etch-pit methods cited by Dr. Hérenguel and M. Lelong will be of great value to everyone interested in textural relationships in aluminium alloys, and it is to be hoped that their contribution will stimulate the wider use of such techniques.

It is interesting to note that mechanical methods of specimen preparation are regarded as unsuitable; although it is obvious that a very heavily worked surface layer could have a disturbing effect, we have observed perfectly formed etch-pits on pure aluminium samples polished mechanically. In our experience, moreover, the validity of the angular measurements is unaltered by such factors as surface strain, though it is undoubtedly true that ease of measurement and the perfection of the etch-pits can be affected.

Although desirable, it is not essential for the measuring microscope to be fitted with a graduated revolving stage; in fact, we prefer in some cases to lock the stage and instead to turn the eye-piece and cross-hair, the angular rotation being measured by an arm attached to the eye-piece and rotating around a co-axial graduated scale.

We agree that care must be taken to ascertain the relation between the observed image and the actual surface being examined, not only because of possible lateral inversion, but also because of possible rotation of the image. The microscope we used produced no lateral inversion, but a 90° rotation of the image.

We have recognized in the past the value of models in allowing a rapid appreciation of orientation, and the apparatus described by Dr. Hérenguel and M. Lelong appears to be very convenient. It will be realized, however, that such methods are of qualitative rather than quantitative value and cannot be used for recording the results of investigations.

Professor P. Lacombe,† Dr.ès Sci. (Member): The authors are to be congratulated, not only on their systematic study of the effect on the shape of etch-pits of the composition of the etching reagent and of the metal itself, but on their method of deriving crystal orientation mathematically from the measured angles of the etch-pits on the surface. Thus modern micrography, profiting by Jacquet's development of the electropolishing technique, is getting nearer and nearer to orientation micrography, leading eventually to three-dimensional micrography. Classical micrography, which was limited to identifying the different phases of an alloy or to determining the crystal boundaries of a polycrystalline aggregate, retained the qualitative characteristics of a descriptive or morphological method. The growing use of etch-pits has greatly increased the interest of micrography, by conferring upon it the status of a quantitative method. Following on our first study,‡ a number of workers have made use of reagents producing etch-pits and have suggested variations in the composition of the reagent for study in various fields: investigations on commercial-purity aluminium and industrial alloys,§ electron microscopy,‖ creep,¶ &c.

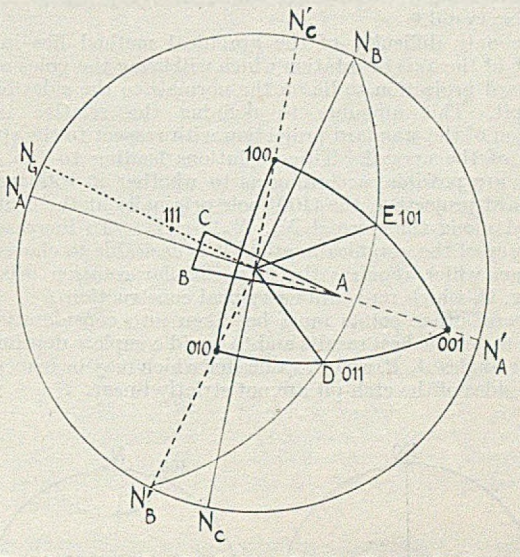

Fig. P.—Stereographic Projection for the Determination of the Orientation from the Direction $N_BN'_B$ of a System of Slip Lines. The great circle passing through the (101) and (011) poles (points E and D) must cut the basic circle at the same points as the direction $N_BN'_B$ of the slip lines.

Great interest attaches to the authors' calculations, which are simpler than those of Kostron;** in particular Table I, which gives values of the angles α, β, and γ, between the cube planes and the plane of micrographic section, as a function of the angles A, B, and C of a triangular pit, is extremely useful. These angles can then easily be plotted on the stereographic projection along the normals to the sides of the etch-pits, thus giving directly the (100), (010), and (001) poles.

In this connection I should like to recall that Beaujard†† and I have suggested a purely graphical method, an example of the application of which was given ‡‡ in relation to Fig. 17 of our earlier paper.§§ Fig. M (Plate C) shows the triangular pits, and Fig. P the corresponding stereographic projection. The procedure is as follows, using the attacked micrographic surface as the plane of stereographic projection.

(i) From the centre of the stereographic diagram are traced the directions parallel to the three sides of the etch-pit, and then the normals N_A, N_B, and N_C to these directions, which

* J. Hérenguel, *Rev. Mét.*, 1950, **47**, 29.

† Director, Centre de Recherches Métallurgiques de l'Ecole des Mines de Paris.

‡ P. Lacombe and L. Beaujard, *J. Inst. Metals*, 1947, **74**, 1.

§ J. Hérenguel, *Rev. Mét.*, 1948, **45**, 505.

‖ R. Castaing and A. Guinier, *Inst. Metals: Symposium on Metallurgical Applications of the Electron Microscope*, **1950**, 156, 157 (discussion).
A. F. Brown, *ibid.*, p. 103.

¶ G. Wyon and C. Crussard, *Rev. Mét.*, 1951, **48**, 121.

** H. Kostron, *Z. Metallkunde*, 1950, **41**, 370.

†† L. Beaujard, *Thesis*, Paris: **1949**.

‡‡ P. Lacombe, *Métaux, Corrosion-Ind.*, 1951, **26**, 392.

§§ P. Lacombe and L. Beaujard, *loc. cit.*, Plate V.

are the loci of the poles of all planes which could produce surface traces parallel to the three sides of the pit. It is also possible, as Tucker and Murphy suggest, to draw the actual shape of the etch-pit, suitably orientated with respect to a reference direction.

(ii) There is superimposed on the stereographic diagram a standard projection of the {100} cube poles, with one such pole at the centre of the projection. By means of the small concentric circles of a Wulff net, this standard projection may be rotated in such a way as to cause the various {100} poles to lie on the three normals to the etch-pit sides. The crystal orientation is then determined.

This construction is similar to that employed to determine the orientation of a crystal from the traces of slip planes, or of orientated needles of a precipitated phase in a solid solution (Widmanstätten structure). An identical method has been used for the case of crystals containing twinned crystals developed on at least three different {111} planes of the matrix crystal.*

The only difficulty of the graphical method lies in the choice of the axis of rotation which will bring the poles of the standard projection to lie on the normals to the sides of the etch-pit. This amounts to defining the relative initial position of the standard projection with respect to the stereogram of the crystal. Three solutions leading to the same result are possible, according as to whether in rotating the standard projection, the (100) pole originally at the centre is moved along the normal N_A, N_B, or N_C. To increase the accuracy of the graphical method it is desirable to choose the position which requires the least angular rotation (case (*d*) of Fig. Q, which represents a typical construction).

Several other points must be taken into consideration in order to get the best results and to avoid complete dependence on the angles *A*, *B*, and *C*, values for which may be inaccurate if the sides of the etch-pit are not strictly linear.

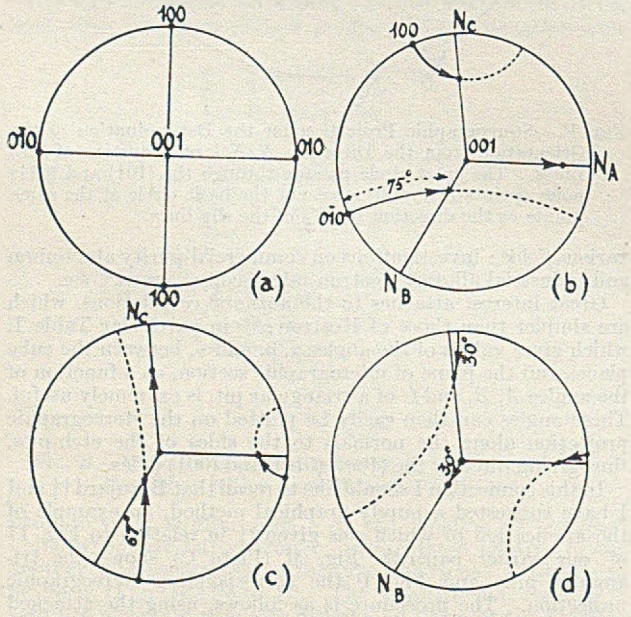

FIG. Q.—General Method of Determining Orientation by Rotation of the Standard Projection of the (100) Poles (Fig. Q (*a*)) to Bring the Three (100) Poles into Coincidence with the Three Normals N_A, N_B, and N_C to the Sides of the Etch-Pit.

In practice, accuracy in determining the (100), (010), and (001) poles depends largely on the size of the three angles *A*, *B*, and *C*, being greatest when these are of the same order of magnitude. If one of them approaches 0° or 90°, a considerable error can be introduced in estimating the position of two poles.

The example given in Fig. P has been specially chosen to make this point clear. The angle *A* (14°) can be measured with great accuracy and reproducibility on several neighbouring etch-pits, but a more difficult problem is presented by

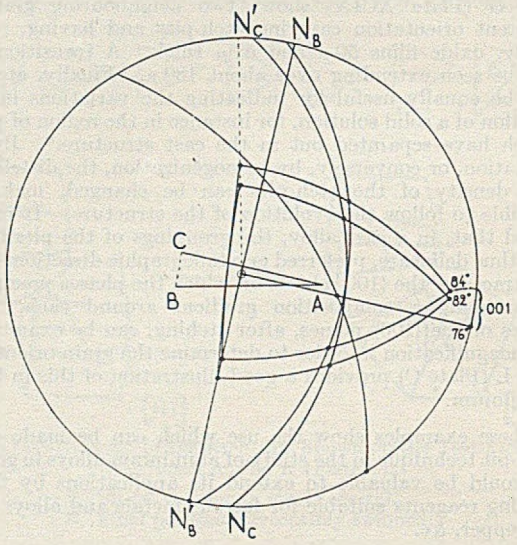

FIG. R.—Illustrating the Large Displacement of the (100) and (010) Poles, in Comparison to the (001) Pole, Resulting from Inaccuracy in the Values of the Angles *B* and *C* of the Etch-Pit. Angle *A* is assumed to be constant and = 14°.

angles *B* and *C*, which are both in the neighbourhood of 90°. The shortness of *BC*, and above all the curvature of sides *AB* and *AC* make accurate measurement difficult. Thus, the value of angle *B* measured on several etch-pits varies from 76° to 84°. Fig. R shows the stereographic plot for the three values, 76°, 82°, and 84°, of angle *B*. While the (001) pole suffers a relatively small displacement, it is far otherwise for the (100) and (010) poles.

In these difficult cases useful verification can be obtained either from the slip-band directions or from the [100], [010], and [001] directions of the three edges of the cubic pit. These can be derived from the three lines of intersection of each pair of etch-pit faces. This is one of the reasons for trying to produce etch-pits of sufficient size to be observed with a low-power lens of great depth of focus. It is then possible to focus at the same time on the unattacked surface and on the bottom of the etch-pit.

It can be clearly seen in Fig. P that one of the ⟨100⟩ lines of intersection almost bisects angle *A*. Therefore angles *B* and *C* should be approximately equal to $\frac{180° - 14°}{2} = 83°$.

Another graphical verification is based on the direction of the slip lines, which are traces of the {111} octahedral planes. In Fig. M (Plate C) the slip lines are almost perpendicular to the side *AC* of the etch-pits. This direction is plotted on the stereographic diagram, where in this particular case it falls on the straight line $N_B N'_B$. It is then necessary to construct the (111) plane, which gives the trace $N_B N'_B$. This plane is represented by a great circle, on which it is sufficient to know two points. If the (100), (010), and (001) poles are joined two by two by arcs of great circles, one of the poles (110), (101), or (011) can be fixed on each arc. The (111) plane is determined by a great circle passing through two of its {110} poles, such as *D* and *E*, situated at 45° from (100), (001), or (010) (Fig. P). If the position of the (100) poles is correct, the great circle representing the (111) plane must cut the basic circle of the stereographic projection at the same

* D. Whitwham, M. Mouflard, and P. Lacombe, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 1070 (discussion).

points $N_B N'_B$. By trial and error it is thus possible to determine with very great accuracy the exact position of the {100} poles, even in a case as unfavourable as this.

It is preferable to plot the (100), (010), and (001) poles on extensions of the N_A, N_B, and N_C normals drawn from the centre O of the projection on the three sides of the etch-pits. In this way the spherical triangle formed by joining the (100), (010), and (001) poles by arcs of a great circle, is orientated in a similar manner to the etch-pit. Moreover, the [100], [010], and [001] directions and also the [110] direction are parallel to the various intersections of the etch-pit faces among themselves or with a slip plane. This similarity of shape and orientation makes the interpretation of the stereographic diagram much easier, especially when trying to determine the relative orientation of two adjoining crystals.

It is in this last case that the use of etch-pits presents most interest, because the orientation can be determined even when the size of the adjoining crystals is extremely small. X-ray methods would necessitate special techniques, such as the microbeam used by Fournier* and by Hirsch and Kellar,† or lengthy exposure times. As an example, mention may be made of the study of so-called "insular crystals",‡ small crystals enclosed within a very large crystal developed either during recrystallization after critical cold working, or by secondary recrystallization. Such small crystals have an orientation closely approaching that of the enveloping crystal, or are exact twins of it.

A characteristic example of these two types of crystal is given in Fig. 5 of the paper by Lacombe and Berghézan.‡ A

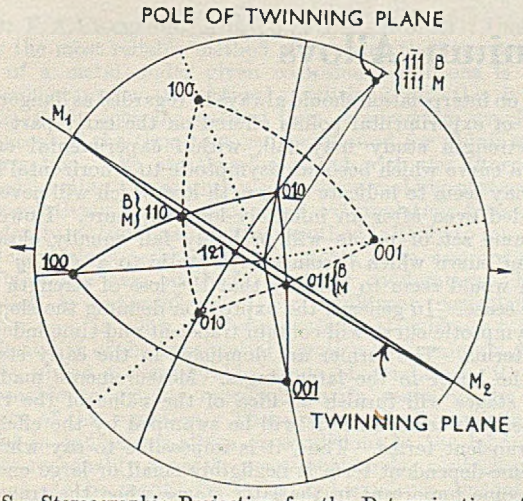

FIG. 5.—Stereographic Projection for the Determination of the Orientation of an Insular Twinned Crystal M in Relation to a Large Crystal B.

Full-line spherical triangle: (100) poles of crystal B.
Dotted-line spherical triangle: (100) poles of crystal M.

large crystal B contains both an insular crystal A of closely similar orientation and an insular crystal M twinned with respect to B (Fig. N, Plate C). It will be noticed that the etch-pits on crystals B and M are almost symmetrical with respect to the rectilinear portion of the grain boundary separating M from B, which is in fact the (111) twinning plane common to both.

As before, it is easy to construct from the etch-pit angles the stereographic projection of the three {100} poles of the two crystals M and B (Fig. S). Also in marking on this projection the direction M_1M_2 of the rectilinear boundary of crystal M, considered as the twin boundary between B and M, the twin relationship between B and M is clearly confirmed. Indeed, the normal N to the direction M_1M_2 passes through a pole P common to the stereographic projection of M and B and having the same (111) indices. The great circle situated at 90° from P can be held to represent the twin plane of B and M, since it passes through three poles common to B and M and having the same (110) indices. This is adequate to define unambiguously the twin relationship. Finally, it may by noted that in this case the twinning plane is at about 4° from the perpendicular to the micrographic surface; this is in agreement with the relatively symmetrical shape of the etch-pits with respect to the rectilinear boundary of the twin.

These examples show the importance of the information that may be obtained from etch-pits when stereographic methods are applied to the interpretation of X-ray diagrams. One further very promising development of the etch-pit technique may be mentioned. This is its use to reveal macromosaic or polygonization boundaries in crystals of pure aluminium § or of its solid solutions. In general the etch-pits do not concentrate on boundaries between two crystals of differing orientation. Rather do they group themselves preferentially at the "intragranular" boundaries associated with polygonization, where it has been suggested by Orowan and by Cahn ‖ that dislocations collect. Thus, it might be visualized that each etch-pit originates at the site of a dislocation. This led Read and Shockley ¶ to suggest that the minimum distance between two etch-pits on a polygonization boundary could be used to determine the very small difference of orientation between adjacent sub-grains. Fig. O (Plate C) shows a crystal of pure aluminium whose surface is parallel to the (111) plane, divided by polygonization boundaries into several sub-grains, the degree of disorientation between which can be precisely determined from the very distinct etch-pits. To conclude, in this last case also the micrographic method has distinct advantages over X-ray methods. It is possible, indeed, to determine the disorientation between two selected sub-grains and to make a systematic study of the distribution of such disorientation between the several sub-grains of a large crystal.

The AUTHORS (*in reply*): Professor Lacombe's remarks are of great interest, especially in defining the uses and limitations of etch-pit techniques.

We agree that the accuracy of positioning of the poles plotted from measurements made on triangular etch-pits is, to a large extent, governed by the shape of the triangle, and we have carried out some calculations which are relevant to this point.

The partial differential coefficients of α, β, and γ may be calculated with respect to angles A, B, and C from equations (5) (p. 239) of our paper. These derivatives are of two general forms, such as:

$$\left[\frac{\partial\alpha}{\partial B}\right]_C = \frac{\sec^2 B}{2 \tan B \tan \alpha} \quad . \quad . \quad . \quad . \quad (1)$$

and

$$\left[\frac{\partial\alpha}{\partial B}\right]_A = \left[\frac{\partial\alpha}{\partial B}\right]_C - \left[\frac{\partial\alpha}{\partial C}\right]_A \quad . \quad . \quad . \quad . \quad (2)$$

It can be shown that when $C \geqslant B \geqslant A$ (the case considered in the paper) the largest of the eighteen possible derivatives, arithmetically, is:

$$\left[\frac{\partial\gamma}{\partial B}\right]_A = \frac{\sec^2 B}{2 \tan B \tan \gamma} \quad . \quad . \quad . \quad . \quad (3)$$

This expression tends to infinity as C tends to 90°, and has a minimum value of $\frac{\sqrt{3}}{2\sqrt{2}}$ when $A = B = C = 60°$. If these calculations are applied to the example cited by Professor

* F. Fournier, *Rev. Mét.*, 1949, **46**, 360.

† P. B. Hirsch and J. N. Kellar, *Proc. Phys. Soc.*, 1951, [B], **64**, 369.

‡ P. Lacombe and A. Berghézan, *Métaux et Corrosion*, 1949, **24**, 1.

§ P. Lacombe and L. Beaujard, *loc. cit.*

‖ R. W. Cahn, *J. Inst. Metals*, 1949–50, **76**, 121.

¶ W. T. Read and W. Shockley, *Phys. Rev.*, 1950, [ii], **78**, 275.

Lacombe in Figs. P and R, it is found that if $A = 14°$, $B = C = 83°$, then

$$\left.\begin{aligned}\frac{\partial\gamma}{\partial B}\Big]_A &= 4{\cdot}01\\ \frac{\partial\alpha}{\partial B}\Big]_A &= 0\\ \frac{\partial\beta}{\partial B}\Big]_A &= -4{\cdot}01\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (4)$$

Thus, neglecting errors in the positions of the radii (which, in any case, affect only the (001) pole), the errors in the (100) and (010) poles are approximately four times the error of measurement of angle B, while the (001) pole is not affected by the error of angle B.

The development of straight-sided etch-pits is, of course, one of the greatest practical difficulties in any method involving angular measurements. The only solution appears to lie in the development of reagents which give a "clean" crystallographic attack. If this is impracticable in any particular instance, then the specimen may have to be regarded as outside the scope of the method; it is in such doubtful cases that useful information can be obtained from observations of the positions of the cube edges. It can be shown that the bottom edges should appear perpendicular to the opposite etch-pit sides, and this property may enable the true direction of a curved side to be determined with greater accuracy. This relationship has, of course, been assumed by Professor Lacombe in calculating angles B and C.

As Professor Lacombe says, slip lines can in certain circumstances provide valuable data for correcting slightly inaccurate measurement or plotting. This is especially true when slip lines which are almost parallel with the shortest side of the etch-pit are present on the specimen. If, however, the only slip lines available are almost perpendicular to the shortest etch-pit side, they are of little value, as alteration of the basal angles (B and C) of the etch-pit will merely cause the {111} pole to move along the radius normal to the slip lines (or across it at a very shallow angle). In this case no accurate estimate of angles B and C corresponding to a "best" fit of the {111} pole can be obtained.

This limitation in the use of slip lines may thus be particularly inconvenient if only one family of slip lines has been developed on the specimen; if, however, three or four families of slip lines are present, then at least one of these will serve as a check. Ideally, all four families of slip planes should be developed, but the practical difficulties involved may be very great, especially in sheet, unless the orientation is such that all the slip lines can be made to appear without undue working of the specimen.

Discussion

Corrosion of Aluminium Alloys *

Dr. U. R. Evans,† M.A., Sc.D., F.I.M., F.R.S. (Member): I am particularly interested in the fact that Mr. Metcalfe attributes the absence of failure in H15-WP to the attack turning in a direction parallel to the specimen face. Mr. Farmery, working with me on aluminium–magnesium alloys in a state more sensitive than would occur in practice, finds that occasionally a specimen may have an abnormally long life (perhaps 1000 times the normal value), and this also seems to be due to the attack spreading sideways, instead of across the specimen. But the phenomenon should not necessarily be regarded as desirable. If the crack turns along a plane parallel and close to the surface, and if the voluminous corrosion product is formed within the crack, the expansion may dislodge the outer layer. Such cracking off of flakes from the surface was, I believe, often met with at a time when wrought iron was an important structural material, since here corrosion tends to follow zones parallel to the surface. The cause of the difference between the behaviours of the Q (quickly corroding), R (resistant), and V (very resistant) zones found in wrought iron is being studied in my laboratory by Mr. Chilton.

Mr. Metcalfe uses his results to test a view, now held in certain quarters, that it is possible, by observations made during relatively short-time experiments, to calculate a thickness which will ensure that the specimens will last for ever. He makes some salutary observations which should be pondered by anyone inclined to adopt this "hope of eternal life" for aluminium alloys. He notes after 12 months' exposure "severe local foliation," constituting "a new type of attack, the incidence of which was much delayed and appeared to be progressing rapidly." This evidently could not have been foreseen from observations at the outset, and it will be recollected that Dr. Vernon,‡ in his early work on aluminium, also noted sudden and unpredicted acceleration in the oxidation after all action appeared to have ceased.

However, quite apart from these special cases, conclusions based on interpolation should always be regarded as dangerous. A set of experimental points offered on the early part of a time/strength study may fall, within experimental error, upon a curve which becomes asymptotic to a horizontal line, and may seem to indicate a strength-loss which will never be exceeded even after an infinitely long exposure. However, the same set of points will probably fall equally close to another curve which becomes asymptotic to a *sloping* line, which would seem to indicate that the loss of strength will never cease. In general, the expression defining the slope of an asymptotic curve will contain transient and time-independent terms. The former are dominant in the early stages, and the latter in the later stages. Measurements made in early stages will furnish no idea of the value of the time-independent term, since it will be swamped by the effect of the transient terms. Thus, it is impossible to say whether the time-dependent term is negligibly small or large enough to become important in the later stages when the transient terms have lost their importance. In the latter case, a slow weakening will continue indefinitely.

In a matter where great expense, and even loss of life, may result from structural failure, it would be altogether wrong to conceal the opinion that the "eternal life" belief is a dangerous one. It is satisfactory to note that Mr. Metcalfe seems to hold very much the same opinion.

Mr. R. Chadwick,§ M.A., F.I.M. (Member): Dr. Brenner and Mr. Metcalfe have adopted somewhat unusual conditions for stress-corrosion testing. In carrying out such a test the use of a highly aggressive corroding medium is undesirable because, if the medium is one causing severe attack on the unstressed specimens, the effective area of cross-section will change during testing, and stress per unit area will thus be far from constant. It is therefore preferable to employ neutral salt solution, or even distilled water, as the corroding medium.

When, in the plotted results of stress-corrosion tests in

* Joint discussion on the papers by P. Brenner and G. J. Metcalfe (*Journal*, this vol., p. 261) and by G. J. Metcalfe (this vol., p. 269).

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‡ W. H. J. Vernon, *Trans. Faraday Soc.*, 1927, **23**, 154.

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acidified salt solution (Fig. 5, p. 267) the curve for stress-corrosion in tension is compared with that for unstressed specimens subjected to a similar corrosive environment, the difference is found to be about 20% in terms of stress. Having regard to the authors' statement (p. 265) on the large observed differences in degree of attack on any one alloy, and their figure of ±20% for the scatter range in determinations of residual tensile stress on corroded specimens, it is doubtful whether Fig. 5 can be regarded as providing any really conclusive evidence that the applied stress significantly affects the rate of corrosion, and indeed the authors do not specifically make any claim that there is such an effect. However, they subsequently discuss the behaviour of the alloys in stress-corrosion as if a real effect were in fact established, and in both the synopsis and the final conclusions a relationship is defined between susceptibility to stress-corrosion and the degree of cold work. The indirect recognition of a stress-corrosion effect is contrary to the evidence of the experimental work, and is likely to be very misleading when the synopsis, or the comments and conclusions, are read without a detailed study of the whole paper.

In regard to the description of the test itself, it is not clear what is meant by "1·2% hydrochloric acid by weight". Is this the content of HCl or of a concentrated solution of HCl? In addition, the volume of corroding medium relative to the surface area of specimens immersed should preferably be stated.

Since even very small amounts of copper may significantly affect corrosion, it would have been most desirable to have determined this element in chemical analysis of the alloys.

Dr. F. A. Champion,* A.R.C.S., F.I.M. (Member): Undoubtedly the most reliable method of assessing the behaviour and life of a metal under given corrosion conditions is direct assessment under the natural conditions, but this is often impractical, since the natural lives required are usually far in excess of the time that can be allowed for obtaining the information. We are therefore faced with the alternatives of accelerating the corrosion process or making observations over relatively short periods and extrapolating from them. Evidently, extreme use of either method is likely to invalidate the conclusions reached, and it seems more appropriate to combine the two methods, each in moderation. Extrapolation is commonly used for rectilinear corrosion/time curves and, in view of the experimental evidence† of the applicability of the exponential equation to aluminium and its alloys under a considerable range of conditions, it seems reasonable to employ extrapolation in assessing the parameters of this equation. These parameters are particularly useful in comparing alloys or conditions in the laboratory, where reasonably accurate assessment under controlled conditions can be made. With natural exposure, uncontrolled variation of the conditions occurs, and the steps in Dr. Vernon's curve to which Dr. Evans (p. 738) referred were evidently due to this cause,† the effect decreasing as film formation on the metal proceeded. Where mechanical properties are to be assessed, relatively thin specimens are required to attain the accuracy desirable for assessing the parameters of corrosion/time curves. Mr. Metcalfe's paper is particularly valuable in giving results of direct interest to the structural engineer, since his metal was just thick enough to be within the engineer's common range, while natural exposure in a wide variety of conditions was employed. Unfortunately, these factors, and the rather wide scatter in the initial mechanical properties, rendered most of the results too insensitive for use in testing the applicability of the exponential equation. Assuming the equation to hold, however, the results from the conditions giving the most severe corrosion did permit the calculation of the parameters. It is encouraging to note that Mr. Metcalfe's calculations on this basis gave for the worst alloy the same theoretical minimum thickness (0·060 in.) as my own.

I feel that the application of the data obtained on this basis to service problems should have the object not only of achieving economy of material by avoiding unnecessary allowances for corrosion, but also of demonstrating the false economy of using metal which is too thin. Taking as an example the thickness of 0·06 in. mentioned above, it is evident that metal 0·072 in. thick will have far more than twice the life of metal 0·036 in. thick. More precise application of these results to design requires the inclusion of an appropriate safety factor, the assessment of which can come only from experience, as with other metals. The fact that one specimen at Sheffield suffered a loss of strength three times the average cannot be taken as representative of scatter liable to occur in service, where the greater cross-sectional area of structural members will have a somewhat similar effect to the averaging of results from these ¼-in.-wide specimens. I feel, therefore, that Dr. Evans need not fear that an increased risk will result from the application of the exponential equation, provided that the application is made intelligently, including recognition of the fact that under some conditions the exponential equation does not hold. In the latter cases other measures are desirable. Thus, the few aluminium alloys which are susceptible to stress-corrosion or exfoliation should be protected under severe exposure conditions by cladding or spraying, to which Mr. Metcalfe has referred.

The second paragraph of Mr. Metcalfe's introduction (p. 269) is liable to be misleading. As far as I am aware, the only useful quantitative data on the initial logarithmic phase of film formation (on film-free metal) was obtained by Steinheil.‡ The work quoted in that paragraph is concerned with the later exponential phase. I should also like to have Mr. Metcalfe's views as to whether the surprisingly greater attack at Christchurch by total as compared with partial immersion was due to contamination of the water in the former case, for example with heavy metals.

The paper by Dr. Brenner and Mr. Metcalfe gives valuable new information on the effect of zinc on the microstructure of the aluminium–5% magnesium alloy, and I should like to ask whether the incomplete boundary observed on ageing homogenized specimens (p. 263) was due to inadequate ageing time. It is much more difficult, however, to extract useful information from the results of their corrosion tests. Thus, Fig. 12 (Plate XXXVIII) of the unaged alloy 4 shows pitting at least 15 mils deep, which is described as "heavy", whereas Fig. 14 (Plate XXXVIII) of aged alloy 4 shows pitting 5 mils deep, which is described as "severe". On p. 266 reference is made to intercrystalline attack in Fig. 17 (Plate XXXVIII), but not in Fig. 14, whereas the photomicrographs tend to show the reverse, though there is very little in either case.

There is doubt as to whether the aluminium–5% magnesium alloy is susceptible to stress-corrosion in the practical sense (e.g. the absence of stress-corrosion failures in extensive Naval use), and it is unfortunate that this paper should describe tests which I feel, for the reasons given below, do little more than confuse the issue.

(i) The corrosion medium has a *p*H below 1, and is, therefore, too far removed from natural exposure conditions to give useful quantitative data.

(ii) A specimen suffering uniform corrosion without any type of selective attack would bend under load owing to the reduction in cross-sectional area, and therefore "endurance for limiting deformation" gives no information on stress-corrosion susceptibility.

(iii) It is not clear whether all the aged alloys failed by fracture or whether some failed by bending.

It would be useful if the authors could give information or comment on the following points:

(1) What were the copper contents of the alloys?

(2) It is concluded (p. 265) that increasing zinc content produced no improvement in corrosion-resistance of the aged and unaged alloys. Figs. 2 and 3 (p. 265) suggest that

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† F. A. Champion, *Metal Ind.*, 1948, 72, 440, 463.

‡ A. Steinheil, *Ann. Physik*, 1934, [v], 19, 465.

increasing zinc content reduced the effect of ageing on the loss of mechanical properties.

(3) A reference to experimental work on the relation between "electrolytic potentials" and cold work on these alloys (as mentioned on p. 267) would be useful.

Mr. E. A. G. Liddiard,* M.A., F.I.M. (Member): The most important fact emerging from the papers by Dr. Brenner and Mr. Metcalfe is the influence of structure on the corrosion and stress-corrosion behaviour of aluminium alloys. It is quite clear from Mr. Metcalfe's paper that the relatively good behaviour of the HE15 material compared to that of HE10, is due to the structure of the former, which has caused the corrosion to take place along planes parallel to the surfaces of the original extrusion. This layer type of corrosion ensures that the effect on mechanical properties is at a minimum. More recent results, obtained from work which Miss W. A. Bell has been carrying out at Fulmer, confirm that once this layer corrosion has reached a certain depth it then proceeds at a much increased rate, and there is no real doubt that the HE10 material is superior to the HE15 when exposed to severe industrial atmospheres. I am not at all sure that the results given in the paper by Dr. Brenner and Mr. Metcalfe can be ascribed to the effect of cold work on structural directionalities. If Figs. 8 and 17 (Plate XXXVIII) are examined, it will be seen that there is a marked tendency for the grain boundaries to be elongated in a direction parallel with the surface, and this probably influences the spread of corrosion crevices so that they are relatively less harmful to the mechanical properties of the test-piece. This effect of cold work in reducing the rate of corrosion damage may therefore have nothing to do with precipitation at grain boundaries. The statement on p. 267 that "bending stresses in service are much more dangerous than tension stresses if they are associated with corrosion attack", needs qualification in view of the results of some experiments started by Mr. Metcalfe when he was at Fulmer, and which are described in greater detail in a paper by Miss Bell and myself.† Typical results are shown in Table A. Some of these were on sheet material,

Table A.—*Influence of Structure on Stress-Corrosion Behaviour of H15 Aluminium Alloy, Using Different Methods of Testing.*

Specimens sprayed daily with 3% NaCl solution.

Type of Test	Average Time to Fail Under Stress of 20 tons/in.², days					
	Extrusions			Sheet		
	Direction of Stressing	Mn-free	Mn-contg.	Mn-free	Mn-contg.	Thickness, in.
Direct-Tension	Longitudinal to extrusion direction	...	...	2	2	0·2
		46	60	3	5	0·1
				2	2	0·05
	Transverse to extrusion direction	5	4			
Four-Point-Load Bend Test	Longitudinal to extrusion direction	...	...	9	97	0·2
		>320	>320	7	13	0·1
		...	...	10	5	0·05
		...	...	12 [a]	38 [a]	0·1

[a] Sheet rolled from extruded bar.

and some on extrusions. In the experiments on sheet the bending was by four-point loading, and the top surface of the specimen was in tension and the bottom in compression. The specimens were in a covered unheated hut and were sprayed daily with a 3% NaCl solution. The times to failure of the H15 sheet, with and without manganese, were very much shorter in direct tension than in bending. I cannot explain why this should be so, unless it is that the directional effects become more marked in bending than in direct tension, and it may be significant that the alloy containing manganese shows a greater disparity between direct tension and bending than the manganese-free alloy.

Turning to the behaviour of extrusions, no failure by stress-corrosion occurred in either alloy in a bend test in which the specimens were cut longitudinal to the direction of extrusion. In direct tension, however, even longitudinal specimens failed in 46–60 days, but specimens cut transverse to the direction of extrusion failed in 4–5 days. It is only fair to state, however, that there is a fundamental difference in the

Table B.—*Stress-Corrosion Tests on Coated H15 Aluminium Alloy Sheet 0·036 In. Thick.*

Specimens sprayed daily with 3% NaCl solution.

Type of Coating	Stress, tons/in.²	No. of Days to Fracture
Sprayed:		
Commercial Al (99·7%	18	>300 not broken
purity)	15	>219 not broken
Al–1% Zn	18	>300 not broken
	15	>219 not broken
Zinc	18	129
	15	132
Zinc paint	18	56
	15	84
Not protected	18	14
Shot-blasted surface	15	38

specimens, the bend specimens were, of course, flat with rectangular cross-section, whereas the direct-tension specimens were circular, and penetration by corrosion at two of the sides would not be delayed by the structural inhomogeneity. In case the layer corrosion and stress-corrosion of the H15 aluminium alloy present too depressing a picture, I should like to quote some recent results (Table B) which show that the provision of a sprayed anodic coating on H15 sheet appears to be completely effective in preventing stress-corrosion, and so far as I know there have been no cases of stress-corrosion failures of clad Duralumin-type sheet. The spraying in this case was done with a powder pistol. It will be seen that zinc spraying, which in this case was only 0·002 in. thick, increased the life by some four to nine times. A metallic zinc paint was rather less effective, but still showed an improvement. These particular tests were carried out using cantilever bending, and not the four-point-loading specimens referred to previously. I should again like to emphasize that these results were obtained on laboratory tests using salt spray, and probably do not represent the behaviour of the material in practice. However, it is clear that anodic protection is effective in preventing stress-corrosion of this type of alloy, and may therefore be highly desirable in certain structural work.

Mr. J. C. Tucker,‡ B.Sc., A.I.M. (Junior Member): The bending stress-corrosion tests on the unaged and aged 5% magnesium alloy without zinc are illustrated graphically in Figs. 4 (*a*) and (*b*) (p. 266) of the paper by Dr. Brenner and Mr. Metcalfe, the initial bending stress being plotted against the time to failure. If we imagine two alloys of widely different tensile properties stressed at the same value under the same conditions of corrosion, and these alloys are attacked at the same rate, then the stronger material will have the greater endurance, since stress-corrosion cracks will have to progress further before the cross-sectional area has been reduced sufficiently for the tensile strength of the material to be exceeded. The alloys in Fig. 4 have been given between

* Director, Fulmer Research Institute, Stoke Poges, Bucks.

† E. A. G. Liddiard and (Miss) W. A. Bell, *J. Inst. Metals*, 1953–54, 82, (9), 426.

‡ Aluminium Laboratories Ltd., Banbury.

0 and 50% cold reduction, and exhibit widely different tensile properties, as shown in Fig. 1 (*a*) (p. 264); the curves in Fig. 4 might be of greater interest, therefore, if instead of plotting the actual stress against endurance, this stress was represented as a percentage of the 0·1% proof stress. If this is done for Fig. 4 (*b*), illustrating the aged alloy, the relative positions of the graphs are altered as shown in Fig. A. The alloy with 30% cold reduction would still remain of lowest resistance but that with no cold reduction would show the greatest resistance, and the graphs for alloys with 10% and 50% reduction with approximately equal resistance would fall between the graphs for 30% and 0% reduction. Similarly, in Fig. 4 (*a*), the differences between the alloys would be not nearly so marked as is shown. Referring still to Fig. 4 (*a*), we have, at Banbury, carried out bending stress-corrosion tests in a similar manner to that described by the authors. Specimens yielded throughout the tests without, however, showing a marked decrease in tensile properties over unstressed specimens after one year's exposure. Fig. 4 (*a*) indicates that the alloys possess widely different stress-corrosion properties, and we should be interested to know,

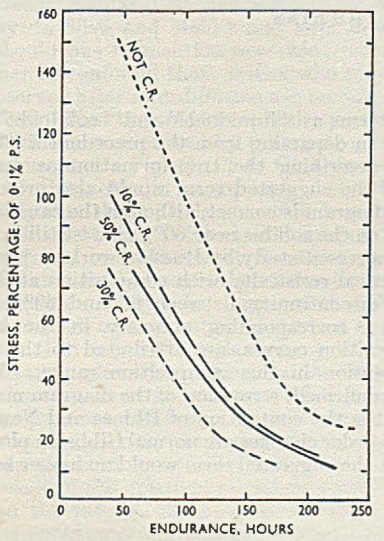

FIG. A.—Bending Stress-Corrosion Tests on 5% Magnesium Alloy Aged at 70° C. (Replotted curves of Fig. 4 (*b*) of Brenner and Metcalfe's paper.)

therefore, whether these specimens were tensile tested after stress-corrosion testing, to determine whether any marked loss of properties was observed as compared with unstressed specimens.

The influence of cold reduction on the corrosion-resistance of the cold-worked and aged alloy without zinc is of interest. The 5% magnesium alloy has useful tensile properties after cold reduction of the order of 30%. However, this alloy had the poorest resistance of the alloys tested by the authors. They have shown that sheet tested in the aged condition after 50% cold reduction has a superior resistance to stress-corrosion as compared with sheet tested in the aged condition after 30% cold reduction, and have correlated this behaviour with the distribution of the precipitate, there being more general precipitation in the alloy cold-reduced 50%. This indicates the desirability of obtaining a property level corresponding to a cold reduction of the order of 30%, by a low-temperature heat-treatment after heavy cold reduction, i.e. by temper-annealing rather than by temper-rolling. I can amplify this by referring to some work carried out at our Kingston Laboratories on a 5·5% magnesium alloy in the half-hard condition. The material was produced by both temper-rolling and temper-annealing, and all material was given a low-temperature ageing treatment of 3 days at 100° C. to simulate exposure under tropical conditions. The stress-corrosion tests were then carried out in a $NaCl/H_2O_2$ solution under direct tension at 75% of the 0·2% proof stress. In the temper-rolled condition the endurance of the specimens varied between 1 and 36 hr., and in the temper-annealed condition between 25 and 60 days, some specimens remaining unbroken at 60 days. The superiority of temper-annealing over temper-rolling is well demonstrated.

The AUTHORS (*in reply*): As suggested by Dr. Evans, it would indeed be wrong to conceal the danger of expecting aluminium alloys to have eternal life, and an effort was made in the paper to emphasize the wisdom of preventive measures when serious corrosion attack, particularly of the foliation type, is observed. One is, however, inclined to favour the view of Dr. Champion that, used intelligently, the exponential equation can be applied, provided that precautions are taken to give suitable protection to alloys susceptible to stress-corrosion or to foliation under severe exposure conditions.

In reply to Dr. Champion's enquiry, the specimens totally immersed in the river at Christchurch frequently became completely buried in river mud owing to variations in the rate of flow of the river causing deposition of silt, and it would not be surprising if under these conditions contamination of the specimens with heavy metals occurred. The examples of the beneficial effects of sacrificial protective coatings given by Mr. Liddiard are particularly encouraging, since the possibilities of using alloys of much higher strength, which are susceptible to stress-corrosion, may be envisaged.

It has been suggested by Dr. Champion that the presence of an incomplete grain-boundary network in the homogenized material described in the paper on the corrosion of aluminium–5% magnesium alloys might be due to inadequate ageing. No information in support of this view was found, and little change in structure was observed after ageing for 28 days at 70° C. as compared with the normal 14 days at 70° C. The copper content of the alloys was, unfortunately, not determined, but as very high-purity materials were used, it is unlikely that the figure exceeded about 0·04%. In reply to Dr. Champion's and Mr. Tucker's criticisms of the use of the accelerated corrosion medium (i.e. a solution of 3% sodium chloride containing 1·2% hydrogen chloride by weight), while it is agreed that the quantitative data obtained should not be compared with service conditions, we believe that such accelerated tests may be valuable in the fundamental investigation of stress-corrosion behaviour, especially in the case of highly corrosion-resistant materials such as the aluminium–5% magnesium alloys.

The plotted results of stress-corrosion tests obtained under these conditions show a real effect of stressing in both tension and bending compared with unstressed specimens exposed for the same period, as the scatter in the accelerated test is smaller than the difference between the three curves. The figure of $\pm$ 20% for the scatter range, mentioned on p. 265, refers to the non-uniform attack of the spray test, and not, as Mr. Chadwick erroneously infers, to the more uniform attack in the accelerated stress-corrosion test.

It is not true that bending under load (" yielding ") occurs only when the attack is uniform and non-selective as it may also occur when corrosion attack penetrates at a uniform rate along all grain boundaries. This type of attack accounts for the fact that not all the specimens fractured in the accelerated test but some failed by yielding.

Considering the high range of scatter in the results after twelve months' exposure, we should not like to conclude from Figs. 2 and 3 (p. 265) that increasing the zinc content reduces the effect of ageing on the mechanical properties, as Dr. Champion suggests.

The relation between electrolytic potentials and cold work on metals and alloys is a well-known phenomenon described by Heyn and Bauer.* It seems, as a result of the later work referred to by Mr. Liddiard, that although theoretically when

* E. Heyn and O. Bauer, *Mitt. deut. Materialprüfanst.*, 1911, 29, 2.

stress concentration occurs in service, bending stresses are more dangerous than tensile stresses, this requires modification when further corrosion leads to release of stress owing to the attack progressing along planes perpendicular to the application of the load.

Our thanks are due to Mr. Tucker for drawing attention to the beneficial effects of temper-annealing as opposed to temper-rolling. Presumably the improvement in properties is due to relief of stress and possibly to break up of any continuous network of the precipitated phase.

By replotting our Fig. 4 (*b*) (p. 266) so that instead of the actual stress, the percentage of the 0·1% proof stress is plotted against endurance (Fig. A), Mr. Tucker has shown that the relative positions of the graphs are altered. This may be of theoretical interest, but in practice only the actual stress is of importance, as this is the basis for calculating the strength of a structure and is the main scale for measuring safety. The specimens were not tensile tested after stress-corrosion testing, since they were sometimes severely deformed or even fractured.

Discussion

The Kinetics of the Eutectoid Transformation in Zinc–Aluminium Alloys

By R. D. Garwood and A. D. Hopkins

(*Journal*, this vol., p. 407)

Mr. A. R. Bailey,* M.Sc., A.I.M. (Member): I should like to raise a small point regarding the terminology used in this paper. Is it justifiable to refer to the isothermal reaction at 275° C. in the zinc–aluminium system as a eutectoid transformation? The relevant region of the equilibrium diagram is identical with that involving a monotectic reaction. I suggest, therefore, that the reaction in question should strictly be regarded as a monotectoid, even though eutectoid-type microstructures may result.

The Authors (*in reply*): We agree with Mr. Bailey that the α/α' phase boundary in the accepted zinc–aluminium equilibrium diagram is similar to the liquidus/liquid-solubility curves in binary systems of the monotectic type. It would thus be terminologically more correct to describe the transformation as a monotectoid. However, in view of the limited use of such terms as "liquidoid" and "solidoid", we do not feel justified in departing from the precedent set by previous workers in describing the transformation as an eutectoid. Adoption of the suggested term would also presuppose that the present diagram is correct, although the cause of the point of inflection on the solidus near 60% zinc is still in doubt. In this respect a recent study by Russian workers † on the variation of electrical resistivity with composition at 360°–422° C. indicates a discontinuity between 66 and 69% zinc. This effect, and a corresponding anomaly in the lattice-parameter/composition curves, are attributed to the ordering of the solid solution in this composition range. Should these findings be confirmed, a revision of the diagram may be necessary, since it is the contention of Rhines and Newkirk ‡ that the order–disorder changes are normal Gibbsian phase changes. In this event the suggested term would no longer be necessary.

Discussion

Diffusion and the Kirkendall Effect §

Dr. Bückle: I should like to illustrate some work which has been done since my paper was published, and which helps to confirm my conclusions.

Fig. A (Plate CI) indicates the general distribution of the holes in a copper/copper–7% aluminium couple after heating at 800° C. for 25 days. However, the Kirkendall effect is much more pronounced when several phases are involved in the diffusion process. Fig. B (Plate CI) shows, in the centre, the polished section of a copper/zinc couple after 1 hr. at 380° C. The Hume-Rothery phases ϵ, γ, and β (very thin) have been formed. A series of microhardness impressions along the length of the specimen serve as markers. After a further 1 hr. at 380° C. the impressions were examined under a microscope having a calibrated micrometer ocular, and their position compared with those before the additional treatment. The results, illustrated by diagram and photograph in the lower half of Fig. B, show a marked contraction on the zinc side (loss of zinc) and an expansion on the copper side (i.e. an expansion of the newly formed γ phase). This represents a displacement of the whole specimen relative to a fixed point of reference. Fig. C (Plate CII) shows the distortion of the microhardness impressions due to the expansion. As the displacement of the diffusion couples takes the form of a relative movement, some means are required of demonstrating its occurrence. Fig. D (Plate CII) shows two copper/zinc couples arranged in such a way that their movements should take place in opposite directions and thus become visible (see diagram (*a*)); experiment confirms that this is so (see photograph (*b*)).

The remaining illustrations show the growth of the various phases, during diffusion at 380° C., in multilayer specimens consisting of about ten thin sheets of copper and zinc placed alternately. In Fig. E (Plate CIII) the thickness of the copper is 140 μ and of the zinc 120 μ, corresponding to the

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† D. A. Petrov and T. A. Badaeva, *Zhur. Fiz. Khim.*, 1947, **21**, 785.

‡ F. N. Rhines and J. B. Newkirk, *Trans. Amer. Soc. Metals*, 1953, **45**, 1029.

§ Joint discussion on the papers by H. Bückle and J. Blin (*J. Inst. Metals*, 1951–52, **80**, 385), and by E. Lardner (this vol., p. 439).

composition of saturated α-brass. After 5½ hr. (Fig. E (*a*)) the zinc has disappeared and broad bands of the γ and β phases have been formed; lines of porosity are to be seen in the region where the zinc originally was. At the end of 120 hr. (Fig. E (*b*)) the γ phase has been replaced by β and the copper takes a more active part in the diffusion process, being converted into α. The second specimen (Fig. F, Plate CIII) (copper 80 μ, zinc 300 μ) corresponds in composition to the ε phase. The development of the phases is markedly different from that of the first specimen. After 30 min. (Fig. F (*a*)) broad bands of γ have already formed, with narrower bands of ε on the zinc side. At the end of 27 hr. (Fig. F (*b*)) the copper and zinc have completely disappeared, giving place to ε, which has also absorbed a large part of the γ phase. As diffusion is governed by the interaction between γ and ε, its rate is much faster and the porosity more pronounced than in the case of the first specimen, in which the interaction between β and α was the dominant factor.

Mr. R. S. Barnes,* B.Sc. (Member): The observations described in the paper by Dr. Bückle and M. Blin are in complete agreement with my own observations on copper/α-brass and copper/nickel couples, first mentioned in the discussion on the paper by da Silva and Mehl † and later described more fully.‡ I should like to mention one point from this latter paper in order to confound those critics who may think that the voids observed after interdiffusion are merely due to some polishing effect. That the voids were really present *inside* the metal after diffusion was proved by taking a microradiograph of the diffusion zone. Fig. G (Plate CIII) is such a microradiograph of the voids in a copper/nickel sandwich and shows, not only that the voids do not result from the polishing process, but also that their polyhedral shape is intrinsic.

While there is no doubt that voids form as a result of interdiffusion, the exact mechanism of their formation may be open to some conjecture. It may be suggested that the voids are formed either by gas coming out of solution or as a result of a gas reaction. The crystallographic shape of the voids is against such an explanation. Also, as the increase in the volume of the couples is independent of the purity of the metals, their previous treatment, and the annealing atmosphere, this explanation is very unlikely to be the correct one. The experimental results all suggest that the voids form as a direct result of the diffusion mechanism itself.

To explain the results, the authors invoke a mechanism involving the simultaneous diffusion of vacancies and interstitial atoms. As theoretical values for the activation energies of formation of vacancies and interstitial atoms favour a simple vacancy mechanism in face-centred cubic metals, it seems unnecessary to invoke such an involved idea, especially as all the results can be adequately explained, much more simply, by considering the migration of vacancies alone.

The results of the experiments can be summarized by Fig. H, which represents a diffusion couple consisting of two metals *A* and *B*, with three reference lines, denoted *x*, *y*, and *z*; line *y* represents the marked interface between the two metals and lines *x* and *z* marked positions in the metals *A* and *B*, respectively. As a result of diffusion, the reference lines shift relative to one another, line *y* moving towards the reference line *z* and away from the reference line *x* (this movement is usually referred to as the Kirkendall shift). In addition to this movement, the two outer reference lines *x* and *z* move apart as a result of a volume increase of the couple, caused by the formation of voids in metal *B* near to the original interface. It is found that the interface *y* always moves towards the metal with the lower melting point and also that the voids appear in this metal.

If we use a simple vacancy mechanism, i.e. a mechanism whereby an atom can diffuse only by exchanging positions with a neighbouring vacancy, all these results can be explained quite simply. The preferential flow of atoms in the positive direction in Fig. H will be accompanied by an equal flow of vacancies in the opposite, negative, direction. Such a flow of vacancies across the interface will disturb the equilibrium conditions in the diffusion zone; the number of vacancies in the region above *y* (in Fig. H) will be depleted, and vacancies will be generated here in an attempt to maintain equilibrium; in the region below *y*, vacancies will accumulate and exceed the equilibrium number, when they will tend to precipitate out of the lattice. The vacancies necessary for this preferential flow can be generated (above *y*) at lattice defects such as grain boundaries, polygon boundaries, and edge dislocations, and precipitated (below *y*) on similar defects; but if the supersaturation of vacancies here is high enough, then some of the vacancies will coalesce and form microscopic voids. The generation of vacancies above *y* and the precipitation of vacancies below *y* would cause an expansion and contraction, respectively, and the formation of voids (below *y*) would in addition result in an increase in the total volume of the couple.

Only if all the vacancies eventually go to form voids, i.e. none are annihilated at lattice discontinuities, will the distance

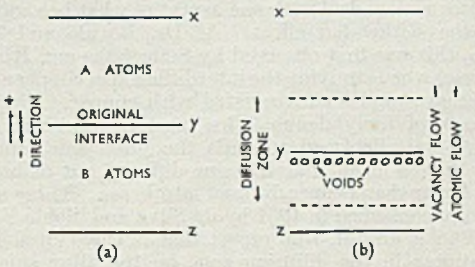

Fig. H.—Diagram to Illustrate Proposed Vacancy Mechanism.

yz (which contains the voids) remain constant. If the above explanation is the correct one, then the distance *yz* must decrease and can never increase. Observations show that this is the case; moreover, the reproducibility of this decrease would be very difficult to explain if the voids were the result of some process, e.g. a gas reaction, not *directly* connected with the diffusion process.

For this mechanism of void formation to be valid, the energy necessary to form the voids must come from the diffusion process. Rough calculations reveal that the energy released by the metals interdiffusing is about 10^4 times the total surface energy of the voids, so that this mechanism is quite feasible from an energy point of view.

With regard to the paper by Mr. Lardner, I should like to propose that the results he obtained can be accounted for in terms of the ideas I have outlined. The cast alloys used contained concentration gradients, and the solution-treatment of these alloys permitted the individual atoms of the alloys to diffuse and the concentration gradients to be reduced. As the melting point of magnesium is less than that of aluminium, it is to be expected that the magnesium atoms would diffuse the faster, or, in terms of vacancies, that the vacancies would flow from the aluminium-rich regions to the magnesium-rich regions. The accumulation of vacancies in the magnesium-rich regions could cause voids to form in this region. The crystallographic shape of the voids which Mr. Lardner observed suggests that these voids are formed in a way similar to those in diffusion couples, and their appearance in the magnesium-rich regions fits in well with this point of view.

After one of the high-temperature solution-treatments (5 hr. at 385° C. + 16 hr. at 420° C. + 16 hr. at 450° C.) (p. 440), it was found that cavities were completely absent. I should like to ask the author whether, in this particular

* Atomic Energy Research Establishment, Harwell, Berkshire.

† A. D. Le Claire and R. S. Barnes, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 1060 (discussion).

‡ R. S. Barnes, *Proc. Phys. Soc.*, 1952, [B], **65**, 512.

case, the absence of cavities might not be due to incipient melting of the alloy? After all other solution-treatments cavities were found, although an increase of time or temperature resulted very often in fewer but larger cavities; this might be expected if large cavities grow at the expense of the small ones.

Mr. Lardner's results suggest that the rate of cooling had no effect on the formation of voids, and if the absence of cavities in this *one* particular case could be accounted for by incipient melting, then the inability to remove already existing cavities would not be unexpected, and there would no longer be any need to look to the cooling of the samples for an explanation of their formation.

These experiments suggest that the voids result from the smoothing out of the concentration gradients, i.e. as a result of the diffusion process. Although other interpretations may be put upon these experiments, it is perhaps significant that the crystallographic nature of the voids is similar to that observed after the interdiffusion of two metals, and also that the position of the voids is in accord with their position in diffusion couples.

Dr. J. C. Chaston,* A.R.S.M., A.Inst.P., F.I.M. (Member): These two papers deal with one aspect of what has come to be called the Kirkendall effect. As Dr. Bückle and M. Blin explain, this was first observed by Smigelskas and Kirkendall in America when studying the interdiffusion of copper and zinc, using brass samples electroplated with copper. They found by means of molybdenum wire markers that the original interface was displaced towards the brass side, and interpreted this to mean that the zinc diffused out of brass into copper faster than copper diffused into brass. These observations were confirmed in 1951 by da Silva and Mehl.

Dr. Bückle and M. Blin report that in these circumstances holes appear in the diffusion zone on the alloy side. It is perhaps proper to point out that, since these observations were made, Hersch † has found holes under the surface of 70 : 30 brass from which zinc had been distilled in a vacuum, and in a more detailed paper Balluffi and Alexander ‡ have described many instances of cavity formation in diffusion couples (and sometimes in the couples before diffusion).

The explanation suggested by all these workers for the appearance of cavities has been well expressed by Balluffi and Alexander: "Porosity appears in α-brass when zinc is removed either by evaporation into vacuum or diffusion into copper. No matter where the zinc goes, it apparently moves out of the alloy by diffusion and leaves voids behind. One is tempted to say that this is a direct result of the unequal diffusion rates of copper and zinc in α-brass and that zinc atoms which diffuse outwards are replaced, not by copper atoms but by vacancies which may precipitate to form microscopic voids. The voids may subsequently be removed by a sintering process, but presumably the sintering process is slower than the diffusional process of forming voids."

In considering these phenomena, I suggest that three questions arise:

(1) Are the observations really consistent with the proposed explanation? As I understand it, the explanation suggests that the copper surface has such an attraction for zinc atoms that they diffuse into it faster than they can be replaced either by copper atoms or by zinc atoms coming from the brass immediately beneath the surface. This surely implies that we should expect to find holes collected immediately beneath the surface, becoming more and more sparsely distributed as we proceed farther from the interface. The distribution shown in Fig. 3 (Plate LVIII) of Bückle and Blin's paper gives no evidence at all, however, of any bunching near the interface. The holes are distributed quite uniformly in a wide zone extending about 0·2 in. below the surface and then abruptly vanish. To me, such a distribution is quite inexplicable on the proposed theory. It should be pointed out, incidentally, that although the authors describe the region containing cavities as the diffusion zone, no evidence is actually given as to the extent of diffusion.

(2) Do cavities actually exist in other circumstances to which the same argument can be applied? I am surprised that none of the investigators of this problem has hitherto extended observations to cored structures. The use of welded sandwiches or electroplated specimens must always raise questions of local entrapment of gases. On the other hand, a sound brass or bronze casting would provide concentration gradients in an ideal form for diffusion studies. As far as I know, cavity formation has never been recorded when a cored brass casting is homogenized.

(3) Can the cavities be explained on established rational grounds without introducing new theoretical ideas? One possibility for the cavities observed by Bückle and Blin is that they may be due to inclusions pulled out during polishing, to leave pits subsequently enlarged by etching. It is significant that these workers polish on felt and velvet, which is particularly likely to drag out inclusions. I would suggest that for studies such as this, the use of diamond-powder polishing techniques is essential.

A second possibility is that gas reactions may be involved. Some of the cavities, such as those on the right of Fig. 4 (Plate LVIII), are undoubtedly due to gas reactions in copper. Admittedly, gas reactions are not normally encountered in brass, but experience has shown that they can occur in unexpected circumstances when catalysed by the presence of impurities or third elements.

On the whole I think that none of the work so far reported can be accepted as incontrovertible evidence for the view that cavities can be formed directly as a result of intermetallic diffusion. That the cavities may be due to side reactions has never yet been completely ruled out.

In this discussion reference has been made only to the paper by Bückle and Blin. It seems difficult to fit Lardner's observations into the general picture, but as the cavities which he observed were formed only during cooling, I suggest that they represent gas cavities produced by a reaction around centres nucleated during the preliminary heat-treatment.

Dr. T. P. Hoar,§ M.A., F.R.I.C., F.I.M. (Member): Strong evidence for the production of voids when two metals interdiffuse is provided by the net increase in volume often observed, for example, in the early stages of the heat-treatment of copper–nickel powder compacts.‖ This fact seems to confirm the metallographic evidence that Dr. Chaston doubts.

The separate diffusion of two metal species in an alloy has received general notice only within the last few years. This is astonishing: the separate diffusion of different species in gaseous and liquid systems has been recognized for a century or so, while the phenomenon was treated theoretically by Wagner for solids generally, and demonstrated by him and by Pfeil for a number of metallic compounds, about 25 years ago. The balance between knowledge of diffusion in metallic and non-metallic solids has now been handsomely redressed by those interested in atom movements in alloy systems; but, much as one may approve the opening up of the metallic field by the paper of Smigelskas and Kirkendall, may one suggest that the "effect" that they demonstrated for a single pair of metals has been somewhat inappropriately named?

Mr. M. C. Inman,¶ B.Sc.: Dr. Chaston has emphasized the importance of accurate measurement of concentration/distance curves for the understanding of diffusion phenomena. At Leeds a group of investigators, under the direction of Dr. R. Shuttleworth, is using radioactive tracers to measure

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* Manager, Research Laboratories, Johnson, Matthey and Co., Ltd., Wembley.

† H. N. Hersch, *J. Appl. Physics*, 1952, 23, 1055.

‡ R. W. Balluffi and B. H. Alexander, *ibid.*, 1952, 23, 1237.

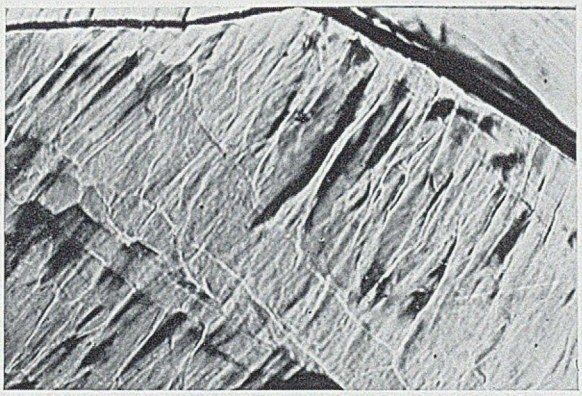
§ Lecturer, Department of Metallurgy, Cambridge University.

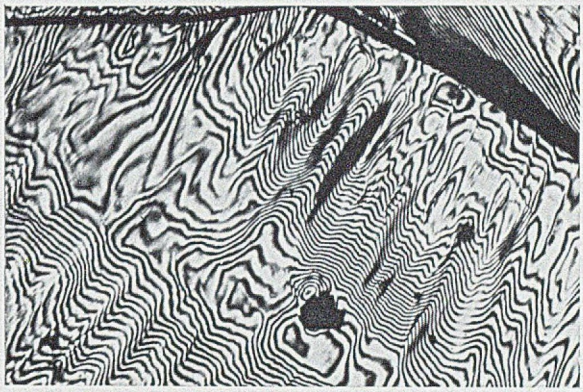
‖ J. M. Butler and T. P. Hoar, *J. Inst. Metals*, 1951–52, 80, 207.

¶ Yorkshire Copper Works Fellow, Metallurgy Department, University of Leeds.

CREEP AND PLASTIC DEFORMATION.

C





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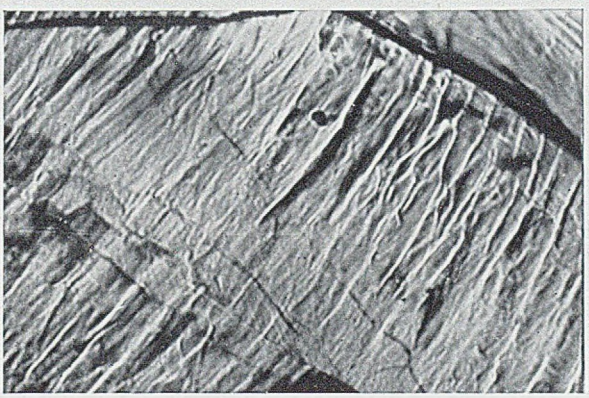
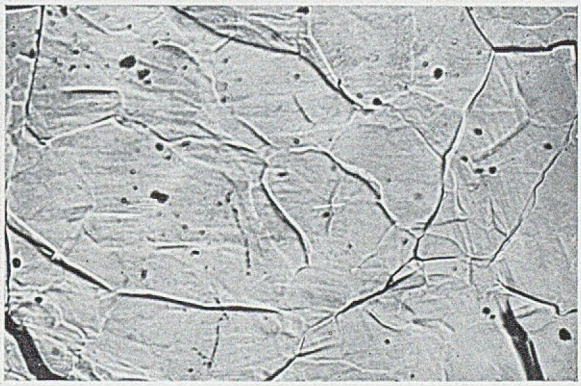




F

FIGS. C–E.—Area on Pure Aluminium Deformed 14% in 75 Hr. at 200° C.

FIG. C.—Inside focus.
FIG. E.—Outside focus.
FIG. D.—Multiple-beam interferogram.
FIGS. C and E.—Narrow-pencil illumination. × 140.

FIG. F.—Aluminium Deformed 12% at 325° C. in 8 Hr., Repolished Flat, Further Strained 3% at 300° C. Outside focus. Narrow-pencil illumination. × 150.

(*Gifkins and Kelly.*)

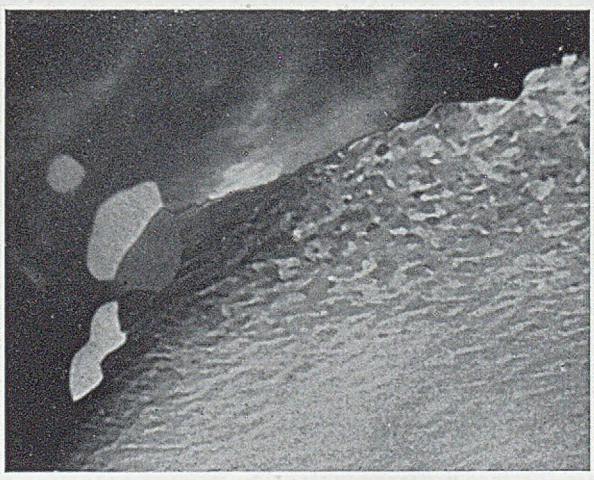


FIG. G.—Super-Purity Aluminium Cold-Rolled 20% and Annealed 1 min. at 375° C. Anodized. Photographed under polarized light. × 200. (*Perryman.*)

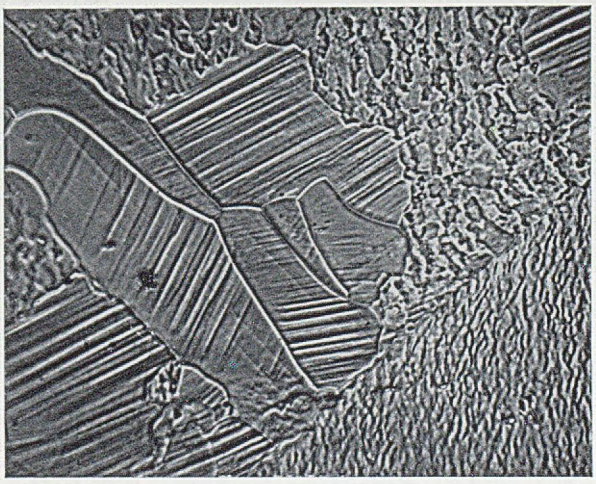


FIG. H.—Super-Purity Aluminium Cold-Rolled 50% and Annealed 10 sec. at 375° C. Etched in 25 HNO_3, 73 H_2O, 2 HF at 50° C. Bent slightly after etching. Photographed under phase contrast. × 200. (*Perryman.*)

[*To face p.* 744

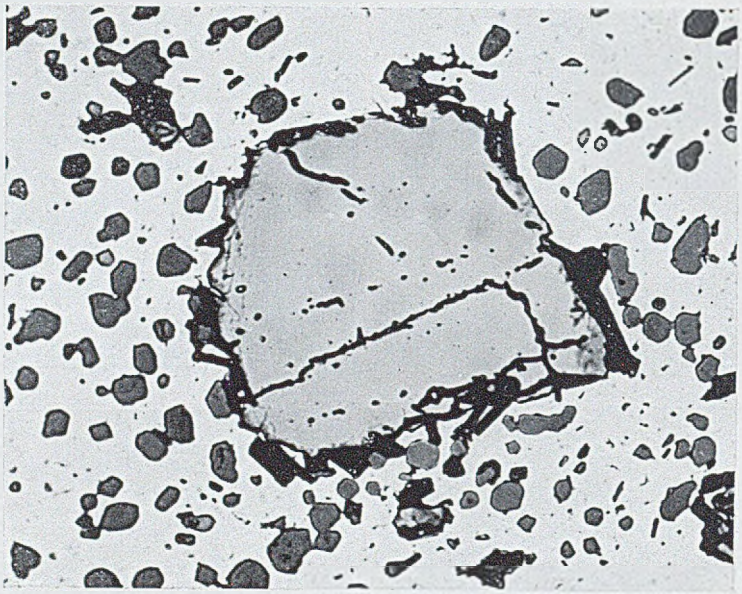


FIG. A.—Primary Manganese-Bearing Constituent in a Eutectic Aluminium-Silicon Alloy. (*Turner on Dudzinski.*)

FIG. B.—Aluminium–6·37% Chromium Alloy, Chill-Cast and Annealed. × 750. (*Dudzinski's reply.*)

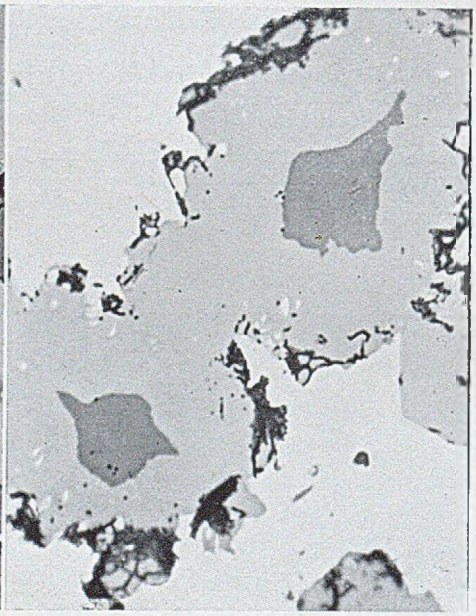


FIG. C.—Aluminium–2·4% Vanadium Alloy, Chill-Cast and Annealed. × 1000. (*Dudzinski's reply.*)

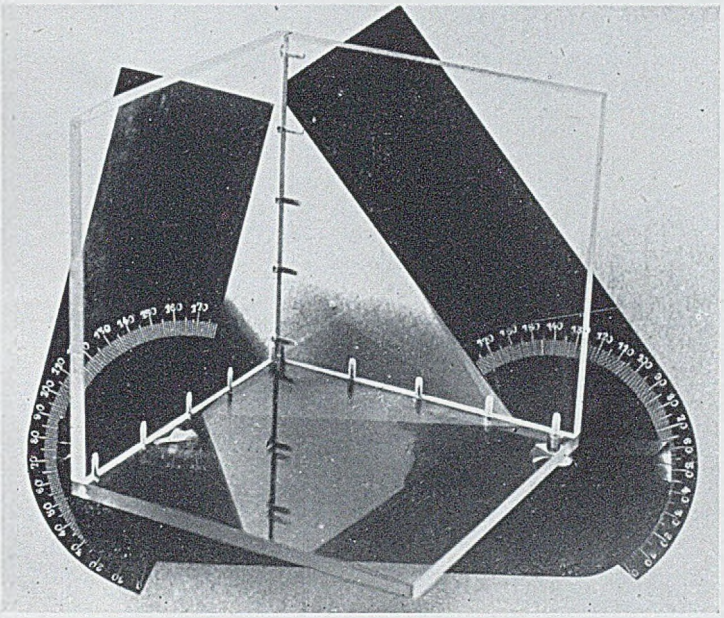


FIG. D.—Jointed Triangle for the Direct Interpretation of Etch-Pits. (Plan.)

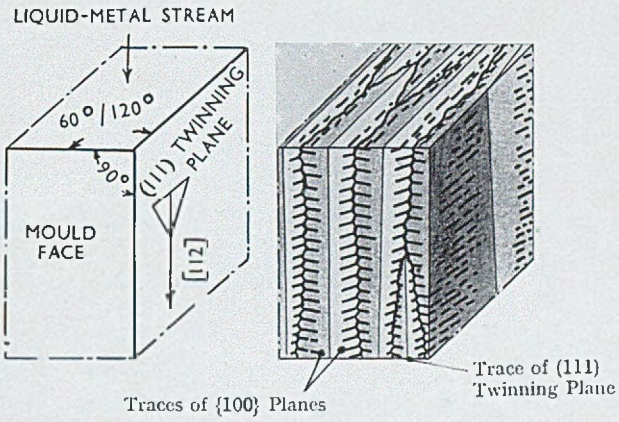


FIG. E.—Twin Texture in 99·5% Aluminium, Semi-Continuously Cast.

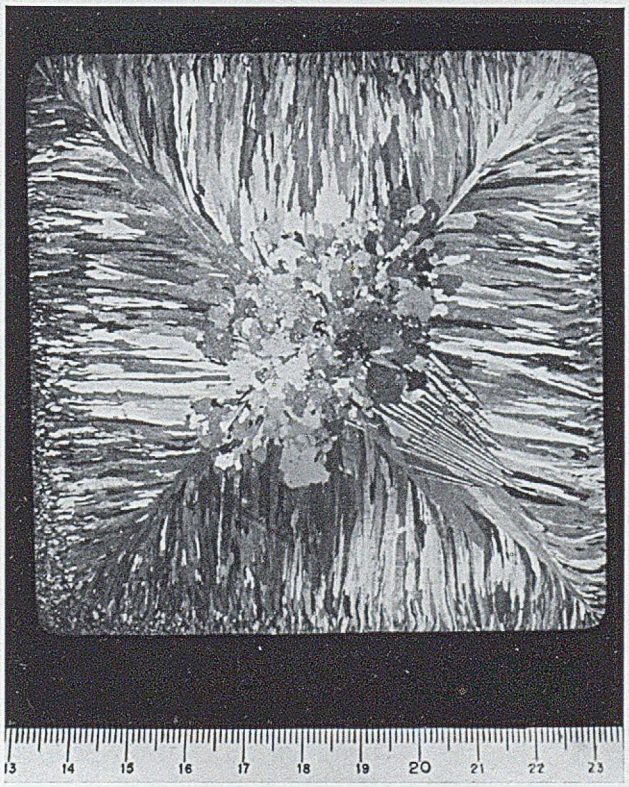


FIG. F.—Fan-like Twinned Structure in a 99·5% Aluminium Wire Bar, Cast in a Permanent Mould.

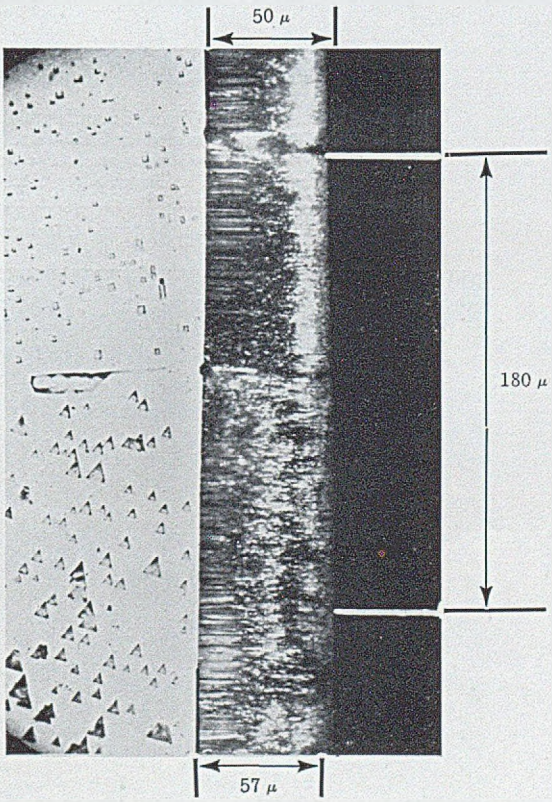


FIG. G.—Illustrating Use of Etch-Pits in Determining the Orientation of Two Neighbouring Grains of an Aluminium–3% Magnesium Alloy, Carrying Anodic Oxide Layers of Different Thickness. × 300.

(Hérenguel and Lelong on Tucker and Murphy.)

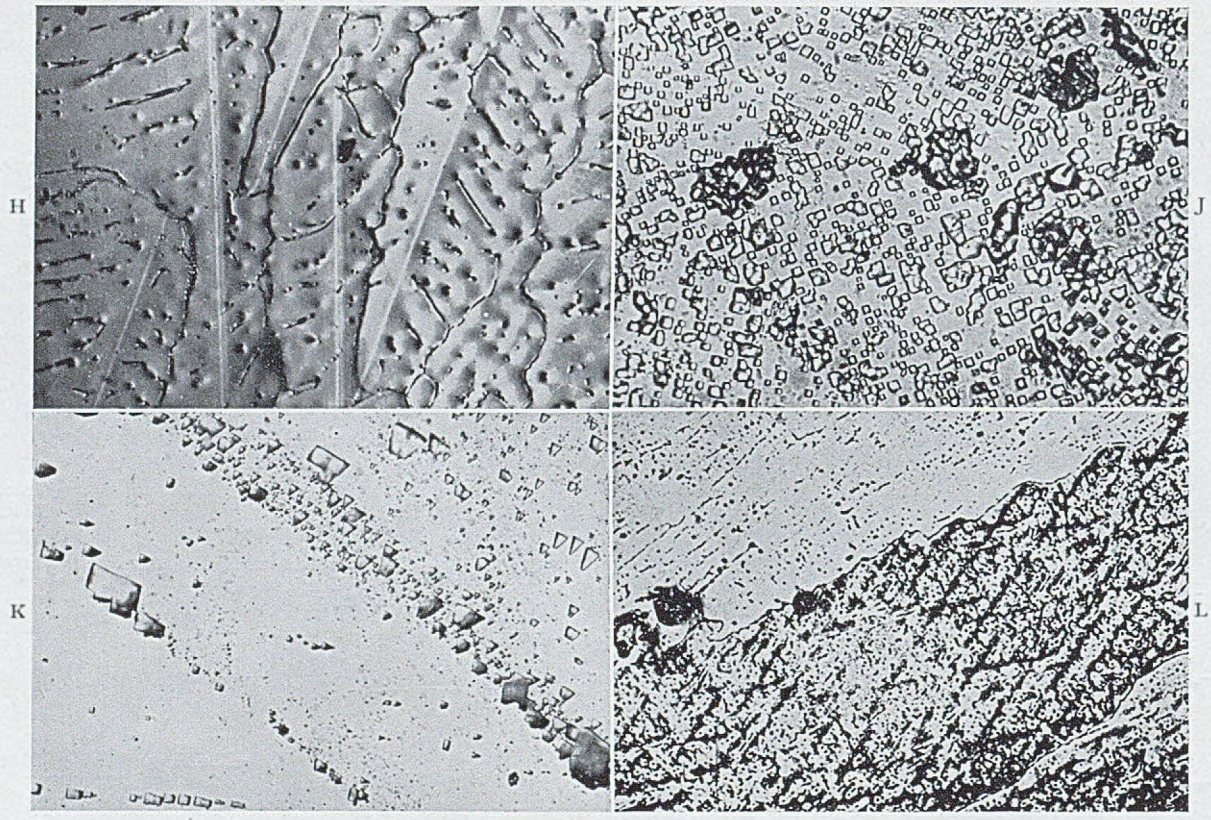


FIG. H.—Junction of Two Twin Elements with a Strong Relative Disorientation. × 120.
FIG. J.—Cube Texture Revealed by Etch-Pits. × 350.
FIG. K.—Zone of Progressive Curvature at the Boundary of a Deformation Band in a Cold-Worked Single Crystal of Aluminium–3% Magnesium Alloy, as Revealed by Etch-Pits. × 600.
FIG. L.—Distribution of Etch-Pits in Alignment Parallel to {100} Traces on As-Cast 99·5% Aluminium. × 25.

(*Hérenguel and Lelong on Tucker and Murphy.*)

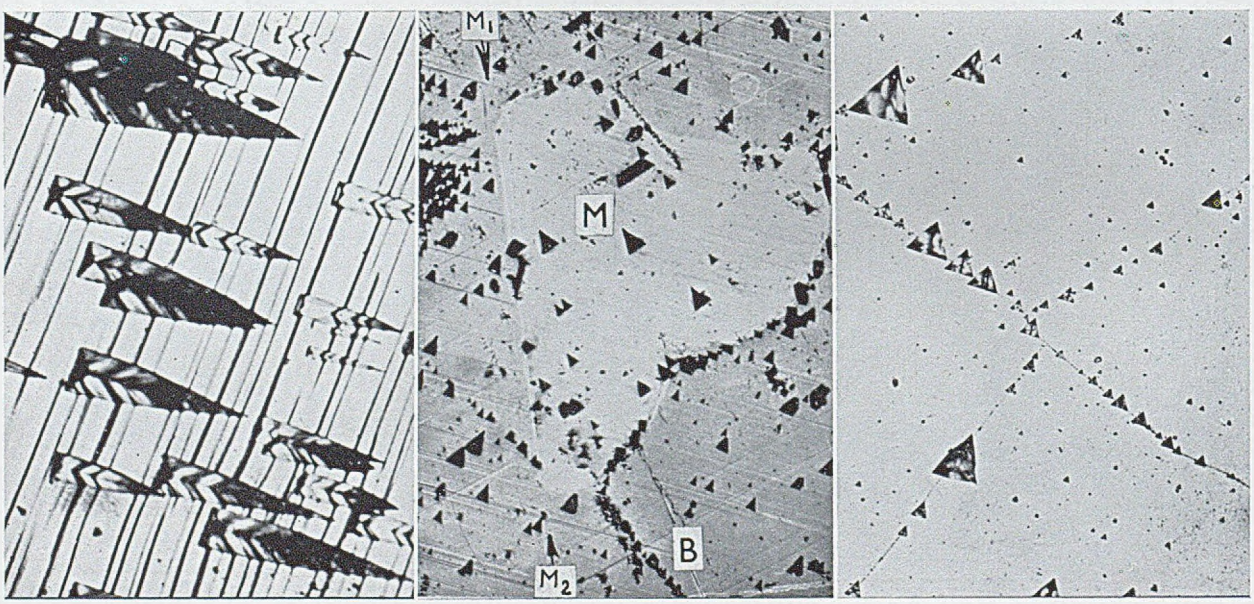
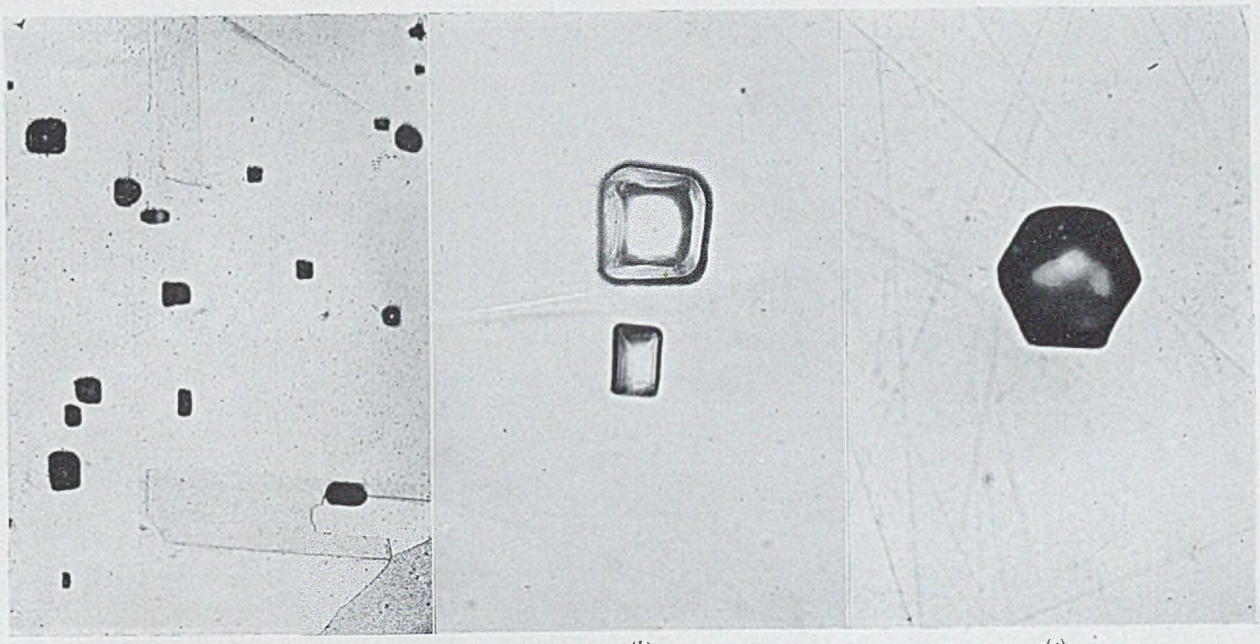


FIG. M.—Etch-Pits and Slip Lines on a Pure Aluminium Single Crystal. × 350.

FIG. N.—Insular Crystal *M* Enclosed in a Large Crystal *B* in a Relatively Twinned Position (M_1M_2 linear boundary represents trace of the (111) twinning plane). × 100.

FIG. O.—Intragranular Polygonization Boundary, Marked by a Series of Etch-Pits, in an Aluminium Crystal with Orientation Approximately Parallel to the (111) Plane. × 500.

(*Lacombe on Tucker and Murphy.*)



(*a*) (*b*) (*c*)

FIG. A.—Size and Distribution of Holes in a Copper/Copper–7% Aluminium Alloy Couple after Diffusion for 25 Days at 800° C. (*a*) × 100. (*b*) and (*c*) × 350. (*Bückle.*)

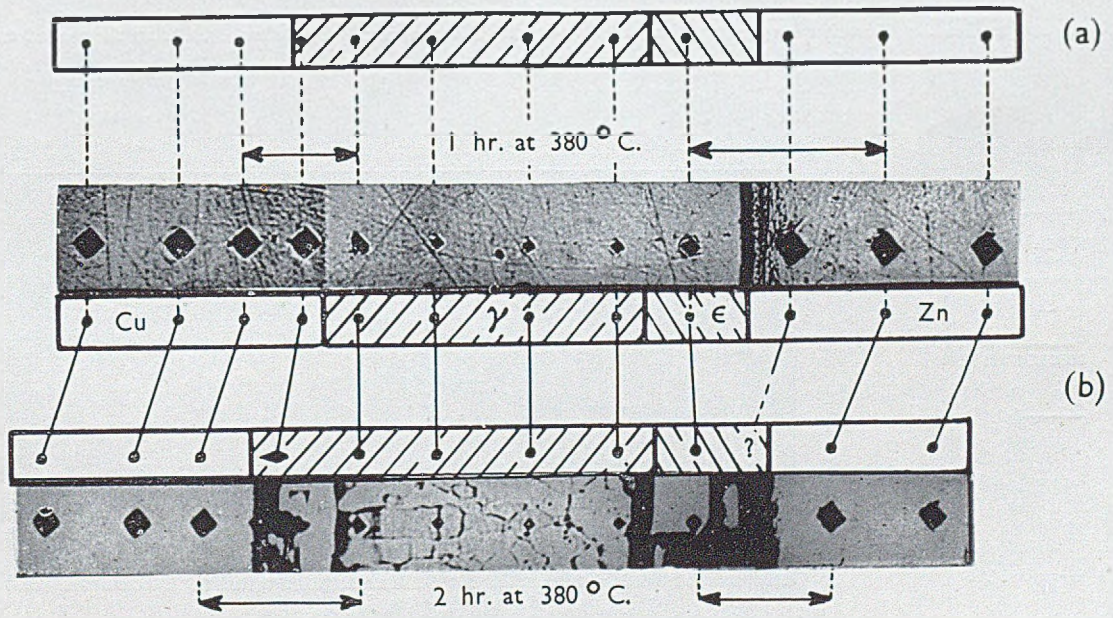
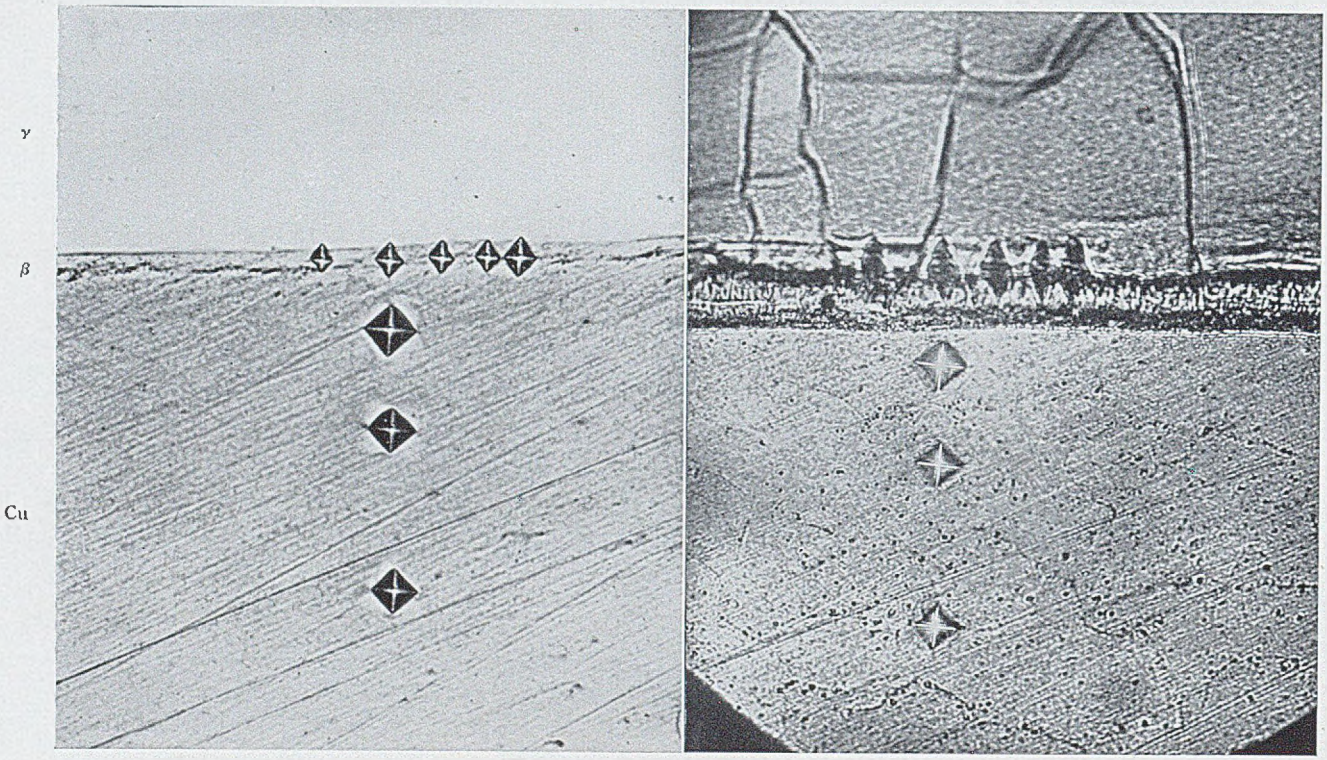
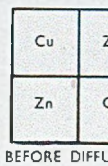


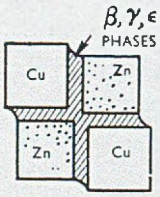
FIG. B.—Multiple-Phase Diffusion in a Copper/Zinc Couple, Showing Anomalous Expansion on the Copper Side (left) and Contraction (Kirkendall Effect) on the Zinc Side (right). (*a*) According to classical theory. (*b*) Actually observed. × 450. (*Bückle.*)



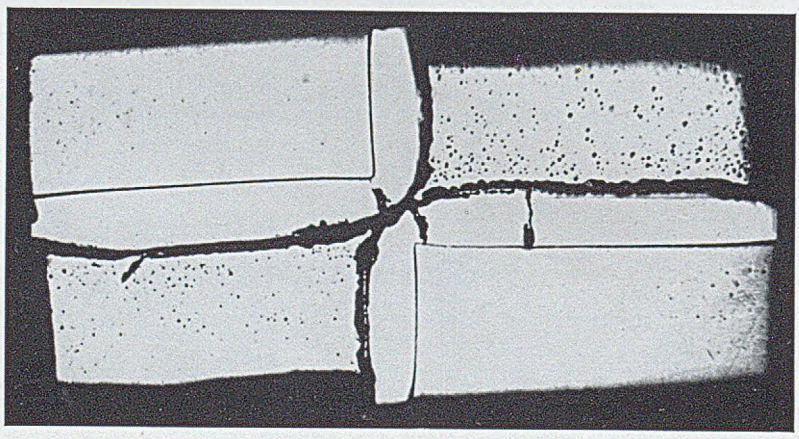
(*a*) (*b*)

FIG. C.—Anomalous Swelling Revealed by Deformation of Micro-hardness Impressions. (*a*) Before. (*b*) After the second treatment. × 650. (*Bückle.*)





(*a*)



(*b*)

FIG. D.—Displacement of Copper/Zinc Couples After Diffusion for 27 hr. at 380° C. (*a*) Diagrammatic. (*b*) Experimental observation. × 10. (*Bückle.*)

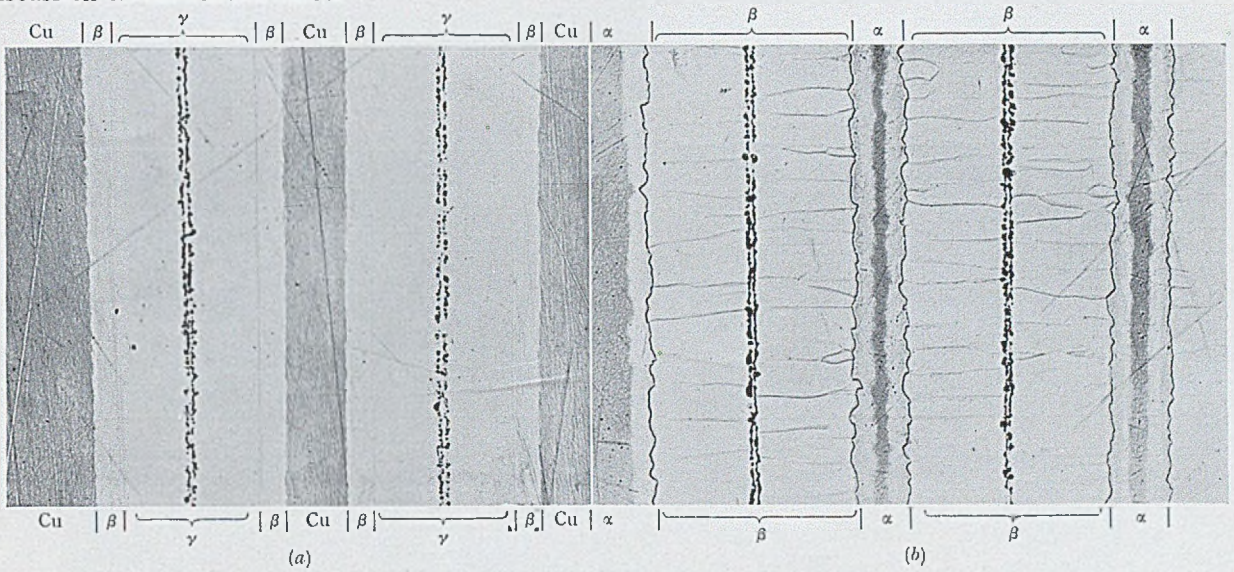


FIG. E.—Copper 140 μ thick, zinc 120 μ thick. (*a*) After 5½ hr. (*b*) After 120 hr. × 200.

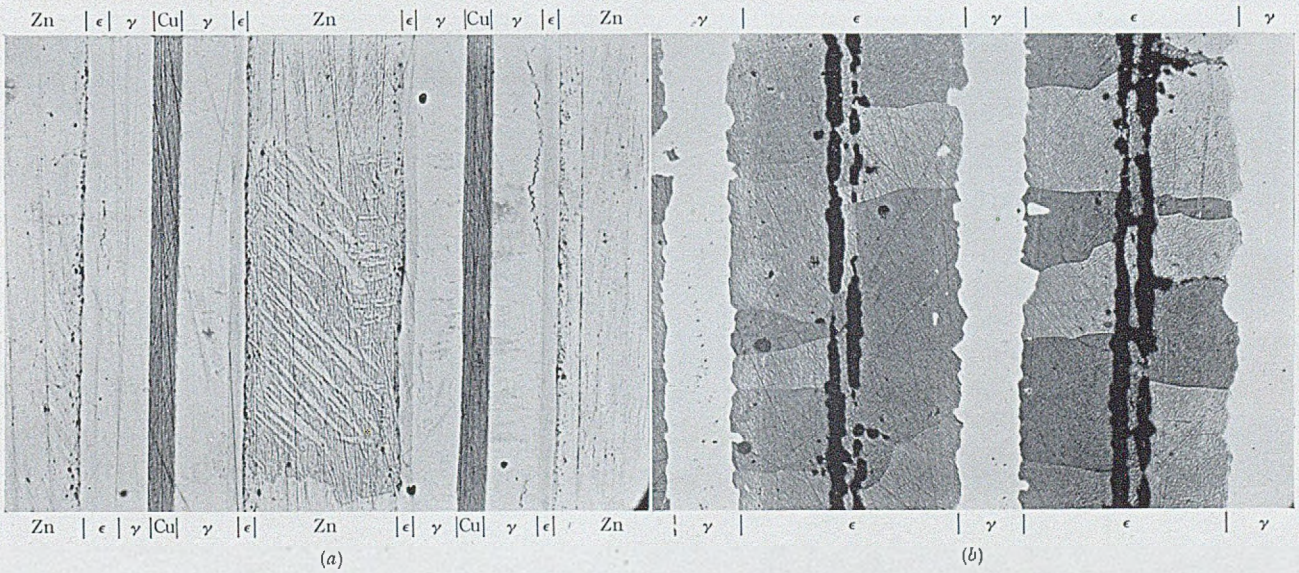


FIG. F.—Copper 80 μ thick, zinc 300 μ thick. (*a*) After 30 min. (*b*) After 27 hr. × 150.

FIGS. E and F.—Showing Evolution of Various Phases Formed During Diffusion at 380° C. in Multi-Layer Specimens of Alternate Copper and Zinc Sheets. (*Bückle.*)

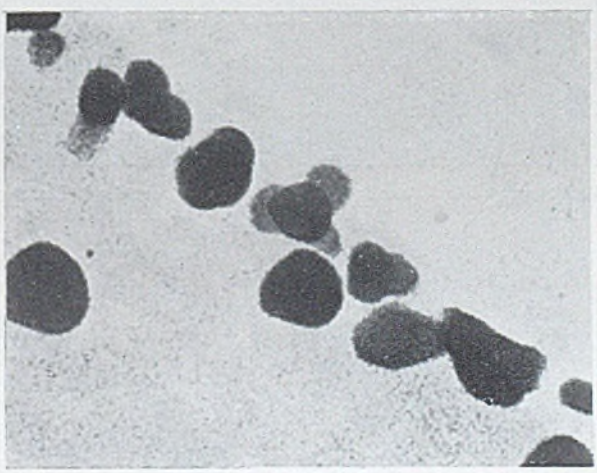


FIG. G.—Microradiograph of Voids in a Copper/Nickel Sandwich, Showing That They do Not Result from the Polishing Process and That Their Polyhedral Shape is Intrinsic. (*Barnes.*)

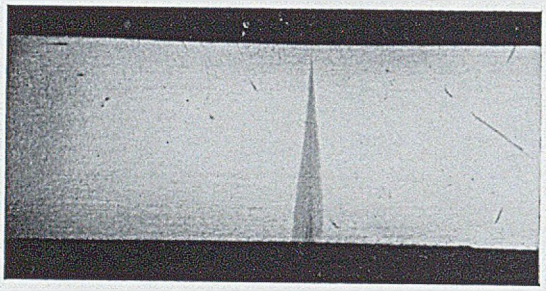


FIG. A.—Standard Tensile Test-Piece of Narrow Central Gauge-Length, Showing Normal Markings First Formed. × 1. (*Chadwick and Hooper.*)

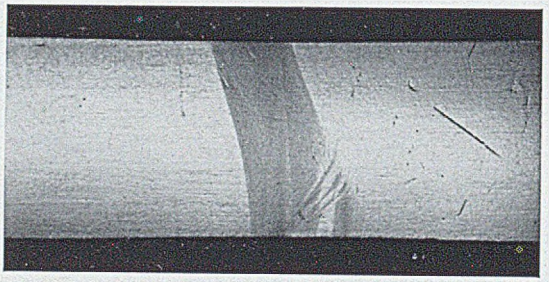


FIG. B.—Illustrating Formation of Tongue-Shaped Markings on Further Stretching of Test-Piece. × 1. (*Chadwick and Hooper.*)

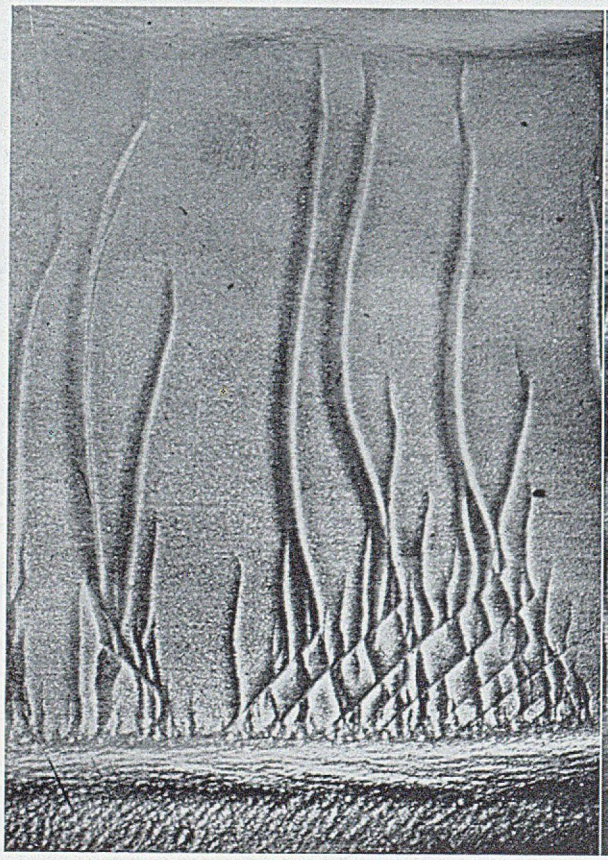


FIG. D.—Stretcher-Strain Markings on a Steel Pressing. × 1. (*Hundy.*)

FIG. E.—Stretcher-Strain Markings on an Aluminium–Magnesium Alloy Pressing. × 1. (*Hundy.*)

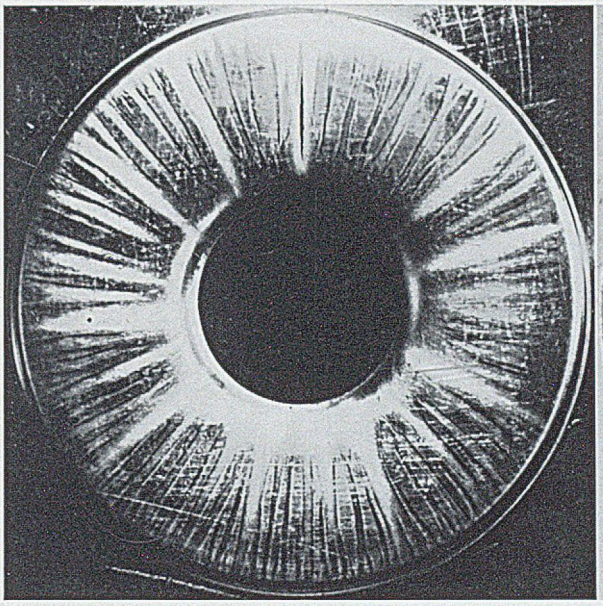


FIG. F.—Steel Pressing Showing Stretcher-Strains, Localized Necks, and Fracture. × 1. (*Hundy.*)

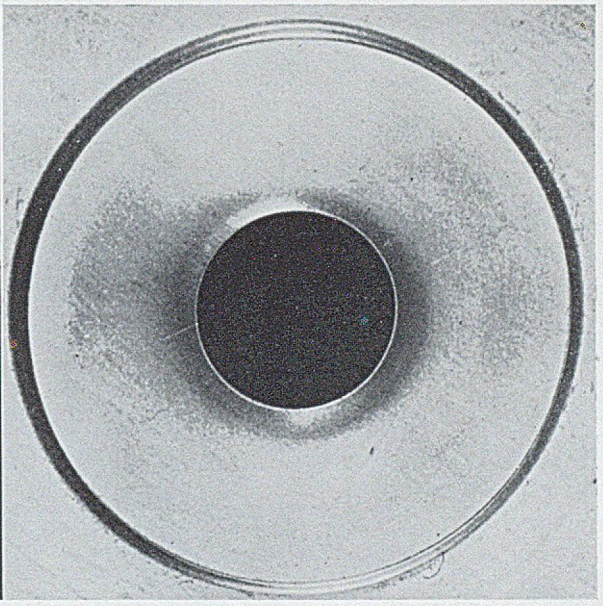
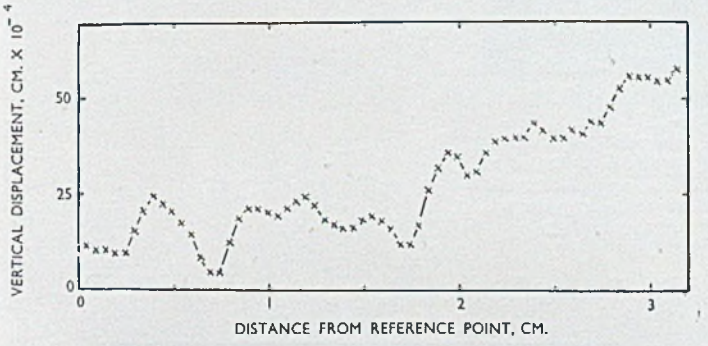


FIG. G.—Similar Pressing to Fig. F but the Steel Was Temper-Rolled Before Pressing to Remove All the Defects. × 1. (*Hundy.*)



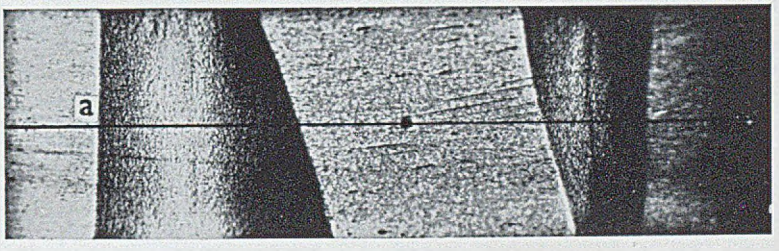
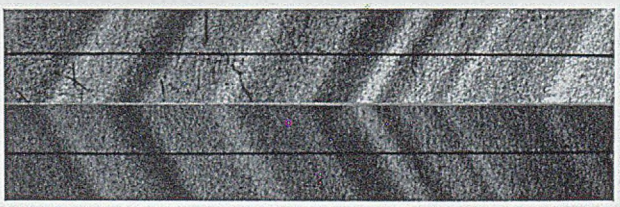


FIG. P.—Two Type-*A* Wedge Markings Formed on Annealed Mild Steel Strip of 0·023 mm. Grain-Size, Stretched Part Way Through the Yield-Point Elongation of 4%. × 2·6. (*Phillips.*)



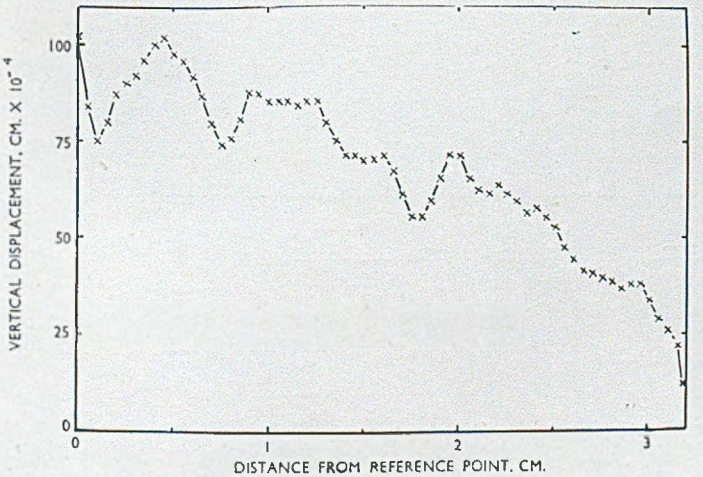


FIG. O.—Relation Between Profile and Type-*B* Markings on Strip of Commercial Aluminium–3½% Magnesium Alloy, Grain-Size 0·018 mm., Rolled to 0·044 in. Thick (~10% Reduction) and Stretched to Fracture. (*Phillips.*)

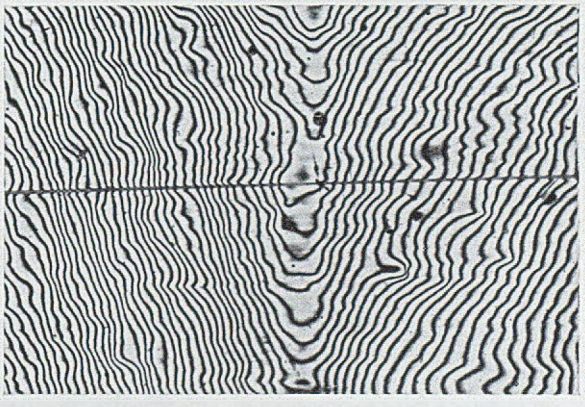


FIG. Q.—Multiple-Beam Interference Pattern Showing Sharp Tilt at Boundary *a* of Fig. P Between Yielded and Unyielded Material. A reference scratch runs across the field. × 41. (*Phillips.*)

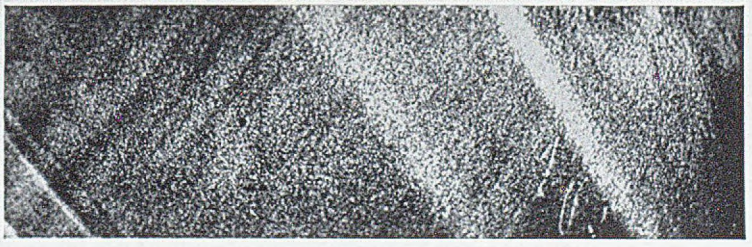


FIG. R.—Illustrating Type-*B* Ripple Markings Formed on Strip of Same Steel as Fig. P, Stretched to Fracture at 170° ± 5° C. × 2·6. (*Phillips.*)

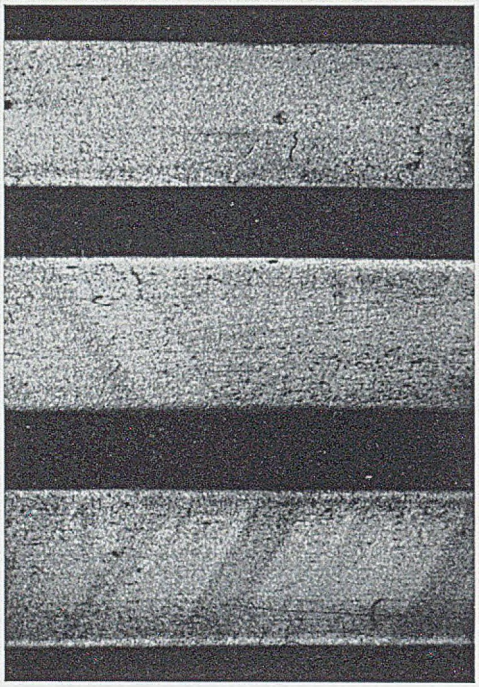


FIG. S.—Effect of Rapid Straining at Room Temperature on the Occurrence of Type-*B* Ripple Markings in Commercial Aluminium–3½% Magnesium Alloy Strip (OZX), Rolled to Approx. 0·012 in. Thick and Annealed. Approximate strain rates (in sec.$^{-1}$) as indicated. × 2·5. (*Eborall and Phillips.*)

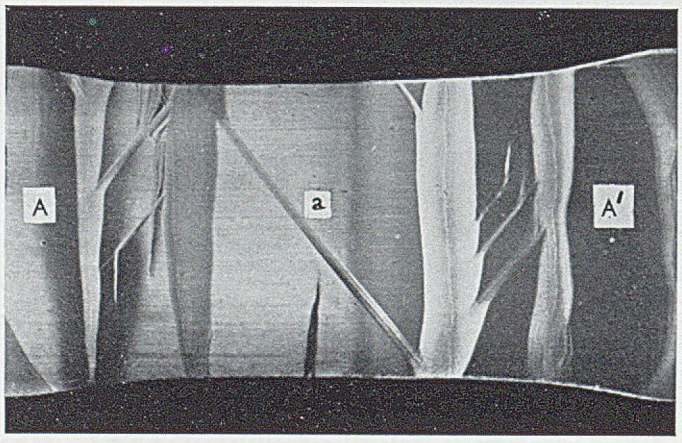


FIG. T.

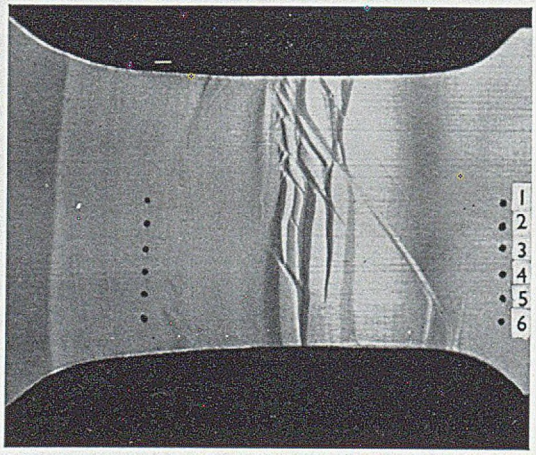


FIG. U.

FIGS. T and U.—Type-*A* and Type-*B* Markings Present Together in Mild Steel. (*Chadwick and Hooper.*)

these curves in copper–zinc alloys. I am studying the self-diffusion of copper and zinc in β-brass, whilst Mr. L. W. Mercer and Mr. D. Johnston are studying two α-brasses containing 1 and 30% of zinc, respectively.

The appearance of pores in the chemical-diffusion experiments of Dr. Bückle and M. Blin and of Mr. Lardner shows that in these systems atom movement occurs by interchange with vacancies. The pores are formed because the preferential interchange of one component with vacancies causes vacancies to be pumped from one side of the couple to the other, and thus produces a vacancy supersaturation so great that some of the vacancies combine to form pores. If the vacancy supersaturation had been less, the vacancies would have been annihilated at dislocations.

Whilst the occurrence of pores and of Kirkendall displacements during chemical diffusion proves that atom movements occur by interchange with vacancies, experiments on the diffusion of isotopes in a chemically homogeneous system have a more immediate interpretation in terms of the interaction of the vacancies with the two kinds of atom in an alloy. For

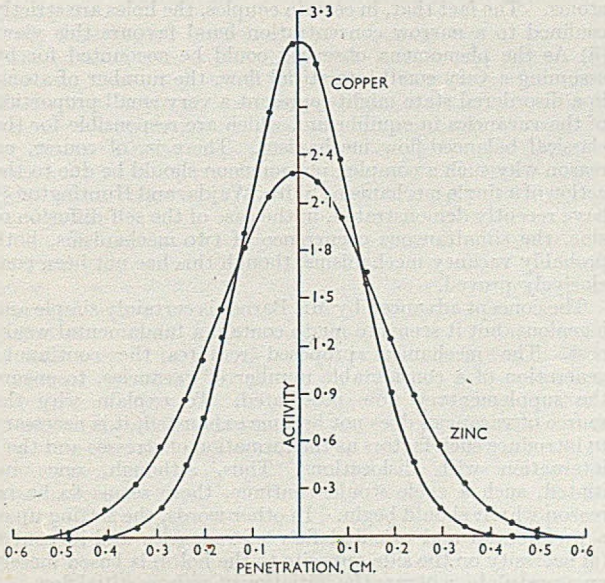


FIG. J.—Normalized Activity/Penetration Curve for Self-Diffusion of Copper and Zinc in β-Brass for 15·7 hr. at 732° C.

$c/c_0'' = (4\pi Dt)^{-1/2} \exp[-x^2/4Dt]$.
$D_{Cu} = 1{\cdot}37 \times 10^{-7}$ cm.²/sec.
$D_{Zn} = 2{\cdot}67 \times 10^{-7}$ cm.²/sec.
$D_{Zn}/D_{Cu} = 1{\cdot}95$.

the self-diffusion coefficient of a component is simply related to n, the frequency with which an atom of that component jumps to adjacent lattice sites, by the equations :

$$D_A = \alpha n_A a^2 \qquad D_B = \alpha n_B a^2 \quad . \quad . \quad . \quad . \quad (1)$$

where D_A and D_B are the self-diffusion coefficients of the two components, a is the cubic lattice constant, and α is a numerical constant (1/8 for body-centred cubic and 1/12 for face-centred cubic crystals).

A technique has been devised to measure simultaneously the self-diffusion coefficients of copper and zinc in brass. A foil of the brass, 0·005 in. thick, is irradiated in a pile so that it contains both copper and zinc radioactive atoms. This foil is then welded between two discs of brass of the same chemical composition and the sandwich annealed for about a day at the diffusion temperature. After this the diffusion-anneal sections parallel to the weld are turned off in the lathe and collected in weighing bottles. The γ activities of these sections are measured by a ring of six Geiger counters, connected in parallel to a single scaler. Since the half-lives of radioactive copper and zinc are 12·9 hr. and 250 days respectively, separate activity/penetration curves for copper and zinc are easily obtained without the need for a chemical separation, for the activity of a section immediately after diffusion is due to both copper and zinc, whilst after ten days the copper has decayed and the remaining activity is due solely to the zinc.

The activity per unit volume c, at a distance x from the origin, is given by :

$$c/c_0'' = (4\pi Dt)^{-1/2} \exp[-x^2/4Dt] \quad . \quad . \quad . \quad . \quad (2)$$

where c_0'' is the initial activity per unit area at the origin and t is the diffusion time. In Fig. J are shown the activity/penetration curves for copper and zinc in β-brass after diffusion for 15·7 hr. at 732° C. Especially to be noticed is the large diffusion distance, comparable to that of interstitial carbon in iron at the same temperature. Values of D_{Cu} and D_{Zn} were calculated by equation (2) from the activity/penetration curves and these are given for various temperatures in Table A.

TABLE A.

Temp. (°C.)	D_{Zn}, cm.²/sec.	D_{Cu}, cm.²/sec.	D_{Zn}/D_{Cu}
678	$1{\cdot}35 \times 10^{-7}$	$0{\cdot}65 \times 10^{-7}$	2·08
732	$2{\cdot}67 \times 10^{-7}$	$1{\cdot}37 \times 10^{-7}$	1·95
777	$4{\cdot}26 \times 10^{-7}$	$2{\cdot}26 \times 10^{-7}$	1·88
831	$7{\cdot}27 \times 10^{-7}$	$4{\cdot}04 \times 10^{-7}$	1·80
870	$1{\cdot}07 \times 10^{-6}$	$6{\cdot}14 \times 10^{-7}$	1·75

It should also be noted that since the values of D_{Cu} and D_{Zn} are measured simultaneously, the ratio D_{Zn}/D_{Cu} should be free from systematic errors. This ratio is important because, by equation (1), it equals n_{Zn}/n_{Cu}, the relative frequency of interchange of the two kinds of atom with the vacancies. The temperature-dependence of the diffusion coefficients is given by the equations :

$$D_{Cu} = 0{\cdot}038 \exp[24{,}900/RT] \quad D_{Zn} = 0{\cdot}024 \exp[22{,}800/RT] \quad (3)$$

The experimentally determined activation energy is the sum of the energy necessary to create a vacancy and the energy required for an adjacent atom to interchange with this vacancy. In 50 : 50 β-brass the energy needed to create a vacancy will be about the same for all sites, and so the difference in activation energy for copper and zinc (2·1 kg.cal.) can be identified as the difference between the energy required for a copper and a zinc atom to exchange with a neighbouring vacancy.

Preliminary measurements by Mr. Johnston on a 70 : 30 brass show that at 830° C. :

$$D_{Cu} = 1{\cdot}50 \times 10^{-9} \text{ cm.}^2/\text{sec.} \quad D_{Zn} = 4{\cdot}83 \times 10^{-9} \text{ cm.}^2/\text{sec.}$$

Dr. F. ROHNER* (Member): The similarity of the phenomena described in these two extremely interesting papers leaves little doubt that they must derive from the same origin.

The observation by Dr. Bückle and M. Blin that formation of porosity is connected with the Kirkendall effect in copper/zinc and copper/aluminium diffusion couples has been substantiated and shown to be true for other diffusion systems.† Those authors who embark upon a detailed discussion of the possible mechanisms involved agree that the pores must be looked upon as agglomerations or precipitates of vacancies, and that some source of vacancies must be operating in the diffusion zone. The concentration of vacancies in metals due to thermal excitation is much too small to account for the

* Research Laboratories, Aluminium Industrie, A.G., Neuhausen, Switzerland.

† L. C. C. da Silva and R. F. Mehl, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 155.

H. N. Hersch, *J. Appl. Physics*, 1952, **23**, 1055.
R. W. Balluffi and B. H. Alexander, *ibid.*, 1952, **23**, 1237.
W. Seith and A. Kottmann, *Angew. Chem.*, 1952, **64**, 379.

development of the pores. Smoluchowski * estimates the normal concentration of vacancies attributable to this cause at a small fraction of 1%. Seitz † has suggested that the vacancies in the case of the Kirkendall effect might be created at the specimen surfaces. This possibility has been disproved by several investigators, notably by Bückle and Blin; their experiments with specimens Nos. 2 and 5 show the Kirkendall effect to operate whether the outer surface is of copper or of brass.

The mere existence of the Kirkendall effect rules out any direct place-exchange or ring-diffusion mechanism.‡ The fact that porosity is associated with the Kirkendall effect is a strong point in favour of a defect mechanism of diffusion, either of an interstitial type, based on the existence of Frenkel defects, or of a vacancy type, based on the existence of Schottky defects. Either mechanism must upset the thermodynamic defect equilibria locally, if two species of atoms with different diffusion rates are involved. This would result in a super-concentration of vacancies on the side with the higher content of the faster-diffusing species. The formation of pores with crystallographic faces can therefore be explained on both hypotheses. Seitz § holds that the experimental facts do not allow any choice to be made between the two mechanisms. Bückle and Blin favour the interstitial type, rightly I think; this mechanism gives a simpler picture, the surplus vacancies being created on the side on which they are actually found as pores.

Porosity has been proved to occur not only in solid diffusion couples and sandwich specimens, but also in gas-phase/solid diffusion systems.|| Mr. Lardner has now shown that the same type of porosity may develop in diffusion connected with the rejection of solutes from supersaturated substitutional solid solutions. In this type of diffusion only one species of atom is involved. The solvent atoms have no incentive to diffuse in any definite direction, because they cannot relieve the supersaturation. This can only be effected by a diffusion of the solvent atoms to spots suitable for their rejection. Formally, it may be said that the difference in the diffusion rates of the two species of atom involved is at a maximum, because the diffusion rate of one species—the solvent atoms—is zero; actually this is not so, but the diffusion of the solvent atoms is not co-ordinated with the diffusion of the solute atoms. There can, of course, be no displacement of an interface here; but Lardner's observation of pores with crystallographic faces shows that the diffusion is again coupled with the creation of vacancies. This is an argument in favour of the interstitial diffusion mechanism, because to explain the creation of vacancies by the vacancy mechanism would lead to difficulties in this case.

In 1947 I postulated the creation of vacancies as a mechanism for the rejection of copper from supersaturated aluminium–copper solid solutions,¶ thereby explaining experimental data obtained bearing on the kinetics of age-hardening. In the aluminium–copper system no pores with crystallographic faces have so far been observed. It seems probable that the vacancies do not agglomerate in this system as readily as in the magnesium–aluminium system. The more pronounced age-hardening effect found with aluminium–copper alloys may be due to this difference. My views concerning the hardening effect of vacancies have gained support from the observations of Billington and Siegel ** and of Dugdale.†† Further developments of my ideas regarding the dependence of mechanical properties on the free path of slip have been published more recently.‡‡

Dr. H. Bückle (*in reply*): The main object in publishing this work was to provide additional experimental data, which might serve to settle certain points hitherto in doubt. I am glad to find that the experimental results are completely confirmed by Mr. Barnes and by those contained in a number of other papers cited elsewhere in the discussion.

There is still considerable difference of opinion, however, regarding the mechanism responsible for the formation of the voids observed in the diffusion zone. It would seem that the concept of an interstitial mechanism is generally rejected as being heretical, although Balluffi and Alexander considered such a mechanism quite independently. I put forward this concept, which avoids certain of the difficulties involved in the idea of a vacancy mechanism alone, rather with a view to its further examination by experts, than as a complete solution of the problem. I agree with Mr. Barnes that a calculation of the activation energies appears to favour a vacancy mechanism. I think, however, that the force of this argument is greatly weakened by two facts: (i) The calculation is valid for a pure metal under ideal conditions, whereas disorder of the Frenkel type, suggested in the paper, might well be associated with the presence of impurity atoms and might be a special function of the concentration of such atoms. The fact that, in certain couples, the holes are strictly confined to a narrow concentration band favours this view. (ii) As the phenomena observed could be accounted for by assuming a very small interstitial flow, the number of atoms in a disordered state might represent a very small proportion of the vacancies in equilibrium, which are responsible for the classical balanced-flow mechanism. There is, of course, no reason why such a complex phenomenon should be due to the action of a single mechanism; Shirn, Wajda, and Huntington §§ have recently demonstrated, in the case of the self-diffusion of zinc, the simultaneous occurrence of two mechanisms, both probably vacancy mechanisms, though this has not been conclusively proved.

The concept advanced by Mr. Barnes is certainly simple and ingenious, but it seems to me to contain a fundamental weakness. The mechanism proposed requires the continuous generation of a considerable number of vacancies, to ensure the supplementary flow postulated. To explain why the source of vacancies does not become exhausted, it is necessary to introduce such factors as the formation of stresses and their interaction with dislocations. Thus, although, once initiated, such a cycle would continue, there seems to be no reason why it should begin. In other words, the setting up of a preferential and oriented flow of vacancies and its source (of necessity on the side opposite to the holes) is based merely on a postulate, whereas the initiation of an interstitial flow and the formation of holes would arise inevitably from the equilibrium structure of the component in which the holes are formed; that the mechanism has its origin in this component is supported by the fact that the holes stop abruptly at the original interface. It does not, however, seem unreasonable to suppose that the two mechanisms may operate concurrently.

It may be noted that the mechanism proposed by Mr. Barnes does not necessarily require different intrinsic diffusion coefficients. In this respect the experiment described by Mr. Inman is of particular interest, because it proves that, at least in the case of self-diffusion of brass, copper and zinc have distinct diffusion coefficients. The mechanism proposed by Mr. Barnes cannot explain the experimental result in this instance, but the assumption of interstitial flow fits the facts very well. The hypothesis proposed by Mr. Inman requires only that the two metals shall have different activation energies, and this can as well be so with an interstitial flow mechanism, partial or total, as with a pure vacancy mechanism. To decide between the two alternatives, therefore, additional factors must be sought. On the basis of the vacancy mech-

* R. Smoluchowski and H. Burgess, *Phys. Rev.*, 1949, [ii], **76**, 309.
† F. Seitz, *ibid.*, 1948, [ii], **74**, 1513.
‡ C. Zener, *Acta Cryst.*, 1950, **3**, 346.
§ F. Seitz, *Acta Met.*, 1953, **1**, 355.
|| H. N. Hersch, *loc. cit.*
R. W. Balluffi and B. H. Alexander, *loc. cit.*
¶ F. Rohner, *J. Inst. Metals*, 1947, **73**, 285.
** D. S. Billington and S. Siegel, *Metal Progress*, 1950, **58**, 847.
†† R. A. Dugdale, *Phil. Mag.*, 1952, [vii], **43**, 912.
‡‡ F. Rohner, *Z. angew. Math. u. Physik*, 1952, **3**, 383.
§§ G. A. Shirn, E. S. Wajda, and H. B. Huntington, *Acta Met.*, 1953, **1**, 513.

anism it is the more difficult to explain a net flow of zinc, the smaller is the concentration of zinc and the greater is the degree of order of the phase; in an ordered phase a net increase in one of the components could be explained only on the basis of the interstitial mechanism. The expansion of the β phase in the case of the multilayer specimens heated to 380° C. which I described (Fig. C, Plate CII), would appear to provide evidence in favour of this mechanism, though without furnishing absolute proof.

In replying to Dr. Chaston's three questions, I shall refer largely to the preceding discussion.

(i) The explanations advanced merely require that the holes should be confined to the diffusion zone. This has in fact been observed in all instances. In the case of the copper/brass couple, the holes are scattered throughout the entire diffusion zone on the brass side, being most numerous near the interface; their distribution along the zones of equal concentration is statistical, although the section shown in Fig. 3 (Plate LVIII) of the paper is too small to bring out this fact. The extent of the diffusion zones is implicit in the data accompanying the illustrations; Fig. 2 (p. 387), however gives a definite example.

(ii) It is indeed surprising that cored structures have not been investigated more extensively. I would point out, however, that such cases do not lead to unequivocal conclusions, since the grains of a polycrystalline structure do not represent a mechanically free system. Zones in which holes are likely to form alternate with zones liable to expand, in such a way that the holes may easily be closed up, the plasticity of the material at the homogenization temperature being very great.

(iii) The microradiograph reproduced by Mr. Barnes (Fig. G, Plate CIII), removes any doubt as to the existence of the holes. I would emphasize moreover, that the holes which we observed were certainly not due to inclusions having been pulled out. Polishing with diamond powder is undoubtedly of assistance in certain metallographic work, particularly in automatic polishing, but skill and experience are nevertheless much more important than details of technique in arriving at a correct interpretation, and there is no likelihood of an experienced investigator confusing polishing imperfections with a true effect. It would, moreover, be hard to believe that inclusions would be torn out exclusively in the diffusion zone and always on the same side of the interface, regardless of the purity of the alloys, and in a manner perfectly reproducible in the dozens of specimens examined. Neither are the cavities shown in Fig. 4 (Plate LVIII) due to a gas reaction, for they are unmistakably characteristic of micro-fissures. They occur only in the corners formed by the copper and the zinc on one side, and by the protective layer of copper enveloping certain of the specimens, on the other. It is obvious that the expansion of the copper and the contraction of the brass set up mechanical disturbances in such areas.

I entirely agree with Dr. Chaston that, in considering this new aspect of the problem of porosity, the classic causes of hole formation should not be overlooked, since in the case of the majority of commercial alloys these are of far greater importance than holes due to diffusion. I also share his opinion that the holes observed by Mr. Lardner cannot be explained on the basis of the Kirkendall effect. Mr. Lardner, by numerous careful experiments, has established the following points:

(1) The holes occurred only in those specimens which originally contained residual Mg_4Al_3 (β) (Section II, 4 of Mr. Lardner's paper).

(2) Time and temperature operated in the same sense; holes appeared only within certain limits of time and temperature; they were no longer found if the time and/or temperature were raised beyond those limits (Section II, 1, 2).

(3) Holes already formed on cooling did not disappear on prolonged heat-treatment (Section II, 2).

(4) Hole formation was associated with a fairly rapid cooling rate. Very slow cooling diminished their number and produced rounded shapes (Section II, 3).

(5) The number and size of the holes increased with increase in grain-size of the specimens (Section II, 4).

(6) Holes were consistently formed at the centre of the grains, in the region poorest in aluminium (Sections I, IV, Fig. 2, Plate LXVIII).

An analysis of these facts does not furnish a single argument in favour of the Kirkendall effect. As regards point (1), this is undoubtedly a question of multi-phase diffusion, a schematic diagram for which is presented in Fig. H. From this, the following conclusions may be drawn:

(*a*) The maximum gradient is always at the original α/β interface.

(*b*) The width of the zone possessing the steepest gradients first increases, passes through a maximum, and then diminishes again.

(*c*) Steep gradients are associated with the presence of residual β.

(*d*) The holes observed are generally situated outside the diffusion zone, at any rate in the region of minimum gradients.

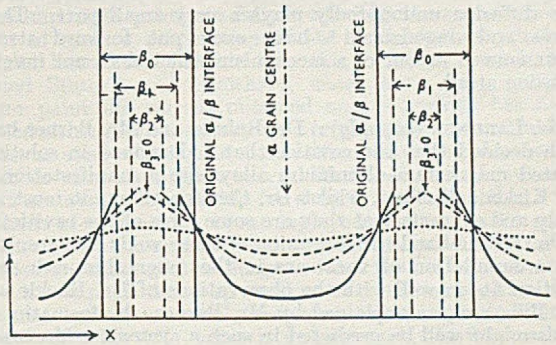


FIG. H.—Showing Evolution of the Concentration (*C*)/Distance (*X*) Curves in the α Grain and Width of the β Phase After Various Solution-Treatment Times.

$t = 0 : \beta = \beta_0$

——— $t_1 > 0$ — — — $t_3 > t_2$ (β has just disappeared)
— · — · $t_2 > t_1$ . . . . . $t_4 > t_3$

Without going into details, it is evident that points (3) (considered together with (2)) and (4), taken in conjunction with points (*a*) and (*d*), exclude any explanation based on the Kirkendall effect. But all the facts point to a simple explanation. The dissolution of β causes a contraction of the lattice which is, at first, confined to the grain boundaries. This results in a high tensile stress at the centre of the grain, liable to give rise either to micro-fissures, when the stresses are released by the mechanical operation of polishing, or to corrosion figures, which might be described as due to local stress-corrosion, polishing being in fact a mechanical-chemical process. The regular shape of the holes is not surprising in a hexagonal phase; similar phenomena are in certain cases observed with zinc, especially in twinned areas. It is obvious that the wider the zone of steep gradients and the steeper the gradients, the higher are the stresses, in complete agreement with the facts (points (1) and (*c*), (2) and (*b*), (5)). The explanation of point (3) now becomes clear, as well as the influence of cooling; only on extremely slow cooling do the stresses become levelled out. It would be interesting to test this hypothesis by means of specially designed experiments.

Dr. Hoar draws attention to the volume changes in sintered compacts. Similar observations have been made in the case of sintered copper/tin and copper/zinc. Fig. D (Plate CII) represents a kind of large-scale model of a sintered specimen, illustrating this phenomenon.

I should like to emphasize the importance of the demonstration first made by Smigelskas and Kirkendall. The earlier demonstration of distinct diffusion coefficients in certain compounds did not make it possible, *a priori*, to draw the same conclusions with regard to substitutional structures having metallic bonding. It was therefore only because this unexpected phenomenon had not been sought, that it was not revealed sooner in metallic structures.

As regards the first part of Dr. Rohner's contribution, I

would refer him to the preceding discussion. I do not think, however, that, if I understand him correctly, I entirely share his views on the mechanism of precipitation. I do not see why in this case only one kind of atom should be involved. Once past the complex stage of nucleus formation, the growth of the nucleus entails diffusion in the surrounding matrix, where the gradients are essentially determined by the equilibrium concentration and the degree of supersaturation. The picture then closely resembles that of Fig. H, but reversed and reduced to the scale of precipitates. That is not to say that the Kirkendall effect will not appear, given the necessary conditions; but it will be much less pronounced, since the volumes involved are very small. These arguments are not applicable to the phenomenon described by Mr. Lardner, since the holes were not observed after precipitation-treatment, but on the contrary after homogenization treatment (see preceding discussion). Age-hardening at room temperature (as in Duralumin) must also be excluded, because here diffusion undoubtedly plays a very small part. Thus, Laves and Jagodzinski * have even put forward strong arguments in favour of a mechanism which does not involve diffusion at all.

Mr. LARDNER (*in reply*): Dr. Rohner and Mr. Barnes have both decided that the cavities that I described in solution-treated magnesium–aluminium alloys are a manifestation of the Kirkendall effect, whilst Dr. Chaston thinks it most unlikely and suggests that they are some form of gas cavities.

On the one hand the formation of these voids as a result of the accumulation of vacancies in the magnesium-rich solid solution fits in well with the observations of Dr. Bückle and Mr. Blin, and, as explained by Mr. Barnes, the formation of voids might well be predicted in such a system. Moreover, the characteristic geometric form and orientation of the cavities, their position, and their obvious connection with the diffusion of aluminium into the grains of the magnesium-rich solid solution, indicate that these voids are closely related to those observed as being associated with diffusion in artificially produced metallic sandwiches.

On the other hand, the magnesium–aluminium system is not unique, and such void formation might equally well be expected in many other common alloy systems, though apparently none has so far been observed. The production of such voids would also be expected to depend upon the concentration gradients existing in the as-cast structure, and as these depend mainly upon casting conditions, such cavities would be expected always to result when castings in the same alloy were solution-treated. In fact, however, the formation of these cavities is comparatively uncommon and is found to be peculiar to occasional casts of alloy. This strongly suggests that some other condition besides the necessary diffusion is required if cavities are to be produced. Dr. Chaston's suggestion of gas cavities is very attractive here, but surely sharp hexagonal-shaped cavities with a well-defined crystallographic orientation are a strange form for cavities due solely to gas to assume.

Evidently the question cannot be decided upon the evidence at present available. The fact that the cavities appeared to form on cooling now seems open to doubt, and Mr. Barnes' suggestion of incipient fusion during the high-temperature solution-treatment obviously needs close attention.

Dr. Rohner's statement that " it has now been shown that the same type of porosity may develop in diffusion connected with the rejection of solutes from supersaturated substitutional solid solutions " indicates a misreading of the paper. What has been demonstrated is that the formation of the same type of porosity is associated with the homogenization of the cast structure.

Discussion

Priming Paints for Light Alloys

By J. G. RIGG and E. W. SKERREY

(*Journal*, this vol., p. 481)

Mr. E. A. G. LIDDIARD,† M.A., F.I.M. (Member): A pellet of magnesium powder containing 20 wt.-% ferric oxide will react violently in a 3% solution of sodium chloride, and, in fact, produces the stoichiometric quantity of hydrogen from the reaction, assuming that all the magnesium reacts in about 3–5 minutes, while there is a very marked heat evolution. Pellets compressed from magnesium powder without additions, and pellets containing 20 wt.-% magnesia, show only a slight reaction, which tends to decrease with time, and there is no rise in temperature. Such pellets will retain their general form in the NaCl solution over a period of several days.

In view of this fact I cannot believe that iron oxide is a suitable material to bring into contact with magnesium, despite the authors' conclusions. Incidentally, mixtures of magnesium metal and metallic iron powder were used during the war for hydrogen generation in sea-water. The process was worked out at the British Non-Ferrous Metals Research Association and is patented.‡ It was subsequently found that ferric oxide was much more effective in stimulating the reaction than metallic iron. This emphasizes the danger in using an easily reducible metal oxide in contact with aluminium or magnesium under conditions in which the hydrogen-evolution type of corrosion attack can take place.

It is very clear from the results reported in the paper that the suitability of the various oxides as primers decreases as the metal of the oxide become more noble. The fact that reasonably good results have been obtained by the authors in their experiments on paints can, I think, mean only that the pigment vehicle is the protecting agent and that it will protect light alloys in spite of the presence of an accelerating oxide. There is no significant difference in the rate of corrosion of a pellet made up with 20% magnesia and one without any admixed oxide, so that the increased rate of corrosion in the magnesium–iron oxide pellet is not due to the greater separation of the individual particles of magnesium metal by the oxide, particularly since the volume of magnesia is, of course, greater than the volume of iron oxide used.

This brings me to my main point. Why do we use a primer at all on aluminium, and if we do so, why do we employ an easily reducible oxide of a more noble metal as a filler? Would it not be so much more sensible to use a primer in which the filler was the oxide of the metal to be painted, or a highly stable oxide, as, for example, titania? It seems to me thoroughly regrettable that nobody has attacked this problem of developing a paint especially suitable for light metals, but that instead priming paints developed for the painting of iron, steel, and wood have been adopted. I was surprised to find that in the earlier paper by these authors,§

* H. Jagodzinski and F. Laves, *Z. Metallkunde*, 1949, **40**, 296.

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‡ British Patent No. **579,246**, 1946.

§ J. G. Rigg and E. W. Skerrey, *J. Inst. Metals*, 1948–49, **75**, 69.

in which the results of the six months' tests are described, they report the use of cobalt naphthenate as a drier for all the paints and for the D.T.D. 260A top coat. I suppose one can be thankful that they didn't use a mercury compound! It may be argued that since the results of their exposure tests are quite good, there is really nothing to worry about, but I do not subscribe to that view. If the results are good it is, I suggest, in spite of the filler and driers used in the paint scheme, and we should be able to do a great deal better if we used primers which were logically suitable for aluminium and magnesium.

In all normal circumstances it is unnecessary to protect aluminium and aluminium–magnesium alloys, and it is only with the high-strength materials, particularly those containing copper, that some form of protection is necessary if they are to operate in an industrial or marine atmosphere. I therefore should have liked to see more work done by the authors on fully heat-treated aluminium–copper–magnesium alloys. The B.S. 5L3 alloy is, of course, only room-temperature aged, and in this condition is not particularly susceptible to intercrystalline corrosion. The alloy more likely to be used for structural work is B.S. 1476 HE15-WP. It is with this alloy that there is serious danger of stress-corrosion or layer-corrosion, and judging from recent experience, the latter form of attack does not seem to have been prevented by painting, even when zinc oxide and chromate primers were used. We do know, however, that the most satisfactory method of preventing attack on these high-strength alloys is by cladding. Less information is available on the effect of anodic sprayed coatings, but such work as has been done is very promising. It has been suggested that a sprayed coating may be even more effective than a clad coating, because of the tendency of inert corrosion products to form in the pores of the sprayed coatings. This appears to be another argument in favour of considering alumina as the ideal inert substance for covering aluminium.

The use of zinc, in the form either of metallic paint or a sprayed coating, to protect aluminium has something to be said for it in that zinc is usually anodic to aluminium under normal exposure conditions, despite the fact that it is some distance away from aluminium in the electrochemical series. My experience has been that zinc coatings on aluminium–copper alloys are less effective than aluminium coatings in delaying stress-corrosion failure, and I think there can be no doubt that zinc is not to be compared with aluminium in its general corrosion-resistance.

I would therefore suggest that the best means of protecting high-strength aluminium alloys against corrosion is to provide an anodic coating, preferably of pure aluminium, either by cladding or spraying, and to use paints which contain no compounds of the more noble metals. More attention should be given to the possible use of alumina in the formulation of paints for aluminium and of magnesia in paints for magnesium.

Mr. A. W. Brace,* A.I.M. (Member): The authors indicate that the medium used might not be regarded as a usual one, and it is perhaps unfortunate that they did not employ more conventional paint vehicles in conjunction with the pigments chosen. In particular, the inclusion of oiticica oil in the medium can be associated with a tendency to embrittlement of the paint film, with consequent flaking during subsequent weathering. It is well established that red lead does not develop its full anti-corrosive properties in the protection of steel with this type of medium; that required by B.S. 1011, however, gives an outstanding performance not excelled by any other vehicle. In tests being carried out by Goodlass Wall and Lead Industries, Ltd., in collaboration with the Aluminium Development Association, the known merit of a B.S. 1011 red lead primer is being exemplified. After 18 months' exposure in marine and industrial atmospheres, one coat of this primer is still in good condition on both steel and aluminium panels. One coat of a red lead primer in a linseed vehicle with a synthetic quick-drying addition has not shown the same good results on steel, although on aluminium the coat is still in fairly good condition. The authors' conclusions, therefore, would appear to be valid only for the particular medium employed.

The use of iron oxide as a major constituent in primers for aluminium should not be dismissed lightly, for although in itself it has no outstanding properties, the addition of a percentage of zinc chromate substantially improves its performance, and in some applications a red oxide primer containing zinc chromate is to be preferred to a straight zinc chromate primer.

An important point not fully studied by the authors is the effect of surface preparation of the metal before painting. Results have been published in this country † and in the United States ‡ and elsewhere, which show that a much longer paint life can be obtained on steel which has been pickled either in a phosphoric-acid or phosphate-base solution, than on steel which has been only weathered and wire-brushed. For aluminium several distinct forms of pretreatment are available, suitable for shop or site use. Had such methods of preparation been employed, the results on paint life quoted by the authors might have been quite different.

It is something of a challenge to learn that B.I.S.R.A. tests show that a paint life of up to 15 years can be obtained with a two-coat system on steel, and that even under industrial conditions a life of 7 years is not unusual. Unfortunately, no comparable test data seem to be available for aluminium.

The phenomenon of the accelerated corrosion of the aluminium and magnesium panels induced by lead pigments is one of some complexity. Tests made by Goodlass Wall and Lead Industries, Ltd., have shown that immersion of aluminium panels in suspensions of lead pigments (red lead, white lead, basic lead sulphate) in water does not produce any rapid attack on their surface. On the other hand, panels immersed in a dilute solution of soluble lead soaps containing 0·15 wt.-% of both lead and organic acids were rapidly attacked, especially if the water contained 0·5–3·0% of sodium chloride. Similar behaviour was observed with a zinc soap solution containing 0·4% zinc and 1·6% of aromatic organic acids. Work carried out by Whitby,§ using potential/time curves, showed that there was a tendency for red lead paints to attack in this way painted aluminium panels immersed in sea-water, distilled water, or a 0·001-*N* sulphuric acid solution. White lead paints showed no such tendency.

It is not easy to find a simple explanation, but it may be that the acids formed by the breakdown of the linseed oil vehicle ‖ release soluble lead soaps from the pigments, which, in conjunction with chloride, produce rapid attack on the aluminium. In observations which I have made on a few examples of the phenomenon it has been noticeable that only when the paint film has suffered decided deterioration does the marked attack on the aluminium begin. There is some indication that it may not be general to all lead pigments. Further studies are in progress.

Zinc chromate primers are fairly widely used on aluminium, but their efficiency obviously depends on the inhibition due to the release of soluble chromate ions produced by the controlled entry of moisture into the paint vehicle. It is not unusual, however, to apply over the chromate primer further

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† 2nd Interim Rep. of Joint Technical Panel JP/1 on "Painting of Structural Steelwork". **1949**: London (B.I.S.R.A.).

J. C. Hudson and T. A. Banfield, *J. Iron Steel Inst.*, 1948, **158**, 99.

J. C. Hudson, *ibid.*, 1951, **169**, 153.

‡ *Official Digest New England Paint and Varnish Club*, **1949** (Nov.), 792.

J. S. Pettibone, *Amer. Soc. Test. Mat. Special Tech. Publ.*, 1952, (**147**).

§ L. Whitby, *Paint Research Sta. Tech. Paper*, 1939, (**125**).

‖ L. A. O'Neill, *ibid.*, 1949, (**159**).

coats which act essentially either as ion barriers or as a continuous protective layer such as that afforded by leafing aluminium, which aims at the exclusion of corrosive agents. It may well be that this combination is not one which gives optimum efficiency. Furthermore, it may be found that the type of paint system which effectively protects the more corrosion-resistant materials, such as the aluminium–magnesium alloys, is less satisfactory on the Duralumin-type alloy. The special chemical properties of aluminium alloys demand paint formulations somewhat different from those commonly employed on steel, and still further adjustments in the protective system used may be necessary for the various groups of aluminium alloys.

Work on the effects of pretreatment and alloy composition on paint life on aluminium-base materials has been undertaken as part of an A.D.A. investigation, but a more fundamental study of the behaviour of different types of pigment and paint vehicles would be welcome. As compared with steel, there is a relative lack of published information of a systematic nature on this subject. Joint action between the metallurgist and the paint technologist is to be encouraged, in view of the growing use of aluminium for structural purposes and in a wide variety of other fields where techniques suitable for site application have to be developed, as opposed to the rather more refined methods used on small assemblies in the shop.

Mr. R. J. Brown,* F.I.M. (Member): It is unfortunate that the authors did not include in their series of paints the modern etch primers, which are very widely used in industry and extend greatly the service life of the paint coating; nor did they investigate pretreatment with phosphoric acid, which is a common alternative to etching in chromic–sulphuric acid solutions. Although their purpose was to evaluate the primers in general use, the performance of any priming coat is very considerably affected both by the pretreatment of the metal and by the coatings subsequently applied over the priming-paint.

In Table VI (p. 486) it is indicated that uncoated steel panels suffered only slight corrosion during a period of 3 months' exposure at the marine site, and in the accelerated tests. This is fantastic, as uncoated degreased steel will rust overnight in most atmospheres, even under cover. Reference is made in the paper to the more severe corrosion experienced on the panel backs. This is hardly surprising, as careful examination of exposed panels during atmospheric tests will show not only that evaporation on the upper surface is more rapid, but that condensation on the under surface is more severe. The effect of direct solar radiation is to promote the breakdown of the vehicle of the paint coating, the degree of breakdown being related to the intensity of corrosion resulting from prolonged exposure. The severity of the corrosion on the panel backs should be attributed directly to the effect of moisture, and not to sheltering from solar radiation.

Dr. F. A. Champion,† B.Sc., A.R.C.S., F.I.M. (Member): Theoretical considerations lead one to expect that lead pigments would be liable to stimulate the corrosion of aluminium, and even more so that of magnesium, and that this would be most marked in environments providing a strong electrolyte, e.g. marine and industrial atmospheres. The work of Dr. Rigg and Mr. Skerrey has confirmed these expectations and provides a valuable assessment of the practical importance of the effects in different types of exposure conditions. It is rather surprising to note signs that they were operative even in the rural atmosphere, as shown, for example, by the greater corrosion at scratch lines with systems using lead primer as compared with those using iron oxide primer (see Table IV, p. 484). Some mechanical damage is usually inevitable before maintenance is justified in service, and it therefore seems desirable to avoid lead pigments for light alloys in all conditions where *protective* paints are called for.

The authors have pointed out that iron oxide or preferably zinc chromate or tetroxychromate should be used all over composite structures of aluminium and steel, and it should be added that they are also required for aluminium-coated steel (e.g. sprayed coatings). In spite of Mr. Liddiard's purist objections, the results confirm the suitability of iron oxide as a diluent for chromate pigments in primers for aluminium and its alloys.

Mr. A. J. Field,‡ M.C., B.Sc., F.I.M. (Member): It is not clear whether, in the priming paint, as the conditions are intentionally of a non-electrolytic character, the pigment has effect on the durability of the medium or of the underlying metal. This suggests that it might be of interest to test the three interactions separately, namely, pigment on metal, medium on metal, and pigment on medium.

Mr. H. Silman,§ B.Sc., F.R.I.C., M.I.Chem.E., F.I.M. (Member): The problem of formulating a suitable priming paint for aluminium cannot be reduced to the simple one of combining an aluminium-base pigment with a drying oil. Many other factors enter into the matter, including in the first place the compatibility of the pigment with the medium, not only from the point of view of the protective value of the finish but also of the stability of the paint itself. Other aspects include covering power and corrosion-inhibiting properties.

Mr. Liddiard tends rather to over-simplify the economic and technical considerations of paint manufacture in the suggestions he makes for the formulation of a satisfactory priming paint for aluminium.

The Authors (*in reply*): We note that Mr. Liddiard considers that we are lacking in caution in advocating the use of iron oxide pigments on light alloys, while Mr. Brace holds that we are too cautious in our objection to the use of red lead. We therefore feel that the discussion, on balance, supports the moderate view we have taken.

The iron oxide pigment was selected as being a non-inhibitive priming pigment in common use. Despite the observation that iron oxide will catalyse the dissolution of magnesium in sodium chloride solution, it did, nevertheless, provide a useful degree of protection in our tests, with no indication of acceleration of corrosion. The inference is not, however, as Mr. Liddiard suggests, that the medium is making up for the shortcomings of the pigment. No medium of this type without pigment could be expected to give such a long period of protection. As has been pointed out, the iron oxide increases the durability of the film.

Mr. Brace does not see any advantage in the use of zinc chromate primers under relatively impervious top coats. Even leafing aluminium top coats are, however, still slightly pervious,‖ and the exclusion of moisture will rarely be 100% efficient. The primer is, therefore, necessary to provide maximum protection under these conditions and above all to take care of accidental damage, since the chromates continue to protect even where the priming film has been rendered discontinuous in places. We agree with Mr. Brace that mixed chromate–iron oxide films give priming paints suitable for most purposes.

Mr. Liddiard's objections to the use of cobalt driers are of a theoretical nature. Unfortunately, efficient drying can be achieved only in the presence of certain metallic salts or soaps and, of the metals available, cobalt is the most active drier and is therefore used in the smallest concentration possible.

We sympathize with Mr. Brace's remarks about red lead giving the best protection to steel in a medium of the type

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‖ V. J. Hill, *Paint, Oil and Colour J.*, 1952, 122, 137.

specified in B.S.1011, and for that reason did not lay stress in the paper on the comparatively poor results obtained with the oiticica oil medium on this metal. Better media could have been chosen for all the other three priming pigments. Since the emphasis was on priming pigments for light metals and the number of panels had to be kept within reasonable bounds, a single priming medium was selected which gave a reasonable degree of adhesion on all these metals, and was at the same time compatible with both types of aluminium top coat. The manufacturer who so kindly formulated the paints drew on a medium in common commercial use at the time—a time moreover when paint oils and resins were in short supply.

The results from tests by Goodlass Wall and Lead Industries, Ltd., which Mr. Brace quotes, in which aluminium specimens were immersed in suspensions of lead pigments or soaps, appear to be in accord with our own results, namely that an electrolyte (e.g. 0·5–3·0% NaCl) is necessary to give the ill effects. In the exposure tests, the serious effects of lead pigment were, similarly, noted only in industrial and marine conditions where the necessary electrolyte was provided for the galvanic cell.

Several contributors have drawn attention to omissions from the paper. We agree with these contributors, and with Mr. Field, that there is scope for further work in all these directions, and we endorse the statement by Mr. Silman that the problems are complex and should not be considered to be as simple as Mr. Liddiard might suppose. Our results (and especially comparison of the high- and low-purity magnesium-base alloys) confirm Mr. Brace's expectation that a paint system which is satisfactory on the more resistant metals gives a shorter life on the less resistant. Since no paint film is completely impervious, the corrosion characteristics of the underlying metal must be added into the sum of the total corrosion-resistance of the entire system. We do not believe that there is a call for special formulation for particular aluminium alloys, other than adjustment of the protective value of the paint film. This can be done by varying its total thickness or the content of inhibiting pigment to the requirements of the underlying metal, in the same way that it is adjusted to the severity of the exposure conditions.

We would emphasize that we have not attempted a general discussion on the painting of light alloys, but have simply recorded an investigation with a limited objective, namely, the comparison of various single primer pigments on light alloys, although a few incidental observations have been included in the paper. The tests were designed to eliminate as far as possible factors irrelevant to this investigation, in order to obtain reliable results as quickly as possible. For example, the inclusion of "etch primers" (not then available in this country) would have delayed information on the primary objective. We entirely agree that there should be no difficulty in designing procedure and paint systems which would provide better and more enduring protection than the best of the range employed for this particular investigation. Choice of different media and mixed-pigment formulation would be two possible steps in this direction.

As a matter of interest, however, a few of the panels have remained on test, and the best systems have continued to give good protection to the more resistant light metals after exposure for seven years at the most severe sites.

We agree that sheltering from direct solar radiation would extend the time for which the backs of the panels remain wet and so contribute to the effect of moisture, as indicated by Mr. Brown, and would also avoid breakdown of the medium by ultra-violet absorption. Mr. Brown finds it difficult to accept our assessment of the attack on plain steel panels after three months' exposure. We wonder whether he has appreciated that our terms of assessment bear a definite relation to numerical values,* e.g. slight attack included infrequent pitting up to 10 mils deep and general attack up to 0·6 mils deep.

Discussion

Stretcher-Strain Markings †

Dr. W. A. Baker,‡ F.I.M. (Member of Council): In reading the several papers on stretcher-strain markings and discontinuous flow, it seems rather remarkable that these phenomena, so long familiar in steel, should previously have received so little attention in non-ferrous metals. The occurrence of the particularly objectionable types of marking in lightly strained aluminium–magnesium alloys has stimulated a good deal of the current work on the subject, and the close analogy between the behaviour of steel and non-ferrous metals is becoming more and more apparent. The authors are to be congratulated on the careful way in which they have studied the nature and mode of occurrence of these markings, because, although we by no means understand the subject as fully as we would like, they have at least shown how the appearance of the markings depends on various factors, and their observations have gone a long way towards dispelling some misconceptions about stretcher-strains not only in non-ferrous metals but also in steel.

There seems to be little doubt that the initial yield occurring in an annealed material is to be distinguished from the yields that succeed it, and from the yield that occurs in a strain-aged steel. Not only are the two types of yielding dependent on different factors, but they give rise to distinctively different types of marking. In the case of steel, this distinction seems to have been obscured in the past, for the observer has frequently failed to distinguish between stretcher-strains in fully annealed material and those which develop in strained and aged material, and even in one of the present papers Dr. Polakowski suggests that the irregular flamboyant or random markings, now clearly shown to be associated with the first yield in a fully annealed material, arise only from heterogeneous stress distribution in the specimen during straining. This author suggests that whenever these local stress concentrations are relieved by a certain amount of plastic flow, the markings revert to the regular parallel-band type. However, Dr. Phillips, Mr. Swain, and Mr. Eborall state that if care is taken to avoid notches in the specimen, the shear deformation involved in the initial yielding will spread continuously through the test-piece and no major strain marking will be visible. Thus, although they show that the highly irregular flamboyant markings, so objectionable in practice, are caused by local stress concentrations which propagate this deformation from a number of points at one time, their observations seem to be inconsistent with Dr. Polakowski's

* J. G. Rigg and E. W. Skerrey, *J. Inst. Metals*, 1948–49, 75, 69.

F. A. Champion, *ibid.*, 1943, 69, 47.

† Joint discussion on the following papers published in the *Journal*: R. Chadwick and W. H. L. Hooper (1951–52, 80, 17); W. H. L. Hooper (this vol., p. 563); W. H. L. Hooper and J. Holden (this vol., p. 648, and *Bulletin*, 1953, 1, 161); N. Krupnik and H. Ford (this vol., p. 601); N. H. Polakowski (this vol., p. 617); V. A. Phillips, A. J. Swain, and R. Eborall (this vol., p. 625); V. A. Phillips (this vol., p. 649).

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suggestion that only one type of deformation occurs and that the differences between the appearance of the markings is dependent only on the conditions of straining.

From the practical point of view it is comforting to find that Mr. Chadwick and Mr. Hooper, and Dr. Phillips, Mr. Eborall, and Mr. Swain, reach essentially the same conclusions about remedial measures for stretcher-strain markings in the aluminium–magnesium alloys. One of the remedies that involves rapid cooling from a high temperature is perhaps of more academic than practical interest. The two groups of investigators appear to interpret this result, and the effect of subsequent reheating of the quenched material to lower temperatures, in different ways. Thus, Mr. Hooper suggests that quenching from high temperatures introduces internal stresses, which in some unspecified way prevent the formation of the objectionable random markings. On his view the effect of subsequent heat-treatment at lower temperatures is to relieve these internal stresses and thereby make the material again susceptible to stretcher-strain marking. The other investigators make no reference to any possible effect of internal stresses but interpret the effects of quenching and reheating in terms of the distribution of magnesium atoms between the grain bodies and the grain-boundary regions. They hold that their observations are consistent with the view that the solute atoms diffuse to, and concentrate at, the grain boundaries during low-temperature heat-treatments, and thereby produce a grain-boundary barrier which impedes the propagation of slip from one grain to another and is thus responsible for the marked initial yield. Their data on the effects of various times and temperatures of heat-treatment seem to me to rule out the suggestion that the effects are due to internal stresses. If one refers to their Fig. 24 (p. 638) and considers, for example, the effects of reheating at 150° and 100° C., it will be found that to restore the yield point to an equivalent degree by heating at these two temperatures, the heating times at 100° C. would have to be roughly one hundred times as long as at 150° C. This fact seems to me to be incompatible with the idea that the relief of internal stress is responsible for the effects noted, because observations on the creep properties of a variety of aluminium alloys, including aluminium–magnesium alloys, show that the resistance of the materials to creep at the two temperatures I have quoted differs by a factor of only about 2, or at most 4. On this score it seems to me that the internal-stress effect, if any, might be disregarded, but I should be very interested to hear the authors' further observations on this point.

Turning to the less objectionable type of strain marking, the parallel ripples or Lüders bands (described by Dr. Phillips and his colleagues as type-*B* markings), there seems to be no doubt that these markings arise from yields, whether single or multiple, occurring in strain-aged material. Until one reads the paper by Mr. Krupnik and Professor Ford the picture seems to be fairly straightforward, in that all the investigators seem satisfied that these yields and their associated markings can be explained in terms of Cottrell's theory of strain-ageing. Krupnik and Ford, however, complicate the issue by showing that at slow, constant rates of loading, and more particularly by straining at constant rates in a very rigid machine, the discontinuous yielding and the associated ripple markings are suppressed. These authors consider that their findings throw doubt on the view that discontinuous yielding can be explained by current theories of strain-ageing phenomena. I do not propose to venture into that particular argument, but I should like the exponents of whatever theory is put forward to explain in a little more detail just how the deformation associated with type-*B* markings occurs. In the description of the behaviour of materials when yielding is observed, Lüders-band markings are described as running up and down the gauge-length of the specimen, although the description of the contours of the specimens after such yielding has occurred makes it clear that what really happens is that a great many small contiguous necks are formed in rapid succession. One then has the picture that the load on the material is increased till the point is reached at which slip occurs in some region, presumably where there is a local stress concentration, and the slip gives rise to a small neck. Why does yielding stop in this region, to be followed immediately by yielding in a similar very small adjacent area? I do not see why, in the light of what is said in the several papers, the boundary of the first necked region does not spread continuously through the metal, and I cannot help wondering whether a more careful consideration of the macroscopic mode of deformation associated with type-*B* yielding might explain the observations of Krupnik and Ford on the effect of straining at slow and constant rates. Could it be, for example, that under their conditions of testing in a rigid machine the volume of metal affected in each of these small necked regions might be smaller still, so that the deformation process became one in which the boundaries of the initially necked region spread right through the material?

Mr. R. Chadwick,* M.A., F.I.M. (Member) and Mr. W. H. L. Hooper,† B.Sc., A.I.M. (Member): Although we clearly stated in our first paper (p. 19) our belief that type-*A* or random markings are, when first formed, at right angles to the direction of stress, this important fact should be repeated and emphasized, because the issue has tended to be obscured for two reasons. First, the terminology suggested, i.e. "random" or "flamboyant", has emphasized the curvature which often develops as stretching progresses and the stress system becomes more complex. Secondly, the flamboyant character of the markings really arises from the employment of wide test specimens. Although such specimens are most desirable for obtaining good illustrations, uniform stressing is inherently difficult, while slight gauge variations cause irregularities even with accurate specimen alignment. On a standard tensile test-piece of narrow central gauge-length, the first-formed markings (Fig. A, Plate CIV) are normal, and diverge from this position only after continued stretching (Fig. B, Plate CIV), forming the tongue-shaped markings such as those illustrated in Fig. 2, Plate III (Chadwick and Hooper) and seen also in Fig. 3 (*a*), Plate XC (Phillips, Swain, and Eborall).

There appears to be no serious divergence in views as to the general form of metal surfaces affected by type-*A* markings, the model illustrated in our first paper (Chadwick and Hooper, Fig. 12, Plate VI) being generally accepted. Dr. Phillips, Mr. Swain, and Mr. Eborall made measurements of the angle of tilt between adjacent surfaces at a strain line produced at an early stage in the stretching of an aluminium–magnesium alloy. Using both optical interferometry and differential focusing, they obtained values ranging from 22′ to 33′. We used the former method only and obtained angles in the same range, i.e. 20′–30′ on both aluminium–magnesium and mild-steel specimens (Hooper and Holden). A somewhat different series of values was obtained from Talysurf measurements on specimens of aluminium–magnesium alloy subjected to a greater amount of stretching, so that type-*A* markings were numerous and fully developed. On these specimens the Talysurf traces show that surfaces generally have significant curvature. The geometry is indicated in Fig. *C* on the usual exaggerated vertical magnification of the Talysurf trace. The angle to a reference surface AA' is obtained from measurement of the tangent of the mean slope ZY/XY of the area between two strain lines X and Z. A typical measured angle, ϵ, is about 1′. The angle α between adjacent surfaces forming the cusp at Z is quite obviously larger than ϵ, but at this stage of stretching is smaller than at the earlier stage where the 20′–30′ measurements were taken.

Again, on the subject of type-*A* markings, Phillips, Swain, and Eborall (p. 628), quote us as having found no thinning of sheet as a result of the formation of markings. This is incorrect, because no measurements of thickness were, in fact, made, but clearly if a specimen is stretched by 1% or so there

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must be some corresponding thinning, which is, however, an overall and not a local thinning. Possibly we were guilty of over-simplification in our synopsis (Chadwick and Hooper, p. 17), but the point we made was that random (type-*A*) markings were due to kinking, in contrast to the parallel bands (type-*B*), which are due to local thinning or necking.

The parallel bands or type-*B* markings have been characterized as occurring in aluminium alloys at a later stage in stretching than the type-*A* markings, and there is general agreement on their topography. We found that these markings first became apparent in Talysurf measurements after type-*A* markings had been largely dispersed and attenuated at about 2% extension. There is, however, a good deal of evidence that strong type-*B* markings appear at a much earlier stage. For example, in the picture by Phillips, Swain, and Eborall (Fig. 3 (*a*), Plate XC) of type-*A* markings, with a 1% extension, many of the finer markings are at angles of 52°–55° and must be regarded as of type *B*; similar but smaller markings are shown by Hooper (Fig. 3, Plate LXXXIII), after ½% extension. As yet very little work has been done on the topography of markings in mild steel, but the work of Mr. Hooper and Mr. Holden suggests that the two types of marking often occur together. Fig. 4 (*Bulletin*, 1953, **1**, 162), for example, shows kinking and necking occurring simultaneously. The central marking is quite definitely a neck

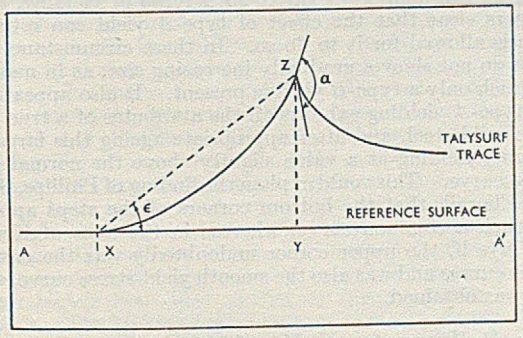

FIG. C.—Geometry of Talysurf Traces on Aluminium–Magnesium Alloys on Which Type-*A* Markings Were Fully Developed.

from the Talysurf traces. Angles measured on Figs 4 and 5 (*Bulletin*, p. 162) range between 50° and 55°.

There has unfortunately as yet been little attempt to correlate the results of topographical measurements with stress/strain curves. The obvious difficulty in trying to relate existing data is the small number of discontinuities in the stress/strain curve compared with the total number of strain markings. Thus Phillips, Swain, and Eborall generally show less than 20 discontinuities in a 5% extension, where there must be literally hundreds of separately identifiable strain lines. It is interesting in this connection to note the finding of Professor Ford that when specimens are stretched under special conditions at constant rate of strain, the discontinuities in the stress/strain curve do not appear, although there were no related topographical observations. It seems possible that the formation of a single strain line, whether it be a kink or a neck, is insufficient to show any effect on the stress/strain curve. Under normal testing methods with a non-rigid machine, however, the sudden yielding when a single strain line forms would cause a disturbance sufficient to trigger-off several more strain lines, which would in total give a visible break in the stress/strain curve. This would be repeated at intervals, and the magnitude of each step in the curve would be largely fortuitous, depending upon the number of strain lines triggered-off, the controlling factors being the mechanical condition and degree of elastic recovery in the testing machine. This would account for the irregularity in size and spacing of steps characteristic of most published stress/strain curves.

Professor A. H. COTTRELL,* B.Sc., Ph.D. (Member): The results presented in this very interesting group of papers contribute substantially to the rapidly accumulating evidence †‡§‖ that yield points can be produced in face-centred cubic metals when these contain substitutional solute atoms. Interpreted in terms of the dislocation theory, yield points are to be expected in such alloys because the dislocations responsible for slip exist in a form (i.e. as pairs of Shockley half-dislocations) in which they are capable of attracting to themselves substitutional solute atoms. However, this attraction is weaker than in the case of interstitially dissolved carbon and nitrogen in ferritic iron, where a notable yield point can be produced. For example, according to elasticity theory, the energy binding a zinc atom to a dislocation in copper is about 0·12 eV., whereas the corresponding value for carbon in iron is about 0·5 eV.‖ This is important, because the concentration of dissolved atoms in equilibrium with a dislocation atmosphere of a given density rises exponentially as the binding energy is reduced. For an atmosphere that will give a strong yield point at room temperature, the amount of carbon or nitrogen in solution in iron need only be about 10^{-7}%. But for zinc in copper, the corresponding concentration has to be about 1%. This means that yield points in face-centred cubic metals are unlikely to be observed at ordinary temperatures unless fairly substantial alloy additions (e.g. up to a few per cent.) are made, and these additions are retained in solid solution. These conclusions agree with the observations that face-centred cubic metals do not normally show yield points unless they contain appreciable amounts of impurity or alloy additions, and that serrated yielding is observed most clearly in freshly cooled specimens, where most of the alloying elements are retained in solution.

Serrated yielding in these face-centred cubic metals has two interesting features. It often does not begin until a small amount of plastic deformation has taken place. Secondly, if we interpret the serrations as being caused by strain-ageing during the course of plastic deformation, as is known to be the case with carbon and nitrogen in iron, the necessary rate of ageing is far too fast to be accounted for by the diffusion coefficient of the solute atoms, as determined from high-temperature measurements. That this fast ageing does really occur is demonstrated in the paper by Dr. Phillips, Mr. Swain, and Mr. Eborall, as well as in some rather similar work in America.‡

Both these features can be explained ¶ on the bases (i) that the diffusion coefficient is too small, at the start of plastic deformation, to give appreciable strain-ageing during deformation, and (ii) that the diffusion coefficient increases during plastic deformation, through the creation of vacant atomic sites and related atomic defects,**†† and after a certain strain becomes large enough to cause strain-ageing during deformation. According to Mott ** and to Seitz †† the concentration of vacancies created by plastic deformation is about $10^{-4}\,\varepsilon$, where ε is the strain, and an estimate ¶ based on this formula gives the expected rate of substitutional diffusion in worked aluminium at room temperature as $10^{-13}\,\varepsilon$ cm.²/sec., in order of magnitude. By analysing published data on serrated yielding in iron, one can show ¶ that it occurs when the rate of diffusion (of carbon or nitrogen) is about $10^{-9}\,\dot{\varepsilon}$ cm.²/sec., where $\dot{\varepsilon}$ is the rate of strain. Let us consider

* Professor of Physical Metallurgy, Birmingham University.

† C. A. Edwards, D. L. Phillips, and Y. H. Liu, *J. Iron Steel Inst.*, 1943, **147**, 145.

‡ O. D. Sherby, R. A. Anderson, and J. E. Dorn, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 643.

§ R. E. Smallman, G. K. Williamson, and G. Ardley, *Acta Met.*, 1953, **1**, 126.

‖ G. Ardley and A. H. Cottrell, *Proc. Roy. Soc.*, 1953, [A], **219**, 328.

¶ A. H. Cottrell, *Phil. Mag.*, 1953, [vii], **44**, 829.

** N. F. Mott, *ibid.*, 1952, [vii], **43**, 1151; 1953, [vii], **44**, 187, 742.

†† F. Seitz, *Advances in Physics*, 1952, **1**, 43.

a typical experiment on an aluminium alloy at room temperature, where the rate of strain is, say, 10^{-5}/sec. Then the rate of diffusion at which serrated yielding occurs should, by analogy with iron, be about 10^{-16} cm.^{2}/sec. Now the diffusion coefficient at room temperature, deduced from the high-temperature data, is of the order of 10^{-23} cm.^{2}/sec.; it is thus far too small to give serrated yielding. But with plastic deformation the rate of diffusion increases, and according to the formula $10^{-13}\ \varepsilon$, a strain of 10^{-3} should be sufficient to cause serrations to appear. A further development * of this theory suggests that the serrations disappear, and that the stress/strain curve becomes smooth again, if the rate of diffusion becomes too high, or the rate of strain too low. In this connection it would be most interesting to know if the smooth stress/strain curves obtained by Mr. Krupnik and Professor Ford at constant rates of strain persist at higher rates, or whether they break down into the serrated type. Are they smooth because the rate of strain is too small, or is there some other effect present?

Mr. A. J. Field,† M.C., B.Sc., F.I.M. (Member): These informative papers will be of assistance to the light-metal sheet-producing industry in dealing with the nuisance of stretcher-strain markings on certain alloys. They bring to mind similar phenomena encountered some 30 years ago in the production of binary aluminium–2·5% and 3% copper alloy sheets supplied in the annealed condition for such uses as camera cases. In some instances the formation of the parallel bands was then observed in the tensile-testing machine, always at an angle of approximately 60° to the direction of the applied force. These bands started with a clink-like noise and thereafter one edge of a band could be seen to run away from the other, which might have remained stationary. The distance travelled was sometimes quite considerable, sometimes less so, the breadth of the band depending on the distance of propagation of the molecular disturbance. After the first disturbance had ceased on a test-piece and following a further period of apparently elastic extension, another oblique band would originate and broaden by propagation of one edge. Sometimes this ran in an opposite direction, and the bands sloping in opposite directions sometimes ran opposite ways. The rate of propagation of the band boundary could be followed, and appeared to be of the order of 50 ft./min. In the case of these alloys, parallel bands did not always occur, there being no doubt some small differences in annealing conditions; there were no instances of flamboyant markings, which supports the observation of Dr. Phillips that these occur only on the aluminium–magnesium alloys. The adjective can be commended as more picturesquely descriptive than "type *A*", which some authors are beginning to adopt, with type *B* for the oblique parallel bands.

The binary wrought aluminium–magnesium alloys were little used in the early 1920s, although their virtues and possibilities had been clearly shown by Schirmeister's results.‡

It is of interest that the flamboyant markings are reported not to register a diminution of thickness, but only to exhibit a change of angle relative to the rest of the sheet. As extension has taken place and no change of density is reported, it is to be supposed that all extension has taken place at the joints between the flamboyant markings and the undistorted sheet.

Use is made in certain of the papers of the term "strain-ageing". The word "age" involves the factor of time, and information as to the relationship of hardness to time would be of interest. It is true that all events have to happen at intervals of time, and that all phenomena unavoidably cover a lapse of time, but unless there is a fairly definite and particular relation of an effect to lapse of time, as in the precipitation-hardening of an aluminium alloy after quenching, and if strain is the causative factor and increase of hardness the effect, perhaps the factor of time is not specific and a more accurately descriptive term should be adopted.

The method of rectification, sometimes adopted in the case of steel pressings, of filling in such defects as flamboyant markings with lead solder would not be acceptable for light alloys. Methods of prevention or avoidance are indicated in some of the papers. One method is to quench the non-heat-treatable aluminium–magnesium alloys from 500° C., but this process has the disadvantage of a rather high cost. The use of material with a somewhat larger grain-size might be undesirable in some instances. Other suggestions made include the use of roller levelling, which was earlier recommended for restraining the "worming" (i.e. flamboyant marking) of steel sheets. Certainly a simple, cheap, and effective solution to the problem is much to be desired.

Professor H. Ford,§ D.Sc., Ph.D. (Member): A study of the various papers shows that the size and progression of the steps in the yield-stress curve, while following the same general characteristics, appear to depend upon whether the material shows both type-*A* and type-*B* yielding. In certain of the experiments made by Dr. Phillips, Mr. Swain, and Mr. Eborall, the materials exhibit both types of yielding, and it appears clear that the effect of type-*A* yield can return, if time is allowed for it to do so. In these circumstances, the steps do not show a gradually increasing size, as in materials in which only a type-*B* yield is present. It also appears that the type-*A* yielding exhibits all the attributes of a true yield, as in mild steel, and after appropriate ageing this large step returns, yielding at a value slightly above the normal yield-stress curve. This could explain the finding of Phillips, Swain, and Eborall, that the bottom corners of the steps appeared to touch a common curve, whereas in the tests of Krupnik and myself, the upper corner undoubtedly was the envelope of the curves and was also the smooth yield-stress curve, where this was obtained.

Mr. D. Humphreys ‖: Manufacturers of sheet metal must have gained a great deal of practical information from the papers on stretcher-strain marking. As producers of aluminium–magnesium alloy sheet we have found that (i) control of grain-size, (ii) small amounts of cold working followed by a non-recrystallizing anneal, (iii) quenching from 500° C., all afford means of overcoming the type-*A* or flamboyant markings. The last method is attractive in that it gives a fully soft, fine-grained sheet.

However, in many plants in this country the only means of quenching from 500° C. is in quench tanks working in conjunction with sodium nitrate salt baths. References in the literature ¶ stress the possible hazards in treating magnesium alloys in salt baths, and afford evidence ** of a violent reaction occurring at 450° C. in the case of the 7% magnesium alloy. I should be glad to learn of the experience of members in this matter, and furthermore, what is likely to be the effect of this rapid quenching on the corrosion-resistance of the alloys.

Dr. B. B. Hundy,†† B.Sc. (Member): At B.I.S.R.A. we are primarily concerned with stretcher-strains in mild steel, and at present we are working to improve the industrial methods of eliminating these markings. The close similarity of ferrous and certain non-ferrous alloys in respect of the yield-point phenomena and of stretcher-strain markings has been pointed out in a number of these papers, but I think that this similarity should be emphasized. A steel pulled in the

* A. H. Cottrell, Chapter in "The Relation of Properties to Structure" (American Society for Metals 1953 Seminar), in the press.

† Works Manager, The British Aluminium Co., Ltd., Falkirk.

‡ H. Schirmeister, *Stahl u. Eisen*, 1915, **35**, 650, 873, 996.

§ Imperial College of Science and Technology, London.

‖ Northern Aluminium Co., Ltd., Banbury.

¶ —— "The Treatment of Aluminium Alloys", *American Military Specification No.* **MIL/H/6088**, 1950.

** —— "Precautions in the Use of Nitrate Salt Baths", *Factory Department Memo. No.* **848**, 1950.

†† British Iron and Steel Research Association, Sheffield.

"blue brittle" range, behaves in a similar fashion to an aluminium–magnesium alloy tested at room temperature; the initial yield point gives rise to the flamboyant type-*A* markings, and the serrations in the later part of the stress/strain curve can be associated with the appearance of type-*B* markings. Measurements of these markings on photographs reproduced in the literature * show that they usually lie between 55° and 60° to the specimen axis. This agrees quite well with the quoted figure of 58° for the aluminium alloys. The fact that these markings all appear at this particular angle can be explained by consideration of Hill's theory of localized necking in thin sheets.† The theory predicts that localized necks should form at an angle of 55° to the specimen axis and as the type-*B* markings apparently have the characteristics of necks, one would expect them to form at this angle. The variation from this figure, which is observed, can probably be explained on the basis of anisotropy in the specimens.

Another point of similarity in the type-*B* markings in steel and the aluminium alloys is that the markings disappear when certain solute atoms are removed from solid solution in the base metal. The addition of aluminium or vanadium to steel stabilizes the nitrogen and prevents the formation of markings; whilst Mr. Krupnik and Professor Ford have shown here that the stepped stress/strain curve of freshly quenched Duralumin, which is associated with these markings, gradually smooths out as ageing proceeds.

The characteristics of the flamboyant type-*A* markings are also very similar in mild steel and in aluminium–magnesium alloys. Two identical box pressings were made in mild steel and in an aluminium–3% magnesium alloy and the appearance of the markings was remarkably alike in the two cases. Figs. D and E (Plate CIV) show the same part of each pressing for comparison. Talysurf tracings across some of these markings showed that the deformation occurred by kinking both in the aluminium alloy and in the mild-steel pressing. The angle of kinking for the aluminium–magnesium pressing was found to be about 31′, which is in reasonable agreement with the figure quoted by the B.N.F. workers but rather higher than that quoted by Mr. Chadwick and Mr. Hooper. The kinking angle for the mild steel was, as might be expected, considerably higher, and was found to be about 2° 30′. There seems to be little doubt that the flamboyant markings, or true stretcher-strains, occur by a kinking or shearing mechanism, rather than, as was thought at one time, by thinning without kinking. The actual amount of kinking is probably dependent on the metal and on factors such as grain-size. A hypothesis to explain why the deformation takes place by a kinking mechanism has been put forward by Lomer.‡

It seems that mild steel differs from non-ferrous alloys in two respects only. First, the type-*A* markings on the aluminium–magnesium alloys are permanently removed by cold rolling, whereas they return when mild steel is aged after rolling. Secondly, mild steel shows a pronounced rise in strength and fall in ductility on strain-ageing, which is not shown by the non-ferrous alloys. Have any of the authors an explanation for this?

I would now like to make one or two more specific comments on the papers presented here.

Have Mr. Krupnik and Professor Ford, or the B.N.F. workers, applied Professor Cottrell's recent theory of the type-*B* yielding in aluminium alloys § to their own results? His theory seems to explain most of the effects associated with this particular type of stress/strain curve, and I should be interested in any comments on this.

I am rather surprised that Dr. Polakowski attributes the sharp yield point obtained after slow cooling from a high temperature to the formation of a precipitate, and the absence of a yield point on quenching to the precipitate remaining in solution. I think that the dislocation theory of the yield point is now generally accepted, and on this theory we should expect quite the opposite effect; for instance, Cottrell and Leak ‖ have shown that ageing a quenched specimen, so as to precipitate the carbon out of solution, can reduce the rate of subsequent strain-ageing by a factor of 5. It is my opinion that the absence of a yield point after quenching is mainly due to its being masked by intergranular quenching stresses, in a manner similar to that suggested by Dr. Polakowski in another paper.¶ This mechanism might also explain why type-*A* markings can be eliminated in aluminium–magnesium alloys by quenching, though the theory put forward by Dr. Phillips, Mr. Swain, and Mr. Eborall is most attractive. Still referring to Dr. Polakowski's paper, I would suggest that the increase of the Lüders strain after each successive strain-ageing treatment is only a reflection of the shape of the stress/strain curve. If the rise in the yield stress after each ageing treatment is constant, then the Lüders strain will increase as the rate of work-hardening decreases.

Can any of the authors suggest why magnesium is the only element that will give rise to a yield point in aluminium? Is this due to the particular type of lattice distortion caused by a magnesium atom, or is it due to some other reason?

Finally, I would like to point out that stretcher-strains can lead not only to bad appearance, but also to failure during pressing. Fig. F (Plate CV) shows a mild-steel pressing where localized necking and fracture has occurred along the radial stretcher-strains. We believe that this will occur when the pressing speed is high enough to raise the yield point above the ultimate tensile strength. Temper-rolling removed the yield point, and Fig. G (Plate CV) shows that the pressing could then be made without failure occurring.

Dr. C. F. Tipper,** M.A. (Member): Some years ago, I †† devised a means of independently recording load and extension against time, for use on the Quinney machine in the Engineering Department at Cambridge University.

The object was to determine the effect of the rigidity of the machine upon the shape of the load/extension curve, when discontinuous deformation occurred, and to investigate the effects of rate of loading, rate of straining, and ageing. The work was never completed, but the results have some bearing on the present series of papers.

The method of recording had the advantage that the rate of yielding was indicated. Moreover, by suitably marking and measuring the test-piece (in all cases round test-pieces were used) the location of the deformation was determined.

In the yielding of iron and steel a very rapid extension was followed by a gradual spread of the deformation, depending upon the rate of separation of the two heads of the machine. In a jump extension of the aluminium alloys, in which no yields of type *A* were recorded, the drop in load was immediately followed by a gradual rise to a slightly higher load, when another jump occurred. This observation is in accordance with the view that the increase in resistance to deformation is associated with the plastic yielding and that ageing is not necessarily involved, a conclusion supported by the curves in Fig. 19 (p. 613) of the paper by Mr. Krupnik and Professor Ford.

Although there is a general tendency for the size of the steps to increase with the stress, probably owing to the greater available strain energy in the machine, the strains are not by any means uniform in a round bar. In any of the spring- or pendulum-type machines, when a test is being made at a constant rate of extension, the time taken to bring the load

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* M. Kuroda, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1938, **34**, 1528.
E. O. Hall, *J. Iron Steel Inst.*, 1952, **170**, 331.
S. Epstein, H. J. Cutler, and J. W. Frame, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 830.

† R. Hill, *J. Mechanics Physics Solids*, 1952, **1**, 19.

‡ W. M. Lomer, *ibid.*, 1952, **1**, 64.

§ A. H. Cottrell, *Phil. Mag.*, 1953, [vii], **44**, 31.

‖ A. H. Cottrell and G. M. Leak, *J. Iron Steel Inst.*, 1952, **172**, 301.

¶ N. H. Polakowski, *ibid.*, 1952 **172**, 369.

** Engineering Department, Cambridge University.

†† C. F. Elam, *Engineering*, 1940, **149**, 325.

back to the same, or a slightly higher, value increases as the strain associated with each jump increases, and here ageing may become important.

I suggest that the absence of steps in the slow tests carried out in the rigid machine of Krupnik and Ford can be attributed to its rigidity. Plastic deformation will presumably cease as soon as the load falls below a certain value, and in a very rigid machine the extension and drop in load, associated with each jump, would be too small to measure.

There seems no valid reason for attributing all discontinuous yielding to strain-ageing. The Cottrell mechanism can account for the onset of the yield without it. There are other examples, such as twin formation in crystals, which give similar stepped curves, where ageing does not enter into the picture.

Another matter of great interest in these papers is that of the inclination of the striations to the direction of loading. It is difficult to determine the slope in the direction perpendicular to the plane of the strip in such thin material. Dr. Phillips, Mr. Swain, and Mr. Eborall are to be congratulated on their method. The subject is discussed by Nadai,* and it would be interesting to know if the effect of the ratio of width to thickness was investigated in any of the alloys.

Mr. R. Eborall: The observations of Mr. Krupnik and Professor Ford on the effect of the rate of stressing

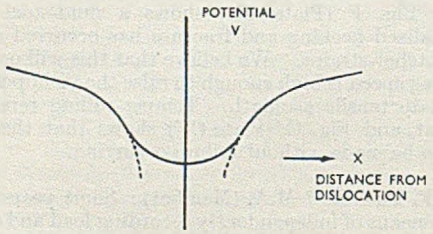

Fig. H.—Potential of a Solute Atom Near a Dislocation.

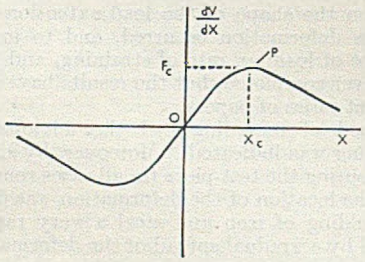

Fig. J.—Restoring Force on a Solute Atom.

might perhaps be explained in the following way. These authors find, in effect, that their stress/strain curves have a common envelope, and that by sufficiently slow, very smooth, stressing they can obtain a smooth curve coinciding with this envelope. Now a solute atom near a dislocation is sited in a sort of potential trough (Fig. H). The restoring force, if it is displaced, is thus given by a curve such as that of Fig. J. Thus, if the dislocation is moved slowly, the solute atom tends to follow, the force dragging it along increasing up to the point P. If the force F_c is sufficient to enable the atom to keep pace with the dislocation there will be no sudden yield, but the dislocation movement is hindered, so that the level of the stress/strain curve is raised.

Putting in some very rough figures, it appears from Mr. Krupnik and Professor Ford's results that at about 1% strain the critical rate of stressing approximates to 0·1 ton/in.^{2}/min. From the stress/strain curve the rate of straining (for smooth straining) is then $\sim 10^{-5}$ strain/sec., and the corresponding dislocation velocity (assuming that there are $\sim 10^{10}$ active dislocations/cm.^{2}) is $\sim 10^{-7}$ cm./sec. To enable the solute atom to keep pace, when acted on by the restoring force available, the diffusion coefficient then has to be of the order of 10^{-15}–10^{-16} cm.^{2}/sec. This is much greater than the value expected by extrapolating the high-temperature values to

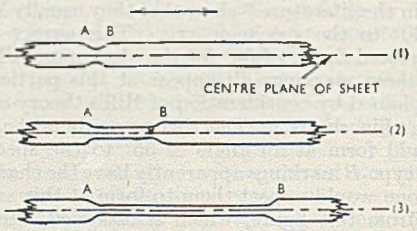

Fig. K.—Stages in the Formation of a Type-B Marking.

room temperature, but the metal is in a worked condition, and Professor Cottrell has already explained how high values of this order may be expected in these circumstances.

An essential feature of this situation is that any shock or disturbance will give rise to a momentarily increased rate of straining and so start off a sudden yield, as Mr. Krupnik and Professor Ford observe.

Replying to Mr. Chadwick and Dr. Baker, what is seen during the formation of type-B markings has been aptly described by Mr. Field. The mode of formation of the markings appears to be as indicated in Fig. K.

At the beginning of a type-B yield, localized yielding occurs as in sketch (1). When the metal within the neck has been stretched sufficiently to carry the applied load, the yielded area starts to spread, one, or sometimes both, of the half-necks A and B moving along the surface as a ripple. A type-B marking is left only if the yielding is halted when either A or B is still within the area under examination. If a strip is stretched in a machine which maintains the load during yielding, in the early stages of deformation the ripples usually travel through a substantial part of the specimen length, or even perhaps the whole of it, before becoming stuck. Later, movements are more restricted. The characteristic rippled appearance of a stretched strip arises when a great many half-necks have accumulated on the surface.

If a strip is stretched in a machine in which the applied load falls off progressively during yielding, the situation is a little different, because when the yielded area has spread a certain distance the load becomes insufficient to produce further yielding and there is a pause during which strain-ageing can take place. The type-B marking has no sharp boundary, so that, in Fig. L, all the material between P and Q

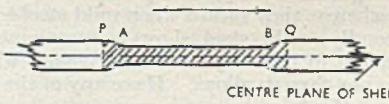

Fig. L.—Limits of Region Hardened by Straining and Ageing After Type-B Yield and Subsequent Pause.

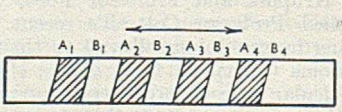

Fig. M.—Plan View of Yielded Regions in Strip Lightly Stretched by Semi-Hard Machine. (Schematic.)

has received some deformation and will consequently strain-age to some extent. When the load is later restored so that yielding again takes place, it would be expected to start outside the hardened region PQ.

As a result, the surface of the strip acquires a whole series

* A. Nadai, "Theory of Flow and Fracture of Solids", Vol. I. 2nd edn. 1950: London and New York (McGraw-Hill).

of separate yielded regions, as in Fig. M. Occasionally, on further increase of the applied load, the next set of yielded regions comes neatly in between the first.

Dr. PHILLIPS (*in reply*): With regard to Dr. Baker's comments, it seems clear that there is a distinct difference in topography between the two kinds of marking which we have called respectively, types *A* and *B*, formed in the annealed aluminium–3½% magnesium alloy of fine grain-size. As illustrated in Fig. 8 (Plate XCII) of our paper, the type-*A* markings form primarily by a shear mechanism, shear occurring parallel to a plane near one of maximum shear stress. Type-*B* markings, the parallel ripple markings formed at higher strains in the same alloy, as shown by Mr. Chadwick and Mr. Hooper, are in the form of incipient necks, and have neither the tilt nor the very sharp boundary associated with the type-*A* or flamboyant markings. This may also be seen in Fig. O (Plate CV), which illustrates rather clearly the relation between the ripple markings and the surface topography. The profile was determined by a microscope-focusing technique, and with oblique illumination it will be seen that the expected sequence of dark and light bands is formed.

With reference to Mr. Chadwick and Mr. Hooper's remarks, I am glad to see that they are now able to confirm that the surface angular change at boundaries between yielded and unyielded material in the case of annealed aluminium–magnesium sheet was in fact similar to our own results. I am also glad to learn that they now agree that thinning occurs within the type-*A* yielded regions, notwithstanding the statements in their papers,*† and in the synopsis ‡ which I also read.

The analogy between the yield-point phenomenon in aluminium–magnesium alloys and in steel is so close that one would expect to find the same two types of marking in steel. Exploratory experiments which we have carried out confirm that this is the case. The steel examined was deep-drawing quality strip, which after cold rolling had been annealed just below the lower critical temperature and had received no subsequent working. By analysis it contained 0·059% carbon, and 0·04% nitrogen.§ This steel had a grain size of 0·023 mm. and a yield-point elongation of 4%. A tensile specimen was stretched part-way through the yield, forming two simple wedge markings (Fig. P, Plate CV). The profile was examined using the microscope-focusing technique and then after being lightly chromium-plated to increase the reflectivity, was examined by multiple-beam interferometry. The profile was that typical of the type-*A* markings formed in aluminium–magnesium alloys. Fig. Q (Plate CV) shows the sharp tilt at a boundary between yielded and unyielded material. The average tilt at a number of such boundaries was 64′ as determined by the microscope-focusing method and 62′ as determined by multiple-beam interferometry.

On stretching to fracture in the annealed condition at room temperature this steel exhibited no ripple markings. A similar specimen tested at 170° ± 5° C. was found to be covered with parallel ripple markings (Fig. R, Plate CV). Examination by the microscopic-focusing technique showed that the visible ripples corresponded to incipient necks in the material, and fracture occurred along one of them. These markings are quite similar to the type-*B* markings formed in aluminium–magnesium alloys at room temperature.

Mr. Hooper and Dr. Holden have observed, at the initial yield in annealed steel, the formation of a channel type of marking, as well as the shear type commonly observed at the initial yield in fine-grained annealed aluminium–magnesium alloys. Although in this channel type of marking (e.g. that denoted *a* in Fig. 4 ‖ of their paper), a depression on one surface of the sheet corresponds to a depression on the opposite surface, it is probable that this marking is of essentially the same form as type *A*, but is caused in this case by two superimposed shears instead of by a single shear (Fig. N). This would account both for the observed contour and for the fact, illustrated in Fig. 9 ‖ of the paper, that the marking *a* consists of plane areas of surface tilted sharply with respect to each other. This would seem to be an essential characteristic of markings formed by the shear process, whereas the type-*B* markings which we have examined are rounded in outline. We have observed a marking which would appear to have been formed by double shear in a lightly stretched strip of aluminium–magnesium alloy.

As shown in our paper, by lowering the temperature so that appreciable ageing does not occur during a test, a basic curve can be determined which passes through the bottom corners of the steps formed at higher testing temperature. Mr. Krupnik and Professor Ford show in their constant-rate-of-loading tests that the top corners of the steps similarly fall on a smooth curve, which will presumably always be the case where the strain rate, total strain, temperature, &c., are such

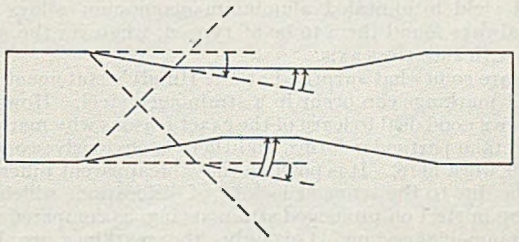

FIG. N.—Schematic Diagram Showing Suggested Double Shear Process for Producing a Type-*A* Channel Marking. Single arrows indicate the first shear and double arrows indicate the second shear.

that substantially complete ageing can occur at each step. Under these conditions the upper and lower envelope curves between them will determine the size of the steps, although inertia effects in the machine may produce overshooting of the basic curve.

Mr. Krupnik and Professor Ford observe that in the as-extruded condition the step size of the stress/strain curves was independent of the amount of alloying element, and they suggest that this contradicts McReynolds' ¶ findings. The apparent contradiction disappears, however, if one takes into account the fact that only that part of the alloying element which is in solution is available for anchoring dislocations. The three copper alloys examined by Krupnik and Ford contained 4·0, 3·8, and 1·4% copper, respectively. The solubility of copper is approx. 1% at 370° C., so that in the extruded air-cooled condition it is unlikely that the amount of copper in solution was very different in the three materials. McReynolds, on the other hand, compared high-purity alloys with 0·025, 0·1, and 0·5% copper, where the whole of the addition would be in solution.

Mr. EBORALL and Dr. PHILLIPS (*in further reply*): We were interested to read Dr. Tipper's contribution, and thank her for her compliment on technique. We believe that, in speaking of strain-ageing, we differ from her only in nomenclature. Some doubts have been raised in the discussion about the occasions on which type-*A* and type-*B* stretcher-strain markings occur. Dr. Polakowski has mentioned in his paper that the kind of marking produced at the initial yield point in an annealed material is influenced by the uniformity or otherwise of the stressing. We would agree with this but

* R. Chadwick and W. H. L. Hooper, *J. Inst. Metals*, 1951–52, **80**, p. 19.

† W. H. L. Hooper and J. Holden, *Bull. Inst. Metals*, 1953, **1**, p. 165; *J. Inst. Metals*, this vol., p. 648.

‡ R. Chadwick and W. H. L. Hooper, *J. Inst. Metals*, 1951–52, **80**, p. 17.

§ An erroneous figure for nitrogen was previously given (*Bull. Inst. Metals*, 1952, **1**, 59).

‖ W. H. L. Hooper and J. Holden, *Bull. Inst. Metals*, 1953, **1**, p. 162 (Fig. 4), p. 164 (Fig. 9).

¶ A. W. McReynolds, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **185**, 32.

consider that the differences produced are in the complexity, not the type, of marking. Similarly, Mr. Chadwick, drawing attention to Fig. 4 of the paper by Mr. Hooper and Dr. Holden,* suggests that type-*A* and type-*B* markings can occur simultaneously at the initial yield point in mild steel and that the diagonal markings (particularly that denoted *a* in the figure) are of type *B*. The authors state, however, and Fig. 9 of their paper shows, that this marking is in the form of a channel, and Dr. Phillips and Dr. Hundy have indicated how such a marking can arise as the result of two superimposed shears; in other words, it is very probably a type-*A* marking. Diagonal markings at the initial yield also often occur in aluminium–magnesium alloy, as Mr. Chadwick and Mr. Hooper point out. Fig. 12 of Hooper and Holden's paper shows a striking example; here the diagonal markings are obviously branches of the main type-*A* marking and are tilted in the same sense. Mr. Chadwick and Mr. Hooper are in fact in error in assuming that markings such as these and the fine ones in our Fig. 3 (*a*) (Plate XC) are of type-*B* because they make angles of 52°–55° with the stress axis. We have examined the profile of many markings formed at the initial yield in annealed aluminium–magnesium alloys and have always found them to be of type *A*, whatever the angle made with the stress axis.

We are somewhat surprised at Dr. Hundy's statement that type-*A* markings can occur in a strain-aged steel. However, we have a good deal to learn of the exact reasons why markings should take particular forms, and there is obviously scope for further work here. It is possible that the apparent difference may be due to the stronger locking of dislocations which can develop in steel on prolonged strain-ageing, as compared with aluminium–magnesium. Certainly, the markings we have seen on a very limited number of lightly strain-aged steel specimens (including those tested at elevated temperatures) are of type *B*. If one considers the propagation of slip from grain to grain in a strain-aged specimen, it is obvious that as the dislocations become more strongly locked the spread of slip depends more and more strongly on the stress concentration near the boundary, and the first dislocations broken free in a newly slipping grain under the influence of the stress concentration then originate from a progressively narrower layer next to the boundary; from the geometrical point of view there is thus a progressive return to the situation in annealed material in which the dislocations, on our hypothesis, originate in the boundary itself.

Dr. Baker has given one good reason for preferring our own explanation of why quenching an aluminium–magnesium alloy from a high temperature removes the initial yield-point effects (viz. through dispersion of the magnesium concentrated in the boundaries) to Mr. Hooper's (viz. through masking by quenching stresses). It might also be mentioned that to produce a quenching stress the temperature gradients must have been severe enough to strain the metal plastically during cooling, whereas the behaviour of our quenched aluminium–magnesium alloy specimens on reheating differed fundamentally from that of the strained material (contrast our Fig. 20 (p. 637) with Fig. 23 (p. 638)). Moreover, from thermal considerations it is rather unlikely that stressed systems of the type considered by Polakowski, in which the skin is in compression with respect to the centre, or vice versa, could be set up in so thin a specimen of an aluminium alloy. Under our conditions, the temperature difference between surface and centre in quenching was probably not more than 5°.

Dr. Hundy asks why only magnesium produces an initial yield in aluminium alloys. There may well be other elements which do so; we have only investigated a few. Copper, in some conditions, can produce a small initial yield. Magnesium, however, is practically unique in that it produces a large lattice strain but is not rapidly removed from solution by an age-hardening or other precipitation process. Considering copper again, a solution-treated and freshly quenched aluminium alloy containing copper would not show an initial yield point, because the copper would be uniformly distributed; on the other hand, when ageing was at all advanced, the effective copper content of the solution would be much reduced through the separation of copper at Guinier–Preston zones or in precipitate. Only at some intermediate stage can the conditions be at all favourable for the formation of an initial yield point, and even then there is competition for the available copper. One would expect zinc to behave similarly to copper. It is perhaps noteworthy that the copper–tin system is similar to the aluminium–magnesium system, in that the tin atom is much larger than the copper atom but considerable quantities of tin can readily be retained in solution.

The effect of rapid straining, at room temperature, on repeated discontinuous yielding is of practical importance because of the high speed of many industrial presses, and Professor Hill has suggested to us that in such presses there might not be time for strain-ageing to occur. This suggestion is in agreement with available data. No visible type-*B* markings were formed (p. 633) on specimens stretched 10% at about 3×10^{-5} strain/sec. at or below — 55°C. From this result and an activation energy for strain-ageing it should be possible to devise a corresponding strain-rate at room temperature, at (or above) which no visible markings should be formed. Sherby, Anderson, and Dorn † found an activation energy initially of 8 kg.cal./g. atom, rising to 15 kg.cal./g. atom as strain-ageing progressed. This variation introduces some uncertainty, but if a value of 11 kg.cal./g. atom is taken as representative, no markings should be visible after straining at about 3×10^{-2} sec.$^{-1}$ at room temperature. The strain rate for a typical crank press would be of the order of 1 sec.$^{-1}$.

To investigate this point experimentally, three small strips of commercial aluminium–3½% magnesium alloy were stretched at approximately 10^{-2}, 10^{-1}, and 10^{2} strain/sec., the first two in a Hounsfield tensometer and the third with an attachment to a standard Izod machine. The surfaces (rather rough, unfortunately) are illustrated in Fig. 8 (Plate CVI), and it can be seen that the markings are much less prominent at 10^{-1} strain/sec. and are absent at 10^{2} strain/sec.

Mr. Chadwick and Mr. Hooper (*in further reply*): In discussion of the effect of quenching on the incidence of type-*A* markings, Dr. Baker, and later Mr. Eborall and Dr. Phillips, have criticized our tentative explanation based on internal stresses and have brought forward further evidence to support their own theory, which supposes that the diffusion of magnesium atoms to and from grain boundaries is involved. Whilst neither theory can be regarded as proven, the further arguments appear to be unsoundly based, and after a critical examination of the evidence, and with additional support from a new and crucial experiment described below, our preference for the quenching-stress theory is maintained.

One of our critics, Dr. Baker, objects to our theory because he assumes that according to it the quenching stresses "in some unspecified way prevent the formation of objectionable markings." We therefore propose to elaborate somewhat on the mechanism, although we had regarded it as elementary, and indeed it has already been explained in some detail by Polakowski.‡ It is first of all necessary to affirm that quenching stresses can be present in thin sheet, a matter which Mr. Eborall and Dr. Phillips have doubted. Quenching of sheet at 500° C. does, in fact, lead to straining, and in industrial practice distortion of large sheets is considerable.

Reference to our original paper § shows that plastic strain before the formation of type-*A* markings, if it exists at all, is

* W. H. L. Hooper and J. Holden, *Bull. Inst. Metals*, 1953, 1, p. 162 (Fig. 4), p. 164 (Figs. 9 and 12).

† O. D. Sherby, R. A. Anderson, and J. E. Dorn, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 643.

‡ N. H. Polakowski, *J. Iron Steel Inst.*, 1952, **172**, 369.

§ R. Chadwick and W. H. L. Hooper, *J. Inst. Metals*, 1951–52, **80**, Figs. 5 and 6 (Plate IV).

extremely small, and up to the point at which yielding first occurs, the straining is purely elastic. Now, any small portion of sheet will consist of a number of elements, some of which are under compressional and others under tensional stresses to varying extents, the sum of such stresses being zero. On the application of an externally applied tension, the elements under the highest internal tensional stress will first reach the elastic limit, and other will follow in succession, so that the condition under which a strain band can spread, i.e. by sudden yielding of a large area, will not be realized. However, after 2–3% extension, the whole of the material will have suffered appreciable plastic strain and the original inequalities will be smoothed out. The absence of any effect on type-*B* markings would therefore be predicted. Heat-treatment at 150° C., which restores the tendency to form type-*A* markings, is known to be effective in relieving internal stresses.

Turning now to the discussion of the atom-migration theory, we note with interest that Professor Cottrell applies it to the serrated or type-*B* yielding only, and quotes figures for atom diffusion rates in strained and unstrained material which indicate that in aluminium–magnesium alloy a plastic extension of at least 0·1% is necessary before this mechanism can operate. Our earlier experiments * showed that before the first large yield point associated with the formation of type-*A* markings, any plastic extension was not more than about 0·02%.

In order to provide fresh evidence on the possible effect of grain-boundary barrier films on the incidence of type-*A* markings, a new experiment has been devised. This was carried out on an aluminium–7% magnesium alloy in which it is readily possible, by thermal treatment, to form a continuous grain-boundary network of magnesium-rich phase, which, unlike that postulated by Eborall and his colleagues, is visible under the microscope. Sheet with such a grain-boundary film was heated in a salt bath at 500° C. for 1 min. and quenched in cold water. This period of heating was sufficient to bring the metal up to the temperature of the salt bath and allow a further time for it to reach a steady temperature condition throughout, but was insufficient to take the whole of the grain-boundary film into solution. Specimens so treated were stretched both in the as-quenched condition and after reheating for a short time at 150° C. The as-quenched specimens were free from random markings, whereas intense markings developed on the reheated specimens. Since, in this experiment, strain markings developed irrespective of the presence of grain-boundary films, it would seem that a barrier of this kind is not in any way a significant factor.

A further point on which discussion has centred is the differentiation between type-*A* and type-*B* markings in mild steel. We have suggested in the discussion that in the samples illustrated by Hooper and Holden,† which are reproduced in Figs. T and U (Plate CVI), both types are present together, as indeed they appear to be in some examples of strained aluminium–magnesium alloys. Dr. Phillips, and later Mr. Eborall and Dr. Phillips, argue that the channel-shaped markings in these figures are, in fact, extensions of type-*A* markings. It should, however, be pointed out that, besides being of the shape typical of type-*B* markings observed in aluminium alloys, i.e. they are necks and not kinks, they also invariably lie at the characteristic angle of type-*B* markings. The contour of the markings illustrated in Fig. 9 ‡ has been cited by Dr. Phillips in this connection, but this has little relevance, since no data are available on the contours of individual type-*B* markings. Our own measurements on specimens of aluminium alloys showing type-*B* markings were invariably carried out on specimens with many partially overlapping markings present. On the other hand, Dr. Phillips' attempt to explain mathematically the mechanism by which the type of deformation found in type-*A* markings can give rise to the characteristic configuration of type-*B* markings, may well contain the germ of an idea which could lead to a rational explanation of the relation between the two types of markings, especially if it could be shown that the two are indeed manifestations of a single deformation mechanism.

Dr. Polakowski (*in reply*): With reference to Dr. Baker's comments, I do not think that it has yet been established beyond doubt whether the two types of yield (*A* and *B*) differ basically or are merely different manifestations of the same phenomenon. Information given in my paper § appears to support the second possibility, although it is agreed that visual observation may not carry sufficient conviction. Dr. Hundy's mention of the occurrence of type-*A* markings on temper-rolled and subsequently aged steel sheet would also indicate that the difference between the two species may not after all prove to be fundamental. I am not convinced on this point, but believe that a definite proof to the contrary is still lacking.

In reply to Dr. Hundy, I agree that the term " precipitate " was not very fortunate. I should have used " segregation " or " grain-boundary segregation " instead.

As far as the reason for the absence of a yield platform in quenched bronze is concerned, I presume that again either of the two alternative explanations may apply. Suitable critical experiments should enable this question, too, to be decided. I should be only too glad if the explanation to which Dr. Hundy referred proved to be universally correct.

I wish to make one point in connection with the remedies for stretcher-straining advocated by Dr. Phillips, Mr. Swain, and Mr. Eborall. These authors recommend, among other treatments, " light rolling (about 5%) followed by a non-recrystallizing anneal ".‖ They thus suggest imparting to the sheet first some 5% cold reduction and then introducing an additional heat-treatment operation in order to eliminate the work-hardening caused by this very temper-pass.

In steel sheet or strip manufacture a 1 or 1·5% skin-pass reduction is sufficient to eliminate some 5% yield elongation. With aluminium alloys the *A*-yield varies between 0·5 and 1·5%, and 1% rolling should be ample for the purpose in view. So small a reduction should render any subsequent thermal softening treatment redundant. It is not clear from the paper whether the authors' reason for recommending the double treatment arose from the difficulties of obtaining and controlling a sufficiently light rolling reduction, or has some more fundamental origin.

Professor Ford (*in reply*): Several views have been expressed about the reason why Mr. Krupnik and I found a stepped yield-stress curve to be absent under steady loading or straining conditions. The views are somewhat contradictory, and it is clear that further experimental work is required before a definite explanation can be put forward. Mr. Chadwick and Mr. Hooper have pointed out that it is difficult to obtain uniform stressing of wide, flat specimens, and it should be remembered that our tests were carried out on round specimens in machines in which, as far as possible, the load was applied axially. Mr. Chadwick and Mr. Hooper comment, however, that we did not make topographical records with our type-*B* yielding or in our steady-strain tests. These authors and other contributors who raised this question may be interested to know that further experimental work is now in hand, using a larger straining apparatus, which will be equally rigid, but in which measurements of the stress/strain characteristics and topographical records can both be taken. It will also be possible to make tests at different strain rates, and these tests should allow the interesting point raised by Professor Cottrell to be decided. It is perhaps significant that the strain rate in our constant-rate-of-strain tests was less than 10^{-6} sec.$^{-1}$.

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* R. Chadwick and W. H. L. Hooper, *loc. cit.*

† W. H. L. Hooper and J. Holden, *Bull. Inst. Metals*, 1953, 1, 162 (Figs. 4 and 5).

‡ W. H. L. Hooper and J. Holden, *loc. cit.*, p. 164.

§ N. H. Polakowski, *J. Inst. Metals*, this vol., p. 623 (footnote).

‖ V. A. Phillips, A. J. Swain, and R. Eborall, *ibid.*, this vol., p. 646.

Dr. Tipper's suggestion that the smooth curve we obtained can be accounted for by reason of the rigidity of the straining gear is unlikely to be correct, because in our apparatus the load was measured on the only non-rigid link in the equipment, i.e. on the small loading bar, which extended about 0·0607 in. at the maximum load. Any sudden yielding of the specimen, therefore, would definitely have been indicated by a fall in the load, or if yielding took place at constant stress, the load would remain constant for a short time, and again this would have been observable. We agree, however, with the rest of her remarks.

Dr. Phillips has pointed out that we used much larger amounts of copper than McReynolds; this was done deliberately, but it clearly explains why McReynolds found that his results depended upon copper content, while ours did not.

Discussion

Properties of Chromium and its Alloys *

Dr. E. Gregory,† M.Sc., F.R.I.C., F.I.M. (Member): In view of the very high melting points of chromium and the chromium-base alloys, one can quite appreciate the difficulties encountered in melting and casting and, in particular, in the selection of the refractory materials having the desired combination of properties to resist chemical attack and contain the molten metal. It should be stressed, too, that the melting problem and that of chemical reaction are both appreciably influenced by the "appetite" chromium has for carbon, oxygen, and nitrogen at the very high temperatures involved. The authors have made a most praiseworthy attempt to overcome these difficulties and to improve on past methods of vacuum melting and casting techniques.

In Part I of the first paper, they lay emphasis on the volatilization of chromium, due to its appreciable vapour pressure near to, and above, its melting point, and state (p. 582) that as much as 25% of the chromium may be lost by this means. This appears to be an extraordinarily high figure, and it would be of interest to have some indication of the vapour pressure of liquid chromium near its melting point. A reason for this request arises from our experiences in connection with the oxygen-lancing of electric-arc-furnace charges consisting of 100% stainless steel scrap, where the molten metal is under both oxidizing and reducing conditions in turn, and where practically 100% of the chromium in the initial charge is recovered, which means, of course, that no chromium is lost by volatilization.

Unfortunately, it is impossible to measure the temperature attained; optical and radiation pyrometers are quite out of the question in view of the amount of fume and flame generated. The temperatures reached are well above the upper limit for the platinum/platinum–rhodium immersion thermocouple, but my estimate is of the order of 2000° C.; even so, we do not lose any chromium by volatilization and, moreover, the chromium recovery is highest when the highest temperatures are used. This may sound paradoxical in view of the remarks regarding our inability to measure the final temperatures, but the answer is really quite simple. From experience it has been determined that a bath temperature of 1600° C., before using the oxygen-lance, gives the best chromium recovery; if the temperature is much below this value before lancing, the chromium recovery is not nearly so good, but even in these circumstances there is no volatilization loss, any chromium not recovered being retained in the slag covering the molten metal.

The method of analysis adopted by the authors for the chemical determination of the oxygen contents of the chromium used in their experiments, although simple, appears to yield reasonably accurate results, but I was glad to note that they took the precaution of making sure by X-ray-diffraction examination that the insoluble residue was indeed Cr_2O_3.

It seems tolerably certain that the reason why the carbon-reduction technique failed to function adequately with alloys containing titanium and zirconium, is connected not only with the high stability of the carbides of these two elements but also with the avidity with which they will search for oxygen and then cling to it in the form of oxides.

In view of the high order of creep-resistance of the binary chromium–iron alloys at temperatures in the region of 900° C. and above, the authors were perhaps justified in hoping that the examination of similar properties of a series of ternary and even more complex alloys having chromium and iron as base might lead to encouraging results.

It must have been with some disappointment, therefore, that their experimental efforts in this direction forced them to the conclusion that material defects, associated with casting difficulties, together with a pronounced sensitivity to shock effects and a relatively low resistance to thermal shock, rendered these alloys unsuitable for use at elevated temperatures even under compressive load conditions.

Observing that the chromium-rich alloys possessed certain undesirable characteristics both at elevated and normal temperatures, features apparently inherent in the chromium itself, the authors naturally desired to find whether these were caused by incidental impurities or were intrinsic in the chromium.

Unfortunately, whilst their investigations have indicated that oxygen (as determined by the simple method used), in amounts greater than 0·002%, has comparatively little influence on the sharp transition from brittle to ductile behaviour of "pure" chromium, the same cannot be claimed for the other incidental elements investigated. Alloying chromium with even small amounts of iron, silicon, aluminium, copper, nickel, cobalt, and tungsten, and varying quantities of manganese, all resulted in a substantial extension of the temperature range within which the alloys are brittle, and the lowest transition temperature for the chromium-rich alloys is still apparently somewhat above normal atmospheric temperatures. It seems most unfortunate that such a valuable technical contribution should have to conclude with the statement (p. 597) that, though a higher degree of purification than that achieved in the present work (if ultimately obtained) may depress the transition temperature below normal atmospheric temperature, it is unlikely that this will result in the production of strong chromium-rich alloys having significant ductility at room temperature.

In only one instance, I think, throughout these papers are the authors guilty of some degree of exaggeration, when they state, on p. 597, that: "the temperature at which it [the transition] occurs is raised by all the elements which could be added to chromium to increase its strength at high temperatures". I cannot find any reference to molybdenum additions, either in Table II (p. 590) or throughout that section of the contribution beginning on p. 573, regarding the properties of the binary chromium-rich alloys. Chromium

* Joint discussion on the papers by A. H. Sully, E. A. Brandes, and A. G. Provan (*J. Inst. Metals*, this vol., p. 569), and by A. H. Sully, E. A. Brandes, and K. W. Mitchell (p. 585).

† Director and Chief Metallurgist, Edgar Allen and Co., Ltd., Sheffield.

and molybdenum form a continuous series of solid solutions, and it would be interesting to have the authors' views regarding the properties of the chromium–molybdenum system.

With reference to the final paragraph on p. 597 regarding the respective parts played by structure and by impurities in inducing brittleness in body-centred cubic metals, I would point out (i) that ductile α-iron at normal temperatures is body-centred cubic, and (ii) that α-iron exhibits maximum ductility only when it is completely deoxidized. I suggest, therefore, that the difficulties experienced in producing ductile chromium at normal temperatures are due to impurity and not to its lattice structure. In an attempt to be constructive, I suggest to the authors a remelting of their chromium, with the addition of about 0·20% manganese, in an argon atmosphere. By this means, it may be possible to produce chromium having an exceedingly low oxygen content.

In neither paper is any reference made to spectrographic analysis, and it would be of interest to learn whether the authors contemplated this method of determining the amounts of other impurities likely to influence the results of their work. It is well known that, in some instances, very small additions of any element may exert a profound influence on the properties of metals, and I need only cite the really enormous effect of as little as 0·002% boron on the hardenability of manganese–molybdenum steels.

It is my earnest hope that the authors will continue their endeavours to produce ductile chromium at room temperatures, even though this may necessitate entirely different techniques. A careful study of Dr. Cook's Autumn Lecture to the Institute of Metals* may perhaps give them some ideas for the furtherance of their own particular investigations.

Mr. A. R. Edwards,† B.Met.E., Dr. H. L. Wain † (Member), and Mr. H. T. Greenaway,† B.Met.E.: Work on chromium has been in progress for several years at the Aeronautical Research Laboratories, Melbourne. The suggestion on p. 574 of the paper on the properties of cast chromium alloys that chromium has a considerable capacity for work-hardening at 900° C., is supported by the results of rolling experiments at that temperature conducted at these Laboratories. Hardness values of chromium strip produced in this way approximated to 200 V.P.N., as compared with 110 V.P.N. after annealing.

Parts II and III of this paper indicate that a remarkably high level of creep-resistance is attainable in chromium alloys. Of particular interest is the general tendency, also found by Parke and Bens, for the alloys to exhibit better creep-resistance in the as-cast condition than after heat-treatment. As noted by the authors, this occurred (with respect to the secondary creep rate) even in the 27·9% cobalt alloy, which is a precipitation-hardening material. A relevant point in this connection is the recent statement by Pfeil ‡ that, in commercially established alloys, optimum creep properties are associated with a fully heat-treated structure. Any comments which the authors may have on this divergence of behaviour would be appreciated.

The thermal-shock test results on the three alloys reported in Part III of the paper (p. 582) are not promising, but it seems possible that the test used was unduly severe. The alloy H.R. Crown Max, cited as a comparison material, is noted for its resistance to thermal shock, and it is felt that a test which causes cracking of this material after only 30 cycles may well be too demanding as an initial test for experimental alloys.

In the paper dealing with the ductility of chromium, it is stated (p. 586) that the use of alumina crucibles for melting chromium resulted in contamination by aluminium to as much as 0·3%. This is not in agreement with our experience that experiments involving contact between molten chromium and alumina ware caused aluminium contamination of less than 0·01% as determined by chemical tests, and a trace by spectrographic methods.

In regard to the iron contamination due to ball milling (p. 587), this troublesome feature can be obviated by the use of chromium-plated steel balls in a chromium-plated mill. This method has proved quite successful at these Laboratories.

Specimens used in the authors' work consisted in the main of sintered compacts in which the final porosity varied from 6 to 15% (p. 587). This porosity may well account for the remarkably low hardness values quoted in several parts of the paper (e.g. 48·5 V.P.N. in Table I, p. 589), and for the low value of 6·76 tons/in.^{2} (15,160 lb./in.^{2}) given for the ultimate tensile strength of chromium at 20° C. (Table V, p. 593). This latter figure may be compared with a yield stress of 51,500 lb./in.^{2} and an ultimate stress of 89,000 lb./in.^{2} obtained at room temperature on rolled chromium strip produced in our Laboratories. Furthermore, it is perhaps not surprising that the authors failed to find any room-temperature ductility in their specimens, as it is well known that porosity has an exceedingly marked effect on the ductility of powder-metallurgy products. For example, work done at the Watertown Arsenal some years ago§ showed that the elongation of sintered iron specimens fell from 34 to 7% and the resistance to impact at room temperature fell from 50 to 7 ft.-lb. as the porosity of the material increased from 5 to 15%. Thus it is entirely possible, in our opinion, for sintered chromium to show significant room-temperature ductility, if the degree of sintering is high enough. Certainly our own experiments || would support this view. We have shown that chromium strip, produced from arc-melted ingots by more or less conventional working methods, exhibits considerable ductility in a bend test and a certain degree of ductility in a tensile test at normal rates of strain and at normal temperatures, provided that absorption of certain impurities is prevented during fabrication. Furthermore, preliminary work has revealed a similar room-temperature ductility in a bend test for a chromium–1% tungsten alloy. In view of these facts we must record our disagreement with the authors' conclusions (p. 597) "that the transition from ductile to brittle fracture occurs (for chromium) at a temperature above room temperature, that it occurs at very slow strain rates, and that the temperature at which it occurs is raised by all the elements which could be added to chromium to increase its strength at high temperatures."

Finally, the authors' contention (p. 597) that "the brittleness and notch sensitivity of creep-resistant chromium-rich alloys is so marked that the alloys have little promise for practical applications" is perhaps an overstatement. Such materials may well be quite ductile at operating temperatures, and the fact that they may undergo a ductile-to-brittle transition between the operating temperature and room temperature would not seem to rule them out as useful high-temperature materials. Although room-temperature ductility is obviously desirable, it has not yet been shown to be mandatory. If a material can be produced in the required form, and if it is strong enough, the extent of room-temperature brittleness may possibly be of relatively minor importance.

Mr. J. H. Rendall,¶ B.Sc., A.R.S.M., A.I.M. (Member): In the second paper, the question is raised as to whether the large effect of temperature on ductility is a property of body-centred cubic metals (p. 597). At the National Physical Laboratory we have carried out bend tests on tantalum at liquid-oxygen temperatures and find the metal to be ductile; in fact, ⅛-in.-dia. rods can be bent to 150° round a ⅛-in. radius. We have also hammered a piece of niobium immediately after removing it from liquid oxygen without any signs of cracking.

Now, if it is assumed that the transition from ductile to brittle behaviour is very approximately a constant fraction of the absolute melting temperature, one would expect the

* M. Cook, *J. Inst. Metals*, 1953–54, **82**, (3), 93.

† Aeronautical Research Laboratories, Department of Supply, Melbourne, Australia.

‡ L. B. Pfeil, *Materials and Methods*, 1953, **37**, (3), 79.

§ A. Squire, *Watertown Arsenal Lab. Rep.*, 1944, (671/16).

|| H. L. Wain and F. Henderson, *Proc. Phys. Soc.*, 1953, [B], **66**, 515.

¶ Metallurgy Division, National Physical Laboratory, Teddington.

transition temperature of tantalum to be higher than that of chromium or molybdenum, whereas it is about 200° C. lower. (The transition temperature of molybdenum is between about 30° and 100° C.)

If it is assumed that this low-temperature brittleness is due to small amounts of an interstitial impurity straining and thus weakening the lattice, an explanation for this difference is available. The tantalum lattice is larger than that of chromium, molybdenum, or iron, i.e. the nearest distance of approach of the atoms is 2·854 Å. between centres for tantalum and 2·493, 2·720, and 2·477 Å. for chromium, molybdenum, and iron, respectively. Thus, there may be larger holes for accommodation of interstitial impurities in the tantalum lattice.

Another point which might be mentioned is the difference between the effect of oxygen on chromium and its effect on iron or molybdenum. In both these latter metals as the oxygen content is increased the fracture changes from transcrystalline to intercrystalline; in molybdenum, for example, this occurs at about 0·0005 wt.-% oxygen (0·003 at.-%). The work of Sully and his colleagues suggests that this is not so for chromium, the fracture with high oxygen contents being always transcrystalline.

Now, if it is assumed, as suggested above, that the brittleness is due to interstitial impurities straining the lattice, one can imagine that, above a certain critical percentage, atoms of the impurity will concentrate strongly at the grain boundary and weaken it. If, on the other hand, the solubility of oxygen in chromium were very much lower than this, the critical percentage might never be reached. We have some slight evidence at the National Physical Laboratory that the solubility of oxygen in chromium is very low. The oxygen content of a piece of hydrogen-reduced chromium was determined by vacuum-fusion analysis and by weighing the chromic oxide residue after solution of the metal in 10% HCl. The results were as follows:

	Oxygen, wt.-%.
Vacuum fusion . . .	0·002
Oxygen in insoluble Cr_2O_3 .	0·001

In other words, if the amount of chromic oxide not in solution in the metal is the same as that insoluble in HCl, the solubility of oxygen in chromium is about 0·001%. The solubility of oxygen in molybdenum is 0·004% * at 1000° C. There appear to be no reliable figures for the solubility of oxygen in α-iron, but there is some evidence for placing it at about 0·004%.† There is a third and last point which might be mentioned. One of my colleagues, Mr. Carrington, hammered a piece of arc-melted chromium and examined the fragments under a microscope. He obtained what we think are Neumann bands,‡ one of which apparently shifted by slip.

The Authors (*in reply*): Dr. Gregory's observations are very interesting. Probably the difference in the amounts of chromium lost by volatilization in our experiments and in the oxygen-lancing of stainless steels can be accounted for by a combination of three factors: (i) the pressure of chromium vapour over stainless steel can be only one-fifth of the vapour pressure of pure chromium, assuming an ideal solution; (ii) whereas our experiments were made in vacuum, Dr. Gregory refers to operations at atmospheric pressure, which would limit the rate of volatilization; and (iii) our melting operation was comparatively lengthy. Our experience in the loss of chromium by vaporization was much the same as that recorded by Parke and Bens.§ The vapour pressure of chromium may be derived from measurements made by Speiser, Johnston, and Blackburn.‖ At 2000° C. it is 22 mm.

We note Dr. Gregory's agreement with our general conclusions and regret that our statement that *all* the elements which might be added to chromium raise the brittle/ductile transition temperature is perhaps unjustifiably general, since we did not include the effect of molybdenum. In work not described in the paper, however, we found that these alloys are also brittle at room temperature.

Trace elements were extensively sought by spectrographic techniques, but none were found whose incidence could be related to the brittleness of the samples examined.

Mr. Edwards, Dr. Wain, and Mr. Greenaway and their colleagues have made a recent and valuable contribution to our knowledge of chromium, in demonstrating that chromium rolled under conditions in which the surface is not contaminated shows ductility at room temperature. We do not, however, agree with some of their comments on the present work. In the first place we cannot accept their suggestion that porosity alone is responsible for the lack of ductility shown by our compacts at room temperature. As explained in the paper, we could find no correlation between porosity and the transition temperature, and the fact that melting of powder compacts in an arc furnace in purified argon raised the transition temperature by about 200° C. (p. 593) does not confirm this hypothesis. The effect can scarcely be explained by the pick-up of impurities during arc melting, since uranium and zirconium could both be melted in this furnace without significant contamination. We are more inclined to the view that the crystalline texture has an effect on the transition temperature, and it appears that the structure resulting from hot working is associated with a lower transition temperature than a sintered or a cast structure of the same purity. What is important is the extent of this depression of the transition temperature and the effect of alloying. We still see no reason to modify our conclusion on p. 597 that although in later work "a higher degree of purification . . . may depress the transition temperature by the further small interval required to take it below normal atmospheric temperature . . . this will not contribute materially to the possibility of the development of strong chromium alloys having any important degree of ductility at room temperature". Before Mr. Edwards, Dr. Wain, and Mr. Greenaway can justifiably disagree with our statement that the transition temperature is raised by strengthening additions, they should first measure the transition temperatures of their alloys, which have not yet been reported. They cannot ignore the possibility that the transition temperature of their alloy with 1% tungsten may be higher than that of pure chromium, although still below room temperature. Certainly much more than 1% tungsten would be required to produce an alloy with good creep properties at high temperatures. It may be noted that Gilbert, Johansen, and Nelson ¶ could not sheath-roll even at 800° C. chromium alloys containing 5–20% of aluminium, iron, molybdenum, or nickel, or 5–10% of copper, manganese, and silicon, and this is in line with our own experience.

We fully agree with the statement that: "Although room-temperature ductility is obviously desirable, it has not yet been shown to be mandatory." There are, of course, degrees of brittleness, and if chromium alloys could be handled as readily as, say, cast iron, they would have potentialities. They are, however, so shock-sensitive and so easily cracked (for example during grinding) that it would, in our opinion, be impossible to use them for a vitally important engineering component such as a turbine blade. The thermal-shock test, which is criticized as being too severe, is in fact intended to simulate conditions to which turbine blading may be subjected on occasions in service, and it is possible to set a minimum standard of performance, not met by the chromium alloys,

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* W. K. Few and G. K. Manning, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 271.

† W. P. Rees and B. E. Hopkins, *J. Iron Steel Inst.*, 1952, **172**, 403.

‡ W. E. Carrington, *J. Inst. Metals*, 1953–54, **82**, (4), 170.

§ R. M. Parke and F. P. Bens, *Symposium on Materials for Gas Turbines* (*Amer. Soc. Test. Mat.*), **1946**, p. 80.

‖ R. Speiser, H. L. Johnston, and P. Blackburn, *J. Amer. Chem. Soc.*, 1950, **72**, 4142.

¶ H. L. Gilbert, H. A. Johansen, and R. G. Nelson, *U.S. Bur. Mines, Rep. Invest.*, No. **4905**, 1952.

which must be attained in such a test before an alloy can be regarded as having any promise for this application.

About the pick-up of aluminium on melting chromium in alumina crucibles we can only agree to differ. The figure of 0·3% aluminium (p. 586) was derived by chemical analysis of an electrolytic chromium sample melted in alumina. Aluminium pick-up by the alloys described in the first paper was much less and of the order described by Edwards, Wain, and Greenaway. This was due to the lower melting point of the alloys. It is worth noting that Parke and Bens used beryllia and zirconia crucibles and that although Adcock used alumina crucibles for melting pure chromium, he lined them with thoria.

We do not hold very definite views on the effect of heat-treatment on the creep properties of the alloys and on the divergence between chromium alloys and commercial creep-resistant alloys in this respect. Possibly the difference is between the behaviour of cast and wrought alloys.

Mr. Rendall makes some very interesting speculations on the role of interstitial impurities in chromium and other body-centred cubic metals. He may well be right. Experimental verification must, however, await the purification of chromium to a higher degree than we could achieve. Mr. Carrington's interesting finding is another example of plasticity induced in chromium by a non-homogeneous stress system, imposed in this case by hammering.

Discussion

Oxidation and Sulphidation of Copper *

Mr. E. C. Williams,† M.Sc., A.Inst.P.: It is clear from the observations of Dr. Tylecote on the oxidation, and of Dr. Hoar and Dr. Tucker on the sulphidation, of copper that there are other important controlling factors besides transport of ions across a growing film of reaction product. The most interesting results of the detailed series of experiments carried out by Dr. Tylecote cannot be explained solely by any theory of ionic transport such as the Wagner theory, and the inadequacy is apparent from Dr. Tylecote's own discussion. I am disappointed, however, in the very last sentence of his paper (p. 700), which suggests that the Wagner mechanism in particular, and the transport of ions in either direction across a film as a rate-determining factor, is still predominant in the author's mind. Something more is required to explain the notable difference reported between the oxidation rates in air and in oxygen, the low rate for electropolished specimens, the low rate for wire as compared with sheet, and the difference again between cold-worked and annealed metal. Too much emphasis has been placed in the past on Wagner's theory, and thought on this subject of oxidation may have been stultified in consequence.

Dr. Hoar and Dr. Tucker have invoked the well-known Hoar–Price electrochemical interpretation of film growth to explain qualitatively the kinetics of sulphidation of copper. While this approach was enlightening fifteen years ago, I feel that to-day there is no fresh understanding of the phenomena of film growth to be gained by unduly pressing the analogy between a galvanic cell and a system metal/oxide (or sulphide)/environment, as the authors have done in deriving the schematic growth curves of Fig. 6 (p. 673) from the hypothetical "polarization" curves of Fig. 5 (p. 672). I suggest in particular that the elaborate analogy of cathodic polarization adds nothing to the authors' principal deductions from the observed rates of growth, i.e. that in the initial stages growth is limited mainly by the rate at which polysulphide ions can reach the film surface through the liquid, and in the later stages by the rate at which copper (and/or sulphide) ions can move through the growing sulphide film. In the present stage of knowledge concerning these complicated phenomena of film growth it is most essential to discover more about the actual physical processes taking place, and in this respect the factual content of the paper by Dr. Hoar and Dr. Tucker is admirable and of great value. Their microscopic studies are particularly impressive.

An aspect of metal-surface reactions which seems to me to have been largely neglected is the effect of heterogeneity of solid surfaces. In wet corrosion heterogeneity is taken for granted, perhaps too much so. In the thinking of physical chemists, particularly with regard to catalytic reactions, it is very much to the fore. The microscopic observations of Dr. Hoar and Dr. Tucker confirm my belief that this factor is important. The polarizing microscope indicates, for example, that in an aqueous attacking medium copper sulphide starts to form at preferred localities, and it seems likely that a film becomes continuous by lateral growth from nuclei. Dr. Tylecote, on p. 683, states that the first stage in the oxidation of copper is the formation of a solid solution with oxygen in the surface layers, followed by the appearance of nuclei of oxide which grow laterally to form a continuous film. In only five lines a world of potentially important effects is suggested, and I would have liked to have read much more in this tenor. The sigmoidal curve of weight-gain against time which Dr. Tylecote has produced for the initial stage of oxidation at high temperatures (Fig. 2, p. 684) may be explained by a process of nucleation and growth. The form of the equation is available from theoretical considerations on recrystallization ‡ and for two-dimensional growth we may write:

$$w = d\rho(1 - e^{-kt^2})$$

where w is the weight increase per unit area, d is the thickness, assumed constant, of the spreading oxide layer of density ρ, and k is a factor involving the rates of nucleation and growth. The fact that the sigmoidal curve has only been observed once or twice does not necessarily mean that nucleation and growth is not a general phenomenon in film formation. The shape of the curve is determined by the factor k, which may well be such that the variation approximates to simple relationships—linear, parabolic, &c. It is also possible that further thickening after an initial layer has completely, or even partly, covered the metal occurs by nucleation and lateral growth of a second layer. One cannot imagine the surface of an oxide film as being any more homogeneous than the solid surface on which it is formed.

In conclusion, I suggest that the driving force in surface reactions should now be more intimately considered in relation to surface free energy, or to the chemical potential of metallic atoms at a free metallic surface and at interfaces with another phase. This quantity will vary from point to point, and will be greatest at local patches of high structural disorder, where nucleation will probably occur. Once a nucleus is formed it may be expected to spread laterally rather than grow

* Joint discussion on the papers by R. F. Tylecote (*J. Inst. Metals*, this vol., p. 681) and by T. P. Hoar and A. J. P. Tucker (this vol., p. 665).

† Technical Officer, Imperial Chemical Industries, Ltd., Metals Division, Birmingham.

‡ J. E. Burke and D. Turnbull, "Progress in Metal Physics", Vol. 3, p. 220. 1952: London (Pergamon Press).

vertically, because the free energy of the metal at the edge of the nucleus may be increased by strain arising from cohesive interaction between the layer of reaction product and its substrate.

Dr. Hoar (*in reply*): Mr. Williams believes that the film-cell concept is past its usefulness and in particular that the "analogy" of cathodic polarization used in the paper by Dr. Tucker and myself adds nothing to our understanding of the phenomena. Now, the process by which polysulphide ions in solution produce sulphide ions in the cuprous sulphide film must be one in which they pick up electrons, and it is highly likely that it takes place on the surface of the growing film. That surface is thus an actual cathode, and the rate of the process may depend on the supply of reactant, on the removal of product, and on an energy-hump related to the electrical potential difference across the surface, i.e. the p.d. between the adsorbed layer of polysulphide reactant and the sulphide film just below its surface. Thus the change of this p.d. with process rate (i.e. current) is not "analogous" to cathodic polarization: it *is* cathodic polarization. Certainly we wish to discover more detail about the actual physical processes occurring during film formation; but I think we shall not do so by forgetting that a reaction between ions and electrons taking place at a conducting interphase is an electrode reaction, that the movement of ions and electrons under a potential gradient are respectively electrolytic and electronic conduction, and that these processes can be treated by simple electrochemical methods whether they take place in conventional "liquid" cells or in cells with solid electrolytes that are at the same time electronic conductors.

The simple film-growth theory given originally by Wagner and subsequently in electrochemical form by Jost and by Price and myself is, of course, an approximation and was explicitly so described by its originators. The usefulness of the "cell" model can, however, be much extended by including in it several refinements. In the simplest and most approximate model, the film cell is assumed to operate at constant e.m.f., with the film specific resistance constant in time and space, and with the field strength in the film small enough for Ohm's law to be valid. None of these assumptions is ever strictly true, and one or more of them may be very far from true in particular cases. The influence of polarization in giving rise to a variable e.m.f. is discussed qualitatively in my present paper with Tucker; Wagner, and Price and I, provided early discussions of the influence of variable specific conductivity. Many more recent papers, notably by Wagner, Mott, Hauffe, and their schools,* have extended the theory by adopting more complex models; the "physical" school have preferred to reason *ab initio* by the methods of electrostatics, while the "chemical" workers have sometimes preferred to begin with the inexact "cell" model and to apply refinements such as may be visualized in terms of real current-producing cells and non-ohmic electrical networks. Either approach can lead to the same result if equivalent assumptions are made, and although the physical method is the more elegant, it is perhaps the less easily appreciated by chemists and metallurgists. Consequently, I do not agree with Mr. Williams that the original Wagner theory and the "cell" model are past their usefulness; *all* models, however abstract, are only "ideas" of truth, and there is often something to be said for the cruder "engineering" kind of model as a better aid to elementary understanding than are the more refined models springing from current fundamental physics.

In the case of Dr. Tylecote's results, it seems to me that one way to interpret the growth curves would be to consider them as deviations from the parabolic curves that can be derived from the ideal model. As well as the refinements for growth by lattice transport referred to above, mechanical factors such as cracking, shearing, and splitting of the film would, of course, have to be taken into account. The well-proved general method of investigating real results as deviations from those to be expected from a simple ideal model, which has been so fruitful in the thermodynamic field, seems to me to be more promising than the fitting of certain of the results by more complex models, such as that leading (in my view, by somewhat dubious reasoning) to a "cubic" growth law. The present results that are approximately fitted by the cubic law do not seem sufficiently clear-cut to lend experimental support to its theory, and appear to be capable of better explanation in terms of deviations from the "ideal" parabolic law.

Dr. Tylecote (*in reply*): I still believe that the Wagner mechanism is the driving force in high- and intermediate-temperature oxidation processes. I regard the mechanical processes that occur owing to internal stresses as complicating factors superimposed on the general Wagner mechanism, and not as a mechanism replacing it. That is the reason for the last sentence of my paper. I feel that such mechanical processes are sufficient to explain the departures from the parabolic law in the higher range of temperatures. I shall be surprised if the application of free-energy considerations gives a better working hypothesis than the Wagner mechanism.

In reply to Dr. Hoar, it appears to me that the deviation from the "ideal" parabolic law is sufficiently large to justify another explanation, such as that given by Mott† and by Cabrera,‡ resulting in the cubic growth law.

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* A good summary and bibliography covering most of the field is provided by O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys". 1953: London (Butterworths Scientific Publications).

† N. F. Mott, *Trans. Faraday Soc.*, 1940, **36**, 472.

‡ N. Cabrera, *Phil. Mag.*, 1949, [vii], **40**, 175.

Discussion

Structure of Nickel Alloys *

Dr. G. Bullock,† M.Sc., A.M.C.T. (Junior Member): Dr. Taylor and Mr. Hinton are to be congratulated on having proved the occurrence of an order–disorder change in the nickel-base 25 at.-% chromium alloy, in spite of the difficulties encountered in X-ray analysis owing to the closeness of the atomic scattering factors for nickel and chromium and the rather unexpected resistivity/temperature relationship. They seem to have explained quite fully certain property changes which accompany this transformation. I would suggest, however, that it would have been worthwhile considering the very real advantages to be obtained by the use of quantitative thermal curves ‡ in place of the Sykes method. An advantage of thermal-curve values is that they may be compared directly with the heating and cooling resistivity values.

The authors' views would be appreciated with regard to the possible effect on the scatter of the experimental points and the shape of the curves shown in Fig. 3 (p. 173), of comparing the temperatures of the specimen and the enclosure at one point only in each.

In Fig. 4 (p. 177) it is possible to draw a curve through the points obtained when plotting resistivity ρ against degree of order S. Inspection shows that this curve obeys neither a linear nor a square-law relationship. It does, however, yield a resistivity value, at $S = 0$, of approximately 101 microhm-cm., which is in the region of that obtained using the relationship $\rho = f(S^2)$. This seems to account for the fairly close agreement at high temperatures between the equilibrium curve and the curve for complete disorder, where $\rho = f(S^2)$, as shown in Fig. 5 (p. 177). At values of S other than 0 or 1, Fig. 4 shows that the relationship $\rho = f(S^2)$ appears to be only a slightly better approximation than $\rho = f(S)$, and this understandably limits the general applicability of equation (9) (p. 178).

Dr. B. R. Coles,§ B.Sc. (Junior Member): The papers under discussion and others by Dr. Taylor and Mr. Floyd have added greatly to the information we possess on the phase equilibria of nickel alloys. With the aid of such work we should shortly be able to understand more clearly the alloying behaviour of nickel, much as the assembly of data on copper alloys made possible the theoretical advances that followed it. In particular, I should like to see more work being done on alloys of nickel with the B sub-Group elements and a comparison of the results with those on corresponding palladium alloys.

The results of Dr. Taylor and Mr. Hinton on the nickel–chromium system are of especial interest, since this system has always seemed peculiarly simple. The complete absence of intermediate phases contrasts strangely with the nickel–titanium, nickel–vanadium, and nickel–manganese systems. In all these systems, however, and in the simple solid-solution systems nickel–iron and nickel–cobalt, ordered structures are found at the composition Ni_3X. Ni_3Ti and Ni_3V are discrete phases, but it seems highly probable that in the other systems effects other than size-factor ones (which are small) lead to the formation of superlattices, and the profound changes in physical properties in the Ni_3Mn and Ni_3Cr structures support this suggestion. In neither of these structures does a fall in electrical resistance take place on ordering, but there is the usual ferromagnetic decrease in resistance in ordered Ni_3Mn some 80° C. below the critical temperature.

The specific-heat curves for the two alloys correspond closely, and the large high-temperature excess specific heat suggests strongly that not all the nickel 3*d*-band holes have been filled in Ni_3Cr.

The results of the electrical-resistance investigations of this alloy are extremely interesting. I agree that the increase in resistivity observed is associated with an ordering process, but I find it difficult to believe that a simple Brillouin-zone restriction of the freedom of the *s*-band electrons is responsible. The change in the effective number of free electrons would have to be enormous to counteract the large decrease in the perturbation of the lattice by random solid solution. The strongest evidence we yet have for superlattice Brillouin zones is the work of Komar ‖ on the magnetoresistance and Hall effect in Cu_3Au. The Hall coefficient even changes sign on ordering, but the resistance decreases in the usual way. I am inclined to attribute the increase to some change in the electronic configuration of the *d*-electrons in the alloy, with a consequent change in the transition probability for scattering, and I suspect that the possibility of such change in electronic structure may be partially responsible for the occurrence of order with such low size-factors. This still leaves unexplained, however, the large value of the residual resistance. There is no theoretical justification for the insertion, into a formal treatment, of ρ_ω " the residual resistance at absolute zero of a completely ordered alloy ". No matter how large the transition probability, when the perturbation of the lattice tends to zero the resistance must also tend to zero. It would be very interesting to examine the Hall coefficient and magnetoresistance of this alloy, and I should also expect the magnetic susceptibility to exhibit strange effects.

Dr. A. Taylor (*in reply*): Regarding Mr. Bullock's suggestion, the method of Sykes for determining the specific heat was chosen in preference to others, since the technique is an absolute one and yields the specific heat directly. Its main disadvantages are that it cannot be used with *falling* temperature and that the accuracy decreases rapidly at temperatures above 1000° C. owing to electrical leakages. This latter difficulty could presumably be overcome with improved types of refractory materials. The thermal-curve method is not so direct as that of Sykes, and, according to Handford ¶ its accuracy is somewhat lower.

Many tests were carried out on the temperature variation from point to point on the specimen. On the whole this was less than 1° C., and since the specimen is enclosed in what is virtually a uniform-temperature enclosure at the same temperature, the errors due to the use of a single reference point on the specimen are negligible compared with those from other sources.

The resistivity is probably more accurately a function of S^2 than of S. Bragg and Williams' ** choice of the latter function was purely arbitrary. However, the S^2 function may be obtained by the application of a rigorous quantum-mechanical argument as shown by Dienes,†† and it is gratifying that the very simple reasoning employed in our paper leads to precisely the same result.

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* Joint discussion on the papers by A. Taylor and R. W. Floyd (*J. Inst. Metals*, this vol., pp. 25 and 451) and by A. Taylor and K. G. Hinton (p. 169).

† Lecturer, Applied Chemistry Department, Manchester University.

‡ C. Handford, *Nature*, 1938, **141**, 368.
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§ Lecturer in Metal Physics, Imperial College of Science and Technology, London.

‖ A. Komar, *J. Physics* (*U.S.S.R.*), 1941, **4**, 547.
A. Komar and S. Sidorov, *ibid.*, 552.

¶ *Loc. cit.*

** W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.*, 1934, [A], **145**, 699.

†† G. J. Dienes, *J. Appl. Physics*, 1951, **22**, 1020.

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PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

THE BULLETIN OF
THE INSTITUTE OF METALS

THE BULLETIN OF THE INSTITUTE OF METALS

VOLUME 1
1951–53

EDITOR

N. B. VAUGHAN, M.Sc.

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LONDON
PUBLISHED BY THE INSTITUTE OF METALS
4 GROSVENOR GARDENS, S.W.1
1953

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CORRIGENDA

Page 13, col. 1, line 19. *For* Hazel, William P., *read* Hazel, William Carl.

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Printed in Great Britain by
Richard Clay and Company, Ltd.,
Bungay, Suffolk.

METALLURGICAL ABSTRACTS

GENERAL AND NON-FERROUS

Volume 20, 1952-53

(New Series)

EDITOR

N. B. VAUGHAN, M.Sc.

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LONDON
PUBLISHED BY THE INSTITUTE OF METALS
4 GROSVENOR GARDENS, S.W.1
1953

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SYMBOLS AND ABBREVIATIONS FOR USE IN "METALLURGICAL ABSTRACTS"

Å.	Ångström units = 1×10^{-8} cm.
abs.	absolute
A.C.	alternating current
addn.	addition(s)
amp.	ampere(s)
amp.hr.	ampere-hour(s)
appn.	application(s)
approx.	approximate(ly)
aq.	aqueous
at.-%	atomic per cent.
at. wt.	atomic weight(s)
atm.	atmosphere(s) [pressure]
A.W.G.	American wire-gauge
B. & S.	Brown & Sharpe (gauge)
b.c.c.	body-centred cubic
°Bé.	degree Baumé [scale]
B.H.N.	Brinell hardness number(s)
b.h.p.	brake horse-power
b.p.	boiling point(s)
B.Th.U.	British thermal unit(s)
B.W.G.	Birmingham wire-gauge
°C.	degree Celsius (formerly centigrade) [scale]
C	coulomb(s)
cal.	calorie(s)
c.c.	cubic centimetre (s)
c.d.	current density(ies)
C.G.S.	centimetre-gramme-second (units)
chem.	chemical
cm.	centimetre(s)
coeff.	coefficient(s)
compn.	composition(s)
conc.	concentrated (adj.)
const.	constant (adj. or noun)
contg.	containing
cryst.	crystalline
crystn.	crystallization
c./s.	cycles per second
cwt.	hundredweight(s)
D.C.	direct current
d	density(ies)
detn.	determination(s)
dia.	diameter(s)
dil.	dilute (adj.)
dm.	decimetre(s)
D.P.N.	diamond pyramid (hardness) number(s)
elect.	electric, electrical(ly)
electrochem.	electrochemical(ly)
e.m.f.	electromotive force(s)
estn.	estimation(s)
eV.	electron volt(s)
°F.	degree Fahrenheit [scale]
F	Faraday's constant
f.c.c.	face-centred cubic
f.p.	freezing point(s)
ft.	foot; feet
ft.-lb.	foot-pound(s)
g.	gramme(s)
g.-atom	gramme-atom(s)
g.-mol.	gramme-molecule(s)
gal.	gallon(s)
grav.	gravimetric(ally)
H.F.	high-frequency
h.c.p.	hexagonal close-packed
H-ion	hydrogen-ion
h.p.	horse-power
h.p.-hr.	horse-power-hour(s)
hr.	hour(s)
in.	inch(es)
in.-lb.	inch-pound(s)
indust.	industrial
°K.	degree Kelvin absolute [temperature scale]
kc.	kilocycle(s)
kc./s.	kilocycle(s) per second
kg.	kilogramme(s)
kg.cal.	kilogramme-calorie(s)
kg.m.	kilogramme-metre(s)
km.	kilometre(s)
kV.	kilovolt(s)
kVA.	kilovolt-ampere(s)
kW.	kilowatt(s)
kWh.	kilowatt-hour(s)
kX	Crystal Ångström(s) = 1000 Siegbahn X-units
l.	litre(s)
lb.	pound(s)
L.F.	low-frequency
liq.	liquid (adj.)
M	molar [solution]
m.	metre(s)
m.amp.	milliampere(s)
math.	mathematical(ly)
max.	maximum (adj. or noun)
Mc.	megacycle(s)
Mc./s.	megacycle(s) per second
mech.	mechanical
met.	metallurgical(ly)
mg.	milligramme(s)
ml.	millilitre(s)
min.	minute(s); minimum (adj. or noun).
mm.	millimetre(s)
m.m.f.	magnetomotive force(s)
mol.	molecule(s)
m.p.	melting point(s)
$m\mu$	millimicron(s) = 1×10^{-7} cm. = 10 Å.
mV.	millivolt(s)
N	normal [solution]
N.P.L.	National Physical Laboratory (Teddington, Middlesex)
No.	number(s)
N.T.P.	normal temperature and pressure
Oe.	oersted(s)
opt.	optical(ly)
oz.	ounce(s)
P.C.E.	pyrometric cone equivalent
p.d.	potential difference [electric]
*p*H	hydrogen-ion concentration
phys.	physical(ly)
p.p.m.	part(s) per million
prepn.	preparation
prodn.	production
pptn.	precipitation
P.S.	proof stress
qual.	qualitative(ly)
quant	quantitative(ly)
°R	degree Réaumur [scale]
recrystn.	recrystallization
ref.	reference(s)
resp.	respective(ly)
r.p.m.	revolution(s) per minute
sci.	scientific
sec.	second(s)
sepn.	separation(s)
soln.	solution(s)
sp.	specific
sp. gr.	specific gravity(ies)
spectrochem.	spectrochemical(ly)
sq.	square
S.W.G.	standard wire-gauge (Imperial)
tech.	technical(ly)
temp.	temperature(s)
t.p.i.	threads per inch
U.T.S.	ultimate tensile stress(es)
V.	volt(s)
VA.	volt-ampere(s)
vol.	volume(s)
W.	watt(s)
Wh.	watt hour(s)
wt.-%	weight per cent.
yd.	yard(s)
Y.P.	yield point(s)
%	per cent.
γ	microgramme = 1×10^{-6} g.
λ	wave-length
μ	micron(s) = 1×10^{-4} cm.
$\mu\mu$	1 millionth micron = 1×10^{-10} cm. = 0·01 Å.
Ω	ohm(s)
°	degree(s) arc
′	minute of the arc
″	second of the arc
/	per
$<$	less than
$>$	greater than
$\not<$	not less than
$\not>$	not greater than
$\leqslant$	equal to or less than
$\geqslant$	equal to or greater than
$\neq$	not equal to
$\equiv$	identically equal to
$\cong$	approximately (or essentially) equal to
$\sim$	about
$\propto$	varies as
$\parallel$	parallel
$\perp$	perpendicular

METALLURGICAL ABSTRACTS

GENERAL AND NON-FERROUS

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1 — PROPERTIES OF METALS

***Impact Tensile Test of Single Crystals of Metal [Aluminium]. I.—Preliminary Experiments.** S. Sakui, Y. Sato, C. Okawa, and K. Sato (*Rep. Sci. Research Inst., Japan*, 1951, **27**, (4), 309–315; *Appl. Mechanics Rev.*, 1953, **6**, 77).—[In Japanese]. The tests were conducted principally on single Al crystals to study the mechanism of deformation, since it was believed that polycryst. specimens would exhibit less noticeable changes. The fractured specimens were examined for grain orientation, number of recrystallized grains, deformation angles, slip lines, asterism in Laue patterns, and time/load relationship, as well as relationships between the ultimate static and dynamic stresses and strains at failure. The latter relationships were determined also for polycryst. specimens.

[Discussion on a Paper by M. E. Fine, E. S. Greiner, and W. C. Ellis:] Transitions in Chromium. —— (*J. Metals*, 1951, **3**, (11), 1066–1067).—See *M.A.*, **19**, 2.

Susceptibility of Non-Deoxidized Copper to the Action of Reducing Atmospheres. J. M. Pouvreau (*Cuivre, Laitons, Alliages*, 1951, (4), 65–67).—Refined Cu contg. 0·02-0·07% O is susceptible to the attack of free H in combustion gases at temp. as low as 500° C. or less. The H penetrates the metal and combines with the Cu_2O to form Cu and H_2O, the latter escaping and leaving voids, which cause loss of strength and extreme brittleness. Care must be taken when using this grade of Cu to ensure that oxidizing conditions are maintained in the flame in contact with the Cu, particularly in flame welding.—W. F. H.

***Effect of Speed of Testing on the Tensile Properties of Copper and Copper-Base Alloys.** N. H. Murdza (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 178–193).—See *M.A.*, **20**, 819.

***Creep-Tension Relations at Low Temperatures of Metals [Copper and 61S-T Aluminium Alloy].** J. D. Lubahn (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 905–932; discussion, 933).—See *M.A.*, **20**, 819.

***The Influence of Lead on the Modulus of Elasticity and the Damping of Copper, Silver, Brass, and Red Brass.** (Köster and Bangert). See col. 994.

***Measurement of the Vapour Pressure and Condensation Coefficient of Iron, Cadmium, and Silver.** Günther Wessel (*Z. Physik*, 1951, **130**, (4), 539–548).—The vapour pressure of Fe was measured in the temp. region 1500°–1800° K., by a method due to Heller, Neumann, and Volmer. The metal is contained in a small vessel suspended in a furnace on a thin Mo wire. The vapour escapes into a high vacuum from two small holes so arranged that the back pressure rotates the vessel through a small angle. The results of the measurements were in good agreement with those obtained by Marshall, Dornte, and Norton (*J. Amer. Chem. Soc.*, 1937, **59**, 1161; *M.A.*, **4**, 482) using the Langmuir method, from which it is concluded that the condensation coeff., α, = 1 for Fe. A modification of the method enables α to be determined directly. Measurements on Cd and Ag show that for both of these metals α is very close to 1. 20 ref.—J. W. C.

[Discussion on a Paper by L. H. Van Vlack:] Intergranular Energy of Iron and Some Iron Alloys. —— (*J. Metals*, 1951, **3**, (11), 1067).—See *M.A.*, **19**, 100.

***The Hall Effect in Iron and Nickel at Low Temperatures.** J. P. Jan and H. M. Gijsman (*Helv. Phys. Acta*, 1951, **24**, (6), 636–637).—[In French]. Cf. *ibid.*, 1949, **22**, 581; *M.A.*, **18**, 84. Detn. have been made of the Hall effect and the resistivity (ρ) of electrolytic Fe and commercial Ni, at 14°, 20°, 64°, and 83° K., and at room temp. The results can be expressed by the equation: $\rho_H = R_0\mu_0 H + R_1 J = R_0(\mu_0 H + \alpha J)$, where ρ_H = the Hall elect. field at unit c.d., R_0 and R_1 = the "ordinary" and the "extraordinary" Hall const., resp. (cf. Pugh, Rostoker, and Schindler, *Phys. Rev.*, 1950, [ii], **80**, 688; *M.A.*, **18**, 692), $\alpha = R_1/R_0$, the field parameter, and is always >1, H = the magnetic field inside the specimen, and J = the observed magnetization. R_0 and α could not be measured for Fe, but for Ni R_0 increases slowly with increase in temp., and α is ~2 at low temp. and 13 at room temp. The magnetogalvanic conductivity transverse to const. intensity of magnetism, $\gamma_H = \rho_H/\rho^2$, has been calculated, and found to increase steadily with decrease in temp. The results confirm and extend the previous detn. 4 ref.—E. N.

***Atomic Magnetic Moments of Iron, Cobalt, and Nickel.** N. S. Akulov and T. I. Kakushadze (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (4), 593–596).—[In Russian]. With the aim of explaining the change in atomic magnetic moment with temp., A. and K. considered the possibility of mutual exchange of electrons in two overlapping bands. Neglecting spontaneous exchanges, the number of migrations from the ith band to the jth band/sec. (W_{ij}) will be given by $W_{ij} = \alpha_{ij} n_i (n_{0j} - n_j)$, where n_i is the number of electrons in the ith band, n_{0j} the max. number of electrons in the jth band, and α_{ij} the mean probability of migration from the ith to the jth band. At sufficiently high temp., $\alpha_{ij} = \alpha_{ji}$, and in the case of thermodynamic equilibrium $W_{12} = W_{21}$; hence $n_1(n_{02} - n_1) = n_2(n_{01} - n_1)$. For the case of only two overlapping bands there is also the condition that the number of electrons is const., i.e., $n_1 + n_2 = n$. From these two equations, $n_1 = \frac{n_{01}}{n_{01} + n_{02}} n$ and $n_2 = \frac{n_{02}}{n_{01} + n_{02}} n$. For the s and d bands, $n_{01} = 2$, and $n_{02} = 10$. Hence for Fe, which has 8 electrons in the $3d$ and $4s$ bands, we have $n_s = 1{\cdot}33$ and $n_d = 6{\cdot}67$. Also for Co ($n = 9$), $n_s = 1{\cdot}5$ and $n_d = 7{\cdot}5$; and for Ni ($n = 10$), $n_s = 1{\cdot}67$ and $n_d = 8{\cdot}33$. Hence the number of unpaired $3d$ electrons ($10 - n_d$) for Fe, Co, and Ni will be 3·33, 2·5, and 1·67, resp.; values determined experimentally, from the magnetic saturation at abs. zero, are 2·23, 1·7, 0·6, resp.; values determined experimentally at a sufficiently high temp. (above the Curie point; 1450° K.; and 1173° K., resp.) are 3·31, 2·36, and 1·16, resp. (Cf. Vonsovsky and Shur, "Ferromagnetism", 1948, p. 138).—G. V. E. T.

Extraction, Alloying, and Fabrication of Magnesium. C. J. P. Ball (*Magnesium Rev. and Abs.*, 1949, **8**, (2), 120–142).—

* Denotes a paper describing the results of original research. † Denotes a first-class critical review.

Reprinted from *Proc. Fourth Empire Min. Met. Congr.*, 1950, (II), 1004; see *M.A.*, 17, 242.—N. B. V.

[Discussion on a Paper by W. M. Fassell, Jr., L. B. Gulbransen, J. R. Lewis, and J. H. Hamilton:] Ignition Temperatures of Magnesium and Magnesium Alloys. —— (*J. Metals*, 1951, 3, (11), 1075–1076).—See *M.A.*, 19, 165.

***Magnetic Properties of Mercury at Low Temperatures.** B. I. Verkin, B. G. Lazarev, and N. S. Rudenko (*Doklady Akad. Nauk S.S.S.R.*, 1951, 80, (1), 45–46).—[In Russian]. The periodic field dependence of susceptibility first found by de Haas and van Alphen in Bi (*Proc. K. Akad. Wet. Amsterdam* 1930, 33, 680, 1106; *Met. Abs.* (*J. Inst. Metals*), 1931, 47, 72, 264) also occurs in Hg. Measurement of the couple acting on a single crystal of Hg suspended in a uniform magnetic field showed that the effect could be observed in fields stronger than ~14,000 Oe., at 1·465° and 1·840° K., but not at 4·2° K. Even at 1·840° K., the amplitude of the oscillation is very small. The inability of earlier workers to observe the effect in Hg is attributed to their using fields <12,000 Oe.

—G. V. E. T.

[Discussion on a Paper by T. H. Hazlett and E. R. Parker:] Nature of the Creep Curve [Especially for High-Purity Nickel]. —— (*J. Metals*, 1953, 5, (11), 1577–1579).—See *M.A.*, 20, 740.

[Physical] Properties of Electrodeposited Nickel. William A. Blum (*Materials and Methods*, 1953, 37, (4), 101–105).—Based on a paper by A. Brenner, V. Zentner, and C. W. Jennings, *Plating*, 1952, 39, 865; *M.A.*, 20, 324.

—R. P. H. F.

***Gases in Electrolytic Nickel.** E. Sh. Ioffe and A. L. Rotinyan (*Doklady Akad. Nauk S.S.S.R.*, 1951, 77, (1), 91–92).—[In Russian]. Discrepancies in the published data on gases in electrolytic Ni can be explained if it be supposed that the so-called gases are really present as organic compounds adsorbed from the bath during deposition. On heating or melting, H, CO, CO_2, and possibly hydrocarbons will be liberated, but the relative amounts produced will depend on the conditions. This hypothesis was verified by analysing Ni deposits with various C contents for H (by vacuum fusion) and O (by H reduction). On plotting the O or H contents (in vol. of gas at 20° C./vol. of Ni) against the C content (wt.-%), straight lines were obtained. That for O passed through the origin (i.e. O content ∝ C content), but for H the graph showed that there was also a small amount (~1·8 vol. H/vol. Ni) of inorganic H present.

—G. V. E. T.

***The Temperature-Dependence of the Energy Constant of the Magnetic Anisotropy of Nickel.** L. V. Kirensky (*Doklady Akad. Nauk S.S.S.R.*, 1949, 64, (1), 53–56).—[In Russian]. The energy const. of the anisotropy of Ni has been investigated between −183° C. and the Curie point. The method used was the automatic recording of mech. moments applied to a disc-shaped test-piece inserted in a strong uniform magnetic field. The equation: $K = K_0 e^{-aT^2}$ had already been derived from former experimental work, with K = const. of anisotropy at the given temp., K_0 = const. of anisotropy at abs. zero (= 80 × 10^{-4} erg/c.c.), T = abs. temp., and a = a certain const. (= 3·4 × 10^{-6}). For low temp., the log K/T curve is linear, but for higher temp. K changes sign (at 130° C.); it reaches a max. negative value of 0·6 × 10^{-4} between 200° and 250° C.—W. J. K.

Rhenium. Karl Wagenmann (*Z. Erzberg. u. Metallhüttenwesen*, 1951, 4, (4), 162–163).—A brief note on the extraction, properties, and appn. of Re.—E. J. E.

***Variation of the Resistivity of Thin Metal [Silver] Films as a Function of Thickness and Temperature.** J. P. Borel (*Helv. Phys. Acta*, 1951, 24, (4), 389–400).—[In French]. Thin Ag films were formed by deposition *in vacuo*, and their elect. resistance was determined as a function of temp. up to 90° C., and correlated with the structure. The results show that below 10–11 mμ the structures are probably granular, with grains separated one from the other, thus making regrouping difficult, and, therefore, there is an irreversible increase of resistance with temp. In the region of 11–14·5 mμ the structures are porous, but there is contact between different grains, and the variations in resistivity as a function of temp. are reversible. At a thickness of ~20 mμ compact structures are formed, and the initial high resistance soon drops to that of the massive metal. 6 ref.

—E. N.

***On the Change of Supraconducting Properties of Thallium under Pressure.** L. S. Kan, B. G. Lazarev, and A. I. Sudovtsov (*Doklady Akad. Nauk S.S.S.R.*, 1949, 69, (2), 173–174).—[In Russian]. The influence of hydrostatic pressure on critical magnetic field and critical temp. was studied for Sn, In, Pb, Hg, Ta, and Tl. To eliminate any experimental errors due to the easy oxidation of Tl, these specimens were encased in a thin skin of celluloid, Bakelite, glass, or other material. The most reproducible results were obtained with the Tl specimens in glass. The percentage of pressure taken by the case was determined by calibrating experiments with Sn (for glass, 15%). In all metals except Tl, increase of pressure led to decrease in critical temp. and magnetic field. The effect in Tl was the reverse, a pressure of 1730 kg./cm.^{2} causing an increase in the critical temp. of Tl of the order of 0·02° C. An effect of pressure on critical temp. of the same sign as that in Tl has been found in the alloys Bi_3Ni and Bi_4Rh by Alekseevsky using K., S., and L.'s method (*Zhur. Eksper. Teoret. Fiziki*, 1949, 19, 358; *M.A.*, 17, 641); K., L., and S. found that $\frac{dH_K}{dp}$ for these alloys also has the same sign as the effect in Tl.—Z. S. B.

***On the Volume Change of Tin During the Supraconductive Transition in a Magnetic Field.** B. G. Lazarev and A. I. Sudovtsov (*Doklady Akad. Nauk S.S.S.R.*, 1949, 69, (3), 345–347).—[In Russian]. The vol. change of Sn during the transition from the supraconducting to the normal state in a magnetic field and its temp.-dependence were studied. The measurements were made using a bimetallic spiral, 4 m. in length, made of Sn and brass welded together with Sn on the outside. The movement of the spiral was transferred to a mirror and read off on a scale. The sensitivity of the apparatus, calculated from the expansion coeff. of Sn and brass and the deflection on the scale/°C., was 3 × 10^{-8}/division. A possible source of error lies in the thin layer of contaminated Sn at the Sn/brass interface, but this is considered not to be serious. The max. vol. change for Sn calculated from the equation:

$$\frac{\Delta V}{V} = \frac{H_K}{4\pi}\left(\frac{\partial H_K}{\partial p}\right)_T, \text{ where } H_K = \text{critical magnetic field,}$$

is 9·1 × 10^{-8}. The experimental value measured at 1·4° K. was 9·06 × 10^{-8}. Heisenberg has stated that the main cause of this vol. change is magnetostrictional and describes it as $\frac{H^2}{8\pi}\chi$, where χ is the compressibility const. For Sn at 2° K. $H_k \cong 200$ Oe., $\chi = 1{\cdot}7 \times 10^{-6}$ c.c./kg. Thus, the vol. change = 2 × 10^{-9}, but a figure of this magnitude accounts only for ~2% of the observed effect.—Z. S. B.

***Some Details of the Supraconductive Transition [in Tin].** A. A. Galkin and B. G. Lazarev (*Doklady Akad. Nauk S.S.S.R.*, 1948, 61, (6), 1017–1018).—[In Russian]. Measurements on single-crystal Sn wires (0·03–0·05 mm. in dia.), very slowly cooled, have revealed that after the customary transition to the supraconducting state, the elect. resistance returns to the normal value and that this is repeated a number of times, the number increasing with the current intensity. The width of a single resistance peak is 10^{-4}° C. or less. It is thought that the phenomenon may be connected with that observed by Silsbee, Scott, and Brickwedde (*J. Research Nat. Bur. Stand.*, 1937, 18, 295; *M.A.*, 4, 178).

—N. B. V.

Titanium. K. G. Hrishikesan (*Trans. Indian Inst. Metals*, 1950, 4, 183–198; discussion, 198–202).—A brief review of the occurrence, methods of extraction, phys. and chem. properties, and uses of Ti. 26 ref.—P. F. N.

[Discussion on a Paper by F. C. Holden, H. R. Ogden, and R. I. Jaffee:] Microstructure and Mechanical Properties of Iodide Titanium. —— (*J. Metals*, 1953, 5, (11), 1562).—See *M.A.*, 20, 743.

***The Determination of the Absolute Coefficient of Ionization on the Surface of Hot Tungsten.** U. Arifov, A. Kh. Ayukhanov, and V. M. Lovtsov (*Doklady Akad. Nauk S.S.S.R.*, 1950, **68**, (3), 461–463).—[In Russian]. The abs. coeff. of ionization of pure Ca vapour on a hot W filament was determined by recording the ion current on an oscillograph fed with impulses of rectangular form. It was shown that the coeff. of ionization is given by $k = I_0 - I_\infty/I_0$, where I_0 and I_∞ are the initial and final values of the ionic currents as recorded by the oscillograph. The plot of abs. ionization coeff. against filament temp. is given. In the interval 1275°–1325° C. the values agree with the calculations of Copley and Phipps (*Phys. Rev.*, 1945, [ii], 48, 960); at higher temp. the experimental curve drops below the theoretical.—Z. S. B.

The Properties of Metallic Coatings Produced by Evaporation and Sputtering. S. Tolansky (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 155–165; discussion, 187–193).—See *M.A.*, **20**, 389.

Periodicity in the Group of Alkali Metals. G. G. Diogenov (*Doklady Akad. Nauk S.S.S.R.*, 1951, **78**, (5), 899–900).—[In Russian]. D. tabulates the values (in kg.cal.) of the thermal effects for the systems M_1, M_2|OH, NO_3 for all 10 possible pairs of alkali metals (M_1, M_2), arranged in four sets, as follows: (I) Li, Na 11·2; Na, K 6·1; K, Rb 2·0; Rb, Cs 3·0; (II) Li, K 17·3; Na, Rb 7·9; K, Cs 4·7; (III) Li, Rb 19·1; Na, Cs 10·8; (IV) Li, Cs 22·0. Evidently, the values within any set decrease on going from the first pair to the last, but on going from set (I) to set (IV) corresponding values increase; i.e. there is a periodicity in the groups of the Mendeleev system as well as that in the horizontal periods.
—G. V. E. T.

Some Fundamental Ideas on the Structure of Atoms and Metals in Relation to the Properties and Behaviour of Metals and Alloys. G. P. Chatterjee (*Trans. Indian Inst. Metals*, 1950, 4, 163–172).—The fundamental theory of the structure of atoms and metals is described in simple terms and illustrated by ref. to the properties of diffusion, plastic flow, and elect. conductivity in metals and alloys. 6 ref.—P. F. N.

The Mechanics of Metal Crystals. E. N. da C. Andrade (*Proc. Roy. Inst.*, 1951, **35**, [i], (158), 237–251).—A short, general account of present knowledge of the structure of metals and of their behaviour under strain.—S. V. R.

***The Mathematics of the Tensile Test.** Hans Kostron (*Arch. Eisenhüttenwesen*, 1951, **22**, (9/10), 317–324; discussion, 324–325).—The real stress/strain curve for polycryst. metals between the Y.P. or 0·2% P.S. on the one hand and the U.T.S. on the other, is taken to follow the equation $\sigma = a \cdot \delta^n$ with reasonable accuracy, where σ is the stress, δ the elongation; a is a measure of the resistance to deformation, while n indicates the work-hardening capacity. With the aid of this equation the values of any agreed proof stress, of the U.T.S., and of the real stress under max. loading, can be stated in terms of a and n; the ratios of various P.S. and, if present, of the Y.P. to the U.T.S., as well as the strain corresponding to the U.T.S., i.e. the strain at which work-hardening and reduction of cross-section are in balance, can be expressed in terms of n alone. Thus the mutual interrelations between these various functions can be expressed in terms which have general validity. The theoretical "balance strain" (strain corresponding to U.T.S.) differs in many cases from the experimentally determined value, which can be derived from elongation values referred to two different gauge-lengths. This difference indicates either that the equation given above for the stress/strain curve does not apply to the metal in question, which usually implies that the real value of the work-hardening capacity is higher, or that there are weak zones present in the specimen.
—K. S.

***Nature of "Viscous" Fracture [of Materials Under Stress].** V. A. Pavlov and M. V. Yakutovich (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (1), 49–50).—[In Russian]. An investigation was made into the influence of plastic deformation on the formation and growth of microcracks in Plexiglas, in which such cracks are more easily observed than they are in metals. Sheet specimens, 2 × 8 × 80 mm., were tested in tension, non-uniform stress distributions being produced by necks or holes. Microcracks formed in places of max. shear stress (i.e. where the plastic deformation is most intense), and were always ⊥ the line of action of the normal tensile stress. Microcracks can be formed in regions of elastic deformation, and in this case they close up on unloading. They are always formed by the action of tensile normal stress. Plastic deformation increases the probability of their formation, even in anisotropic substances. Microcracks form only at the surface.—G. V. E. T.

***Anisotropy of the Elastic Modulus of Ferromagnetic Single Crystals.** N. S. Akulov, I. P. Mazin, and Ya. I. Fel'dstein (*Doklady Akad. Nauk S.S.S.R.*, 1950, **71**, (5), 851–854).—[In Russian]. The importance of the magnetomechanostriction in the detn. of the elastic const. of ferromagnetic substances is discussed. As it is difficult to obtain single crystals of alloys for experimental purposes, a method is developed for calculating the true const. from data on polycryst. specimens. It is shown that $\dfrac{T(\phi_1) - T(\phi_2)}{1/E(\phi_1) - 1/E(\phi_2)} = K/\varepsilon$, where $T(\phi_1)$ and $T(\phi_2)$ are free energies of magnetization in two arbitrary directions, $E(\phi_1)$ and $E(\phi_2)$ are the moduli of elasticity in those directions, K is the const. of energetic anisotropy, which can be determined from the law of approach to saturation, ε is the const. of true elastic anisotropy given by $\varepsilon = 1/(c_{12} - c_{11}) + 1/2c_{44}$. The free energies were obtained from a magnetogram for which an Akulov anisometer was used. The value of ε for annealed Ni was determined as $-6{\cdot}6 \times 10^{-5}$ mm.²/kg., which agrees well with Bozorth's result (B. *et al.*, *Phys. Rev.*, 1949, [ii], **75**, 1954; *M.A.*, **17**, 53).—Z. S. B.

Report on A.S.T.M. Task Group for Determination of Elastic Constants. Walter Ramberg (*A.S.T.M. Symposium on Determination of Elastic Constants*, **1952**, 3–9).—See *M.A.*, **20**, 823.

The Fracture of Metals. Paul Feltham (*Iron Coal Trades Rev.*, 1950, **161**, (4302), 399–403).—A review. 24 ref.
—N. B. V.

***Characterization of the Brittleness of Steel [and Non-Ferrous Materials] by Means of Tension and Impact Tests on Notched Bars.** Wilhelm Kuntze (*Arch. Eisenhüttenwesen*, 1951, **22**, (11/12), 387–392; discussion, 392–393).—A material is brittle if the process of relaxation which transforms elastic into plastic deformation is slower than the rate at which the stress is applied. Thus brittleness depends both on the material and on the test conditions. K. distinguishes three characteristic types of brittleness: (1) Natural brittleness, which is due to the presence of particles of a hard and brittle phase in the structure and can be detected metallographically; it leads to low values of the reduction of area in ordinary tensile tests on smooth bars. (2) Notch brittleness, which depends on the response of the material to tri-axial stresses; it leads to a low ratio of values for the reduction of area determined on smooth and on notched bars. (3) Latent brittleness, which is due to lattice disturbances of submicroscopic dimensions and can be detected only at high rates of strain. This group includes impact brittleness, low-temp. brittleness, ageing embrittlement, &c., and it is claimed that a low ratio in the values of the reduction of area determined on notched bars in ordinary and in impact tension tests indicates this latent brittleness at normal temp. and in the un-aged condition, so that low-temp. testing and ageing tests can be avoided. Tests of these types were carried out on a variety of steels, on Cu, Al and Al alloys, Mg, and Zn. K. believes that brittle fractures in service can be accounted for on the basis of this test procedure.
—K. S.

The Creep of Metals. P. Feltham (*Iron Coal Trades Rev.*, 1950, **161**, (4300), 305–309).—A review. 31 ref.—N. B. V.

The Creep of Metals and Creep-Resistant Alloys. A. H. Sully (*Murex Rev.*, 1951, **1**, (9), 211–228).—The historical development of creep studies, the form of creep curves, interpretation of data, and theories of creep are reviewed. Structural changes occurring during slow deformation and

the development of creep-resistant alloys are discussed. 9 ref.—D. M. P.

***Prediction of Creep Curves from Stress/Strain Data.** Yoh-Han Pao and Joseph Marin (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 951–957; discussion, 958–961).—See *M.A.*, **20**, 746.

Fatigue of Metals: Consideration of Orowan and Dehlinger Theories. Paul Feltham (*Iron Coal Trades Rev.*, 1950, **161**, (4308), 599–604).—A review. 35 ref.—N. B. V.

***An Investigation on the Coaxing Effect in Fatigue of Metals.** G. M. Sinclair (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 743–751; discussion, 752–758).—See *M.A.*, **20**, 746.

***The Fatigue of Metals: Notched Parts—Test Results, 1948–50.** Mirko Roš (*Met. Ital.*, 1951, **43**, (12), 512–520).—The results of tests are reported which have been made on various types of steel, pure Al, and Avional D to find the fatigue limit for various uniaxial stress ranges as a function of the notch coeff. The notched test-bars were almost homogeneous and testing temp. normal. 22 diagrams illustrate the values obtained.—I. S. M.

Plasticity. James B. Kelley (*Physics Today*, 1951, **4**, (3), 17–23).—A brief introductory account of the plastic flow and fracture of metals.—J. M. C.

***The Basis of the Mathematical Theory of Plasticity.** Fritz Stüssi. P. P. Bijlaard (*Z. angew. Math. Physik*, 1950, **1**, (4), 254–267; 1951, **2**, (2), 114–117; 118–119).—Experiments were carried out on a hollow cylinder of an Al alloy (Avional M) which was subjected to internal pressure and/or longitudinal tension or torsion. S. claims that the experiments show that the effective Poisson's ratio in plastic flow is not $\frac{1}{2}$, so that there are vol. changes associated with flow, and further that the behaviour under combined stresses is not quasi-isotropic, as is usually assumed. He criticizes Bijlaard's treatment of plastic buckling of struts. 11 ref. B. claims that S.'s experimental results are not new, and can be explained fully in terms of the assumptions of plasticity theory. He explains very carefully his method of finding the strain increment from the stress increments, and finally cites experimental evidence in favour of his theories, pointing out that the experiment quoted by S. is at variance with others. S. claims that B.'s theory is not self-consistent in as much as a change of orientation of the stress deviator during plastic deformation leads to a deformation which is not quasi-isotropic, as had been assumed The experimental work was deliberately done on a material with a long plastic range, since it is then that the effects are most important, and this is why the departure from theory was observable.—W. M. L.

***The Interaction of Stress and Deformation Gradients. II.—Influence of Shape and Size.** Franz Bollenrath and Alex Troost (*Arch. Eisenhüttenwesen*, 1951, **22**, (9/10), 327–335).—Cf. *ibid.*, 1950, **21**, 431; *M.A.*, **20**, 824. Hitherto, the study of the effect of stress and deformation gradients on the resistance to plastic deformation, which depends on the size of the component, required an excessive number of tests. It is the object of this work to help achieve a position where the design of components of varying size and shape can be based on the results of a few simple tests of basic mech. properties. It has been possible to set up fairly simple equations showing the influence of non-uniform distribution of stress and strain on the resistance to plastic deformation in a variety of stress appn. and with cross-sections of different shapes. An expression for the dependence of the fatigue strength on the strain gradient, and thus a simple formulation of the size-effect, was also derived. For any given material, the necessary data for the required calculations can be obtained from a tension and a compression test, and two further tests in which geometrically similar specimens of different size are subjected to bending or torsion. For fluctuating stresses, corresponding types of fatigue test must be carried out.—K. S.

***Increase in the Velocity of Plastic Flow of Metals [Lead, Zinc, Silver, Gold, and Platinum] in Electrolytes During Electrochemical Polarization.** August Pfützenreuter and Georg Masing (*Z. Metallkunde*, 1951, **42**, (12), 361–370).—A study has been made of the velocity of plastic flow under const. load—in air, and in KCl or KNO_3 electrolytes at room temp.—of Pb (99·9%) foil, and wires of high-purity (99·99%) Zn, Ag, Au, and Pt all of which had been extensively recrystallized by heating in air; the apparatus and the techniques employed are described in detail. The results show that under cathodic and anodic (for Au and Pt) polarization, the flow rate is increased up to a factor of ten, depending on the metal and the electrolyte, while the Y.P. is decreased. The observations, therefore, confirm and extend the scope of those made by Rehbinder on Sn. The phenomenon is discussed in relation to previously published hypotheses as to its origin, none of which, it is considered, afford an adequate explanation. It is suggested that the effect is probably associated with the formation of an elect. double layer at the metal/electrolyte interface; there is an electrocapillary reduction of the surface energy which leads to a corresponding decrease in the activation energy for slip in the surface of the specimen. 11 ref.—E. N.

Thermodynamics of Plastic Deformation. N. S. Fastov (*Doklady Akad. Nauk S.S.S.R.*, 1951, **78**, (2), 251–254).—[In Russian]. Math. F. deduces equations for the dependence of Y.P. and max. elastic deformation on the speed of deformation, the dependence of stress on deformation and speed of deformation, and also the form of the creep curve.—G. V. E. T.

The Influence of the Surrounding Medium on the Plastic Deformation of Metals. Georg Masing (*Met. Ital.*, 1951, **43**, (11), 467–470).—[In French]. Studies have been made to confirm the Rehbinder effect. Positive results were obtained up to a point. The mechanism is explained by a decrease in slip activation energy; no clear indication, however, has been forthcoming of any influence on elect. resistance. 6 ref.—I. S. M.

***The Influence of Experimental Conditions on the Adsorption Effect in Facilitating Deformation of Metal Single Crystals.** P. A. Rehbinder and V. I. Likhtman (*Doklady Akad. Nauk S.S.S.R.*, 1949, **69**, (2), 219–222).—[In Russian]. The importance of choosing the most suitable experimental conditions for work on the influence of surface-active media on deformation processes is discussed. The negative results of Kemsley (*Nature*, 1949, **163**, 404; *M.A.*, **17**, 6) are explained by: (*a*) wrong etching of the single crystals, (*b*) unsuitable rate of extension (0·2–0·35%/min. instead of 5–10%/min.), and (*c*) failure to use non-polar grease in the control experiments. Maslennikov showed that the deformation of Sn single crystals with no surface prepn. exhibits strong dependence on the presence of surface-active media. The critical stress rises by approx. 100% in an atmosphere saturated with *n*-butylic alcohol vapour, whereas no hardening is observed if the test is carried out *in vacuo*. R. and L. have recently shown that the properties of surface-active media are well studied in respect of their effect on creep. This is explained by the fact that the microcracks cannot close. Venstrem showed that the creep rate of Sn single crystals immersed in a 0·2% soln. of oleic acid in kerosene is approx. twice that in pure kerosene. In the presence of a 0·3% soln. of cetylic acid in paraffin, the creep rate accelerates earlier than in oleic acid.—Z. S. B.

Friction. F. P. Bowden (*Proc. Roy. Inst.*, 1950, **34**, (IV), (157), 634–646).—A review of the present state of knowledge of sliding friction. The main points discussed are the real area of contact between solids, friction and adhesion, the effect of surface films, the surface temp. of sliding solids, friction on ice and snow, and the frictional properties of plastics.—S. V. R.

***Viscosity of Molten Metals.** G. M. Panchenkov (*Doklady Akad. Nauk S.S.S.R.*, 1951, **79**, (6), 985–988).—[In Russian]. According to the theory developed by P., the dependence of the abs. viscosity (η) of a liquid on the abs. temp. T is given by the expression:

$$\eta = A'\rho^{4/3}T^{1/2}e^{\varepsilon_0/RT}(1 - e^{-\varepsilon_0/RT}),$$

where $A' = \dfrac{12\sqrt{R}}{\sqrt{\pi}\sqrt[3]{N_0}}\omega^{2/3}M^{-5/6}e^{\Delta S/R}$. In these equations, R is the universal gas const., N_0 Avogadro's number, ω the natural

vol. of 1 g.-mol., ρ the d of the liquid, M the mol. weight, ΔS the change in entropy on bond formation (per mole), and ε_0 the bond energy of a mol. of liquid. A' can be considered const., especially over a small temp. range, since ΔS changes little with temp. To verify the application of this relation to molten metals, for each metal the experimentally determined viscosities at any two temp. are used to calculate ε_0 and A'. These values are then used to calculate the viscosities at other temp.; and the calculated values are compared with the experimental data. This has been done for Na at 371·2°–628·2° K. ($\varepsilon_0 = 1153$ cal./mole, $\log A' = \bar{4}{\cdot}00200$), K at 337·4°–625·7° K. ($\varepsilon_0 = 887{\cdot}5$ cal./mole, $\log A' = \bar{4}{\cdot}12400$), Ag at 1273·2°–1433·2° K. ($\varepsilon_0 = 4666$ cal./mole, $\log A' = \bar{5}{\cdot}02170$), Cd at 623·2°–873·2° K. ($\varepsilon_0 = 1156$ cal./mole, $\log A' = \bar{5}{\cdot}58633$), Hg at 253·2°–623·2° K. ($\varepsilon_0 = 286{\cdot}3$ cal./mole, $\log A' = \bar{5}{\cdot}64700$), Sn at 533·2°–1073·2° K. ($\varepsilon_0 = 1210$ cal./mole, $\log A' = \bar{5}{\cdot}44150$), Pb at 623·2°–873·2° K. ($\varepsilon_0 = 2303$ cal./mole, $\log A' = \bar{6}{\cdot}92237$), Sb at 973·2°–1373·2° K. ($\varepsilon_0 = 2585$ cal./mole, $\log A' = \bar{5}{\cdot}08854$), and Bi at 577·2°–874·2° K. ($\varepsilon_0 = 1447$, $\log A' = \bar{5}{\cdot}10295$). Calculated and experimental values agree satisfactorily. The small values of ε_0 compared with vaporization energies are noted.—G. V. E. T.

***The Change in Wettability of Metals and Sulphide Minerals Under the Action of Various Gases.** I. N. Plaksin and S. V. Bessonov (*Doklady Akad. Nauk S.S.S.R.*, 1948, **61**, (5), 865–868).—[In Russian]. The contact angles θ between surfaces of Ag, Au, and Cu and a drop of water were measured at intervals up to 180 min. in atmospheres of O, N, and CO_2. Only O appeared to have any effect on θ; for Au θ increased from 61° to 78° in 60 min.; for Ag θ increased from 52° to 68° in 30 min. Results with Cu were somewhat erratic, owing to the presence of an oxide film.—N. B. V.

***Experimental Researches on "Wetting Effect" and "Liquostriction".** Carl Benedicks and Robert Härdén (*Arkiv Fysik*, 1951, **3**, (22), 407–440).—[In English]. Experiments on a variety of solids (sugar, gypsum, glass, steel, &c.) showed that the bending strength was usually reduced by immersion in a liquid, though oils generally raised the strength. The magnitude of the weakening effect was roughly proportional to the surface tension of the liquid, being therefore particularly high for water and aq. alkali soln. For steel there was a 20% strength reduction in water. This "wetting effect" is attributed to a redn. of the surface tension of the solid as a consequence of wetting it. From this a "liquostriction" effect was predicted and discovered. Wires of quartz and various metals (Pt, Fe, Ni, steel) lengthened spontaneously by several p.p.m. on immersion in a liquid; the effect sometimes takes some time to build up. On drying, the wire contracts, sometimes below the original length. The effect is the greater, the higher the surface tension of the liquid. Oil (e.g. in traces in water) reduces and slows down the effect, which is attributed to thermal agitation in the solid being less restrained at the surface.
—R. W. C.

***Experimental Studies of the "Wetting Effect" and "Liquostriction".** Carl Benedicks and Robert Härdén (*Met. Ital.*, 1951, **43**, (9), 383–397).—Cf. preceding abstract. Results of studies made have shown that the "wetting effect" on solids is a function of the surface tension of the wetting fluid. Experimental data appear to support the theory of "liquostriction", which is the expansion of a solid body caused by a wetting fluid. 13 ref.—I. S. M.

A Study of Gases in Metals. W. Baukloh (*Trans. Indian Inst. Metals*, 1950, **4**, 231–237; discussion, 238).—The basic theories of solubilities of gases in metals and methods of degasification are briefly reviewed. 5 ref.—P. F. N.

***Adsorption and Hydrogenation of Gases on Transition Metals.** M. E. Winfield (*Australian J. Sci. Research*, 1951, [A], **4**, (3), 385–405).—Several principles are suggested which determine the location, and to some extent the behaviour, of gas atoms chemisorbed at the surface of a transition metal. With these as basis, and the published experimental evidence, the structures of adsorbed O, H, C_2H_4, and CO are deduced. For a diatomic mol. three kinds of chemisorbed product are distinguished: adsorbed mol., adsorbed atom, and adsorbed ion. Bond energies, together with solid models of surface and adsorbate, are used to arrive at the probable mechanism of C_2H_4 hydrogenation on Ni and of the Fischer-Tropsch hydrocarbon synthesis.—Author.

Symposium on Thin Films. F. A. Hamm (*Analyt. Chem.*, 1950, **22**, (7), 958–959).—A brief report of a Symposium sponsored by the Armour Research Foundation of Illinois Institute of Technology in June 1950.—N. B. V.

***The Investigation of "Thick" Metal Films and Their Surface Layers with the Aid of the Absolute Phases.** Herwig Schopper (*Z. Physik*, 1951, **130**, (4), 427–444).—An opt.-interference method is described which allows the refractive index, n, to be determined in the interior of a metal film. For Ag $n = 0{\cdot}11$ for $\lambda = 546$ mμ. Methods are also described for measuring the thickness of the transition layer between the metal and support, and of the surface oxide or other corrosion film. The surface film can be measured down to thicknesses of a few mol. 16 ref.—J. W. C.

***Thermal Conductivity of Metals at High Temperatures.** P. H. Sidles and G. C. Danielson (*U.S. Atomic Energy Commission Publ.*, 1951, (**ISC-198**), 24 pp.).—The limitations of the static methods of Forbes (*Trans. Roy. Soc. Edinburgh*, 1865, **23**, 133) and Kohlrausch (*Ann. Physik*, 1900, [iv], **1**, 132) are discussed, and King's dynamic method (*Phys. Rev.*, 1915, [ii], **6**, 437) was employed in the present investigation. Measurements were made on rods approx. 0·32 cm. in dia. and at least 50 cm. long, enclosed in a vessel evacuated to 5×10^{-4} mm. Hg. A detailed description is given of the heating unit designed to give a sinusoidal temp. variation in the specimen; the limitations of the unit are considered, a typical operating condition being a period of 110 sec. and a power input of 0·30 W. resulting in a sinusoidal temp. variation of 0·5° C. Measured in this way, the thermal conductivity of Cu is $3{\cdot}988 \pm 0{\cdot}049$ W./cm./°C. at 36° C. and $3{\cdot}517 \pm 0{\cdot}009$ W./cm./°C. at 561° C., in good agreement with previously published figures. Values for Th are also given over the temp. range 20°–410° C. 15 ref.—J. W. T.

***New Method for the Determination of Hall Effects in Series and in Parallel.** A. L. Perrier (*Helv. Phys. Acta*, 1951, **24**, (6), 637–641).—[In French]. Math. The theoretical and practical aspects of the method are discussed.—E. N.

***On the Dependence of the Thermoelectric Power of Thin Metal Films on Their Thickness.** E. Justi, M. Kohler, and G. Lautz (*Naturwiss.*, 1951, **38**, (20), 475–476).—A theoretical and experimental examination has been made of the effects of film thickness on the thermoelect. power of films of Bi and Pb as measured against Cu. It is concluded that the effects cannot be explained theoretically on a thermodynamic basis, but can be accounted for in terms of electron theory.
—S. V. R.

***Measurements in the Transition Region to Superconductivity.—I–III.** Walther Meissner, Fritz Schmeissner, and Hans Meissner (*Z. Physik*, 1951, **130**, (4), 521–528, 529–538; 1952, **132**, (5), 529–541).—[I.—] The external magnetic field produced by an elect. current in polycryst. coils and straight single crystals of Sn was unchanged when the specimens were cooled through the superconducting transition region. The change of flux in straight polycryst. specimens due to an external longitudinal magnetic field was also investigated in the transition region. The flux was expelled from a specimen in the normal way if it carried no elect. current, but there was an increase in flux before expulsion in specimens carrying 15 and 25 amp. [II—.] Further measurements of the change in flux were made with polycryst. Sn and Hg specimens. The increase in flux occurs only when there is a min. current J_0 flowing through the specimen. J_0 is given by $J_0 = J_g + \gamma Hd$, where J_g and γ are characteristics of each specimen, H is the field strength, and d the specimen dia. Values of J_g and γ are given for Hg, Sn, In, and Tl, those of the latter elements being obtained from the results of Steiner (*Z. Naturforsch.*, 1949, [A], **4**, 271; *M.A.*, **19**, 352). [III.—] Hollow Hg cylinders show an increase in flux in the cavity when cooled through the

transition range. This proves the flux increase is due to a circular component of the current and not to a vol. magnetization. There is no critical current J_0 for increase in flux in the cavity; a small increase occurs with very small currents. By cutting longitudinal slots in hollow cylindrical specimens, the increase in flux was prevented. The increase in flux is believed to correspond to the amalgamation of separate supraconducting regions. Some experiments with impure Ta specimens are also described.—J. W. C.

On the Theory of Supraconductivity. Max Born and Kai-Chia Cheng (*Doklady Akad. Nauk S.S.S.R.*, 1948, **62**, (3), 313–318).—[In Russian]. See *M.A.*, **16**, 328.—N. B. V.

***Observations on Fröhlich's Theory of Supraconductivity.** M. R. Schafroth (*Helv. Phys. Acta*, 1951, **24**, (6), 645–662).—[In German]. Math. It is shown that the interaction between the conduction electrons and the lattice vibrations in a metal, if treated by perturbation methods, can never yield the London equation for the supracurrent in a magnetic field. This deviation from a result obtained by Fröhlich (*Phys. Rev.*, 1950, [ii], **79**, 845; *M.A.*, **18**, 502) is considered to arise from F.'s having made an erroneous choice of the approximation for the expression relating to c.d. However, since the basic idea of F. is considered to be true, other approximations have to be made, and these are discussed. A general expression for the diamagnetic susceptibility of a gas of freely charged particles is derived by a new method; it is valid in any system of statistics. 8 ref.—E. N.

***Semi-Metallic Materials Having a Continuous Transition of [Electrical] Properties from Metal to Ceramic. V.—Capillary [Type] Semi-Conductors.** Eberhard Meyer-Hartwig (*Z. Metallkunde*, 1951, **42**, (10), 302–308).—The basic principles for assessing the possibilities of metal–ceramic combinations in respect of their elect. properties are discussed and illustrated. When the various types of semi-conductors are considered—metal–insulator combinations of multilayer, sandwich, powder, and capillary types—the last-mentioned are seen to be very simple to manufacture. Their prodn. by special sintering processes, which improve metal–ceramic and ceramic–metal diffusion, enables new materials with a wide range of variations in properties to be developed. The basic constituents and characteristics of such semi-conductors with elect. properties designed for sp. purposes (e.g. whose resistance increases or decreases with increase in temp., or which are to be used as corrosion-resistant high-temp. heating elements) are outlined.—E. N.

†**Electronic Conduction in Non-Metals.** Georg Busch (*Z. angew. Math. Physik*, 1950, **1**, (1), 3–31; (2), 81–110).—A very thorough review of theoretical principles and of experimental results on semi-conductors of both ionic and valence crystal types. The elect. conductivity, Hall effect, and change of resistance in a magnetic field are dealt with in [I.—]. The special cases of ZnO, Cu_2O, SiC, Si, and certain spinel-type oxides are discussed in detail. [II.—] The thermo-elect. properties are briefly discussed. 131 ref.
—W. M. L.

***Emission of Electrons and Reflection of Ions from Metal Surfaces.** M. A. Eremeev (*Doklady Akad. Nauk S.S.S.R.*, 1951, **79**, (5), 775–777).—[In Russian]. Ta or W targets, previously annealed at 2500° K. and placed at the centre of a spherical collector for secondary particles, were bombarded with narrow beams of ions of the alkali metals. At moderate temp. the targets were always coated with ions adsorbed from the primary beams, the amount being measured by the ballistic throw of a galvanometer on sudden overheating of the target to vaporize the ions. The number of electrons emitted by the targets increased linearly with the energy of the incident ions. With increasing target temp., the number of electrons emitted and the number of ions adsorbed both decreased. Up to 800° K. the reflection coeff. of the ions is independent of the nature of the target and of the energy of the ions. Above 1000° K., the reflection coeff. for Ta and W with K ions are different, but independent of the energy of the ions between 1 and 13 keV.; for Li ions of these energies, the reflection coeff. remains the same at all temp. At high target temp., ions of very high energy are reflected. Experiments were also made with a target of molten Sn; diffusion prevented the formation of an adsorption layer of alkali metal atoms. Repeated purification of the surface by decantation reduces the reflection of slow ions and the emission of electrons; only fast ions are reflected from completely pure surfaces. The max. energies of these ions correspond to the values obtained in an elastic collision of a K ion with an isolated Sn atom. With Sn the reflection coeff. is again independent of the energy of the ions. The electron emission is due to the presence of adsorbed ions, for no electrons are emitted from Sn surfaces freed from the adsorbed layer. The energy distribution of ions reflected from solid surfaces was studied by magnetic analysis; graphs of the results are given for K and Li ions incident on a Ta target at 45°. The energy corresponding to the max. on a curve is given by $E = \frac{m_1 - m_2}{m_1 + m_2} . E_0$, where E_0 is initial energy of the incident ions, m_1 the mass of an atom of the target, and m_2 the mass of an incident ion. By experiment, values of $\frac{m_1 - m_2}{m_1 + m_2}$ for K and Li were found to be 0·60 and 0·82, resp. (calculated values 0·64 and 0·92). E.'s results indicate that there are elastic collisions between the incident ions and individual free atoms of the target.—G. V. E. T.

***Structure of the [Electron] Emitter of the Kubetsky [Electronic] Tube.** S. M. Fainshtein and L. I. Tatarinova (*Doklady Akad. Nauk S.S.S.R.*, 1951, **79**, (3), 435–438).—[In Russian]. The secondary-electron emitter consists of a film (~10^{-5} cm. thick) produced by reaction of electro-deposited Cu (on Ag basis metal) with an aq. soln. of H_2S, and then activated by treatment with Cs vapour *in vacuo*; this is thought by Kubetsky (*Izvest. Akad. Nauk S.S.S.R.*, 1944, [Fiz.], 8, 357) and by Badikova (*Zhur. Tekhn. Fiz.*, 1939, **9**, 24, 2163) to consist of the system Cu–S–Cs. F. and T. have investigated the nature of the film and the mechanism of its formation, by a reflection method of electron diffraction, using MgO as a standard. After the treatment with H_2S, the film consisted mainly of Cu_2O with some Cu_2S, CuS, and CuO, though in some samples Cu_2S was absent. Cu deposits obtained from neutral $CuSO_4$ at c.d. ~0·3 amp./dm.^{2} were found to be coated with a thin film of Cu_2O even before treatment. The Cu_2S in the emitter layer must be formed by the reaction: $Cu_2O + H_2S \rightarrow Cu_2S + H_2O$. Films of Cu_2S were prepared on NaCl single crystals by condensing separately vapours of S and Cu, then heating *in vacuo* to ≯300° C.; these films contained traces of Cu_2O and were unchanged after heating in air or water vapour for 1 hr. The effect of vacuum heat-treatment before activation in making the colour of the emitter lighter must be due to the reaction $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$.—G. V. E. T.

***Electron Emission from Metal Surfaces as an After-Effect of Mechanical Working or Glow Discharge.** O. Haxel, F. G. Houtermans, and K. Seeger (*Z. Physik*, 1951, **130**, (1), 109–123).—As reported by Kramer (*ibid.*, 1949, **125**, 739; *M.A.*, **20**, 350), metal surfaces rubbed with emery emit electrons, the c.d. decreasing with time. The effect was investigated, using an arrangement in which the surface was placed inside the counter tube used to measure the electron current. For any one metal, the emission current J and the time t since abrasion were simply related by the equation: Jt = const. This const. decreased for different metals in the order Pb, In, Al, Au, Cu, Mo, Sn, Fe, Wood's metal, and graphite. The dependence on temp. of the surface was also investigated; a sudden increase in this temp. gave a sharp rise in electron emission, followed by a rapid decrease. A glow discharge in the counter tube also produced a time-dependent electron emission, but the effect was more marked. The results are interpreted by assuming that the mech. deformation or the glow discharge removes a layer of adsorbed O, which is then re-formed during the electron emission.
—J. W. C.

Magnetic Materials and Ferromagnetism. A. E. De Barr (*Research*, 1951, **4**, (8), 366–371).—A short review. 20 ref.
—N. B. V.

***Effect of Tension on the Magnetization of Ferromagnetic Substances in the Region of the Para-Process.** K. P. Belov (*Doklady Akad. Nauk S.S.S.R.*, 1948, **61**, (5), 807–809; *C. Abs.*, 1949, **43**, 4529).—[In Russian]. Elastic deformation should affect the magnitude of saturation magnetization (region of the para-process). This is indicated by the fact that the exchange forces corresponding to the spontaneous orientation of spins depend on interatomic distance, and the fact that magnetostriction takes place on account of the para-process. Tests were made of the effect of tension on the spontaneous magnetization of ferromagnetic materials. By testing near the Curie point it was possible to eliminate the "commercial" magnetization by means of a relatively small magnetic field. The testing procedure consisted in applying a field, H_s, greater than that for commercial magnetization. The change of saturation magnetization, ΔI_s, produced by quickly applying an elastic stress was measured by a system of sensitive coils and a ballistic galvanometer. The specimens were wires, 2 mm. in dia. and 250 mm. long, and the stress was 8–10 kg./mm.^{2}. Tests were made over the temp. range −200° to +400° C.; points obtained on heating coincided with those on cooling. Curves of $\Delta I_s/p$ against temp. (p in dynes/cm.^{2}) were obtained for (1) Ni, (2) 80 : 20 Ni–Cu, (3) 64 : 36 Fe–Ni, (4) 44 : 56 Fe–Pt, in a field of 1000 Oe. Metals (1) and (2) showed small negative effects, $\Delta I_s/p = -10 \times 10^{-10}$ Oe. cm.^{2}/dyne, (3) and (4) +75 and +200, resp. These max. values occurred near 250° C. At 0° C. the values should be zero. In (3) and (4) the curve of exchange forces against interatomic distance must have a steep slope, in (1) and (2) a flat slope.

***Temperature Dependence of Magnetic Viscosity of Ferromagnetic Metals.** E. F. Kuritsyna (*Doklady Akad. Nauk S.S.S.R.*, 1951, **79**, (2), 233–236).—[In Russian]. Experiments to verify Telesnin's first law of magnetic viscosity (*ibid.*, 1950, **75**, 659; *M.A.*, **20**, 77) which states that relaxation time $\tau = A \cdot \frac{\chi_d}{T}$, where A = coeff. of magnetic viscosity, T = abs. temp., and χ_d is the differential magnetic susceptibility, dI/dH. K. gives curves of magnetization, hysteresis, τ, χ_d, and A for Fe and Co at 86°, 293°, 473°, 673°, 873°, and 1013° K. Curves showing the variation with temp. of max. values of τ and χ_d are also given. The τ curve for Fe falls from a high value at 86° K. to a min. in the region 300°–500° C., and then shows only a slight increase. The curve for Co is similar, but the values are less. Values of A for Fe and Co show more scatter than those for Ni (T. and K., *ibid.*, 1950, **75**, 797; *M.A.*, **20**, 78).—G. V. E. T.

***The Influence of Elastic Internal Stresses on the Law of Approach to Magnetic Saturation.** L. V. Kirensky and L. I. Slobodskoy (*Doklady Akad. Nauk S.S.S.R.*, 1950, **70**, (5), 809–811).—[In Russian]. A calculation of the intensity of magnetization of polycryst. aggregates at high field strength, taking into account the magnetostrictive effect, is given. The internal stresses present in the sample are shown to alter the shape of the magnetization curve at high field strengths to a significant extent at room temp. The shape of the curve can indicate whether the original stresses are opposing or relieving those set up by magnetostriction.—Z. S. B.

***Magnetism of Free-Charge Carriers in Semi-Conductors.** G. Busch and E. Moser (*Helv. Phys. Acta*, 1951, **24**, (4), 329–331).—[In German]. The results of magnetic-susceptibility/temp. measurements on grey Sn show that the temp.-dependent and the const. (temp.-independent) terms in the susceptibility relationship arise from the magnetism of the free-electron carriers and the diamagnetism of the Sn atoms, resp. This conclusion enables an equation to be derived for the magnetic properties of the holes and conduction electrons in semi-conductors; its validity is confirmed by the experimental observations.—E. N.

Solid-State Electronics. Robert G. Breckenridge (*Physics Today*, 1951, **4**, (9), 7–11).—The band theory of conduction (for conductors, semi-conductors, and insulators) is explained simply, and recent work in this field at the National Bureau of Standards is reviewed.—J. M. C.

Correction to the Paper by A. E. Glauberman and I. I. Tal'yansky on: The Theory of the Escape of Electrons from a Metal in an Electric Field. A. E. Glauberman and I. I. Tal'yansky (*Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, (2), 124).—[In Russian]. See *M.A.*, **19**, 440.—G. V. E. T.

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2 — PROPERTIES OF ALLOYS

***Effects of Machining Specimens on the Results of Tension Tests of Annealed [Aluminium and] Aluminium Alloys.** G. W. Stickley and K. O. Bogardus (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 1079–1085).—See *M.A.*, **20**, 751.

***Fatigue of 76S-T61 Aluminium Alloy Under Combined Bending and Torsion.** William N. Findley (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 818–833; discussion, 833–836).—See *M.A.*, **20**, 832.

***Effect of Prior Repeated Stressing on the Fatigue Life of 75S-T Aluminium.** Thomas J. Dolan and Herbert F. Brown (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 733–740; discussion, 740–742).—See *M.A.*, **20**, 831.

***The Presence of Molecular Formations in Ternary Primary Solid Solutions of Aluminium.** T. A. Badaeva (*Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, (4), 533–536; *C. Abs.*, 1949, **43**, 4534).—[In Russian]. Analogously with binary solid soln., in which a high value of the heat of formation indicates a deviation from statistical distribution, in the direction of a distribution akin to chem. mol. formation, the ternary system Al–Mg–Si, along the section of const. Al = 99 at.-%, shows, at all temp. between 480° and 550° C., in unquenched samples, a distinct min. of the elect. resistivity ρ at the Mg : Si ratio corresponding to Mg_2Si. Consequently, the ternary solid soln. contains mol. of Mg_2Si; their max. amount corresponds to the section Al–Mg_2Si. The effect is not masked by an interaction between Al and Si; the binary diagram shows absence of compound formation. In the ternary system Al–Mg–Zn, along the section Al = 90 or 92%, ρ decreases continuously with increasing Zn (decreasing Mg) at all temp. between 410° and 440° C. The isotherms are nearly rectilinear and show no anomalies either in the concentration range of equilibrium between the solid soln. and the T phase or of equilibrium with $MgZn_2$ and $MgZn_5$. Consequently, both the T phase, commonly considered as close to $Al_2Mg_3Zn_3$, and the binary Mg–Zn compounds, are dissociated into atoms in the ternary solid soln. in Al.

***Q Phase of the System Aluminium–Copper–Magnesium.** M. S. Mirgalovskaya (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (2), 289–292).—[In Russian]. In a previous investigation of the central part of the Al–Cu–Mg equilibrium diagram (Urazov and M., *Referaty Nauchno-Issled. Rabot. Otd. Khim. Nauk Akad. Nauk S.S.S.R.*, **1944**, 24), a new intermetallic phase was observed and designated Q. It greatly resembles the U and T phases, not only in crystal form but also in its behaviour towards the usual etchants. Using alloys annealed at 400° C. for 45 days and air-cooled, M. has now established the extents of the phase fields by microscopy. The solid-soln. region of the Q phase is very small (~1·5%). A Thomson bridge was used for elect.-resistance measurements on alloys along the section U–βAl–Mg at 18° and 100° C. The temp. coeff. of elect. resistance/compn. (wt.-% Al) curve for these alloys shows a singular max. at the compn. Al 35·5, Cu 36·8, Mg 27·7% (corresponding almost to $Al_2Cu_2Mg_5$), indicating that the Q phase is intermetallic. An X-ray study of the almost single-phase alloy of compn. Al 36·5, Mg 27·2, Cu 36·3% shows that the Q phase has a b.c.c. lattice (a = 12·087 Å.); the space group is of class *Th-m*3 or *Oh-m*3*m*. The number of atoms in the unit cell, calculated from the observed sp. gr. (3·022 at 25° C.), is 94; i.e. it contains 6 $Al_7Cu_3Mg_6$ groups.—G. V. E. T.

***Region of Primary Crystallization of the *Q*-Phase of the System Aluminium–Copper–Magnesium.** M. S. Mirgalovskaya (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (6), 1027–1030).—[In Russian]. M. investigated the nature of the processes in which the *Q* phase (see preceding abstract) participates, by the microscopical examination and thermal analysis of ~60 alloys. Because of the difficulty in distinguishing the *Q* phase from the *U* and *T* phases, the following etchants were used: 27% HNO_3 + 7% HF, 0·5% HF + 1·5% HCl + 2·5% HNO_3, and 25% HNO_3 + 0·5% HF. With the first etchant, the centres of the grains of the *T* phase were tinted more darkly than their external layers. The phenomena observed by Urazov, M., and Nagorskaya (*Izvest. Sekt. Fiziko-Khim. Anal.*, 1949, **19**, 523) are the result of a typical peritectic transformation of the darker *Q* phase into phase *T*. The *Q* phase takes part in the following invariant processes: liquid + U + $S \rightarrow Q$ (520° C.; Al 51·1, Cu 15·0, Mg 34·0%); liquid + $Q \rightarrow S + T$ (472° C.; Al ~61·5, Cu 12·5, Mg 26·0%); liquid + $U \rightarrow Q + \delta$ (~435° C.; Al ~27·8, Cu 6·2, Mg 66·0%); liquid + $T \rightarrow \gamma + Q$ (~430° C.; Al ~32·2, Cu 6·2, Mg 61·6%); liquid $\rightarrow \gamma + \delta + Q$ (425° C.; Al 31·0, Cu 6·0, Mg 63·0%). The liquidus diagram for the region studied is given.—G. V. E. T.

The System Aluminium–Copper–Magnesium. G. G. Urazov and M. S. Mirgalovskaya (*Doklady Akad. Nauk S.S.S.R.*, 1952, **83**, (2), 247–250).—[In Russian]. Gives the equilibrium diagram, isothermal section at 400° C., and liquidus surface for the system, based on results published in previous papers (see preceding abstracts). With the exception of the region lying near the Cu corner of the Al–Cu system, the Al–Cu–Mg system consists of the following 15 "individual" ternary systems: Cu_2Mg–$CuMg_2$–U, $CuMg_2$–U–δ_{Mg}, U–Q–δ_{Mg}, Q–γ_{Al-Mg}–δ_{Mg}, T–Q–γ_{Al-Mg}, β_{Al-Mg}–T–γ_{Al-Mg}, S–U–Q, S–Q–T, α_{Al}–S–T, α_{Al}–T–β_{Al-Mg}, α_{Al}–θ_{Al-Cu}–S, θ_{Al-Cu}–V–S, V–U–S, η_{Al-Cu}–ε_{Al-Cu}–V, ε_{Al-Cu}–V–U (in the solid state, at 400° C., θ_{Al-Cu}–η_{Al-Cu}–V and η_{Al-Cu}–V–U exist). Conclusions of other workers are criticized.—G. V. E. T.

The Production of Aluminium–Silicon Alloys in the Electric Furnace. Y. Dardel (*J. Four élect.*, 1951, **60**, (2), 37–39; (3), 68–70).—D. reviews available information relating to the reactions involved in the direct prodn. of Al–Si alloys by reducing Al_2O_3–SiO_2 mixtures with C in the elect. furnace. 37 ref.—N. B. V.

Aluminium–Silicon Alloys. P. P. Bhatnagar and T. Banerjee (*Trans. Indian Inst. Metals*, 1950, **4**, 209–230).—A review of methods of prodn. and modification of Al–Si alloys. Phys. properties of the alloys and the effects on the 5% and 13% Si alloys of minor elements within the A.S.T.M. specification are described. The characteristics and appn. of the binary and complex Al–Si alloys are also discussed. 37 ref.—P. F. N.

***Antimony–Lithium Photocathodes.** N. Schaetti and W. Baumgartner (*Z. angew. Math. Physik*, 1950, **1**, (4), 268).—A letter. The spectral-sensitivity curves of Sb–Cs and Sb–Li photo-cells are given, and show that in the near ultra-violet, at ~3600–4500 Å., there is a distinct advantage in the latter. This is the range of wave-lengths produced by cathode-ray tubes, &c.; for example, the flying-spot microscope or a scintillation counter.—W. M. L.

***Photo[-Electric] Effect with Cs–Ga, Cs–In, and Cs–Tl Photocathodes.** N. Schaetti, W. Baumgartner, and Ch. Flury (*Helv. Phys. Acta*, 1951, **24**, (6), 609–613).—[In German]. The photoelect. characteristics of Cs–Ga, Cs–In, and Cs–Tl photocathodes have been determined. Their sensitivity is relatively low, being of the order of 1·0, 1·5, and 0·5 μ amp./lumen, resp., as compared with 30 μ amp./lumen for a Cs–Sb cathode. Although the shapes of the S-shaped spectral sensitivity curves are very similar, and, therefore, are almost independent of the nature of the element used in conjunction with Cs, within the region 5500–4500 Å., there does appear to be a slight relationship between emissivity and at. wt. Anomalous results are obtained when the photocathodes consist of thin evaporated films.—E. N.

***Properties of Cs–Sb Photocathodes at Various [Low] Temperatures.** N. Schaetti and W. Baumgartner (*Helv. Phys. Acta*, 1951, **24**, (6), 614–619).—[In German]. Previous detn. (cf. *ibid.*, 1950, **23**, 524; *M.A.*, **18**, 597) of the spectral-sensitivity characteristics of Cs–Sb photocathodes, which were carried out in the temp. range +20° to −120° C., have been extended to −131°, −183°, and −196° C., and compared with the values at room temp. (+25° C.). The results are given in tables and graphs. They show that: (1) in all cases cooling produces a recession in the long-wave limit of sensitivity, and (2) if the cathode layer contains an excess of Cs and is slightly oxidized, the characteristics deviate from normal in having a relatively low blue, and a much higher red, sensitivity.—E. N.

***On the Electrical Conductivity of a Ferromagnetic Chromium–Tellurium Alloy.** I. G. Fakidov, N. P. Grazhdankina, and A. K. Kikoin (*Doklady Akad. Nauk S.S.S.R.*, 1949, **68**, (3), 491–492).—[In Russian]. F., G., and K. studied the influence of temp. and magnetic field on the sp. resistance of the alloy contg. Te 48·5, Cr 51·5 at.-%, which was prepared by melting under A in a silica tube at 1250° C. The sp. resistance of the alloy at room temp. was $5 \cdot 10^{-4}$ ohm/cm. and the temp. coeff. of resistance was positive, changing sharply at 58° C., the Curie point. $\Delta R_{\perp}/R$ plotted against temp. for fields from 3 to 15 kOe. shows a max. near 58° C. The alloy differs from other ferromagnetic materials in that $\Delta R_{\perp}/R$ and $\Delta R_{\parallel}/R$ are both negative and of almost equal magnitude at 20° C. Vonsovsky (*Zhur. Tekhn. Fiziki*, 1948, **18**, 145) explained this anomaly as being due to a "volume" effect. Though the results do not agree with those of other workers, owing to different methods of prepn., they are consistent with heat-capacity and magneto-caloric measurements on the same alloy.—Z. S. B.

***Exploratory Investigation of High-Temperature Sheet Materials [Cobalt-Base Alloys].** D. Preston (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 962–986; discussion, 986).—See *M.A.*, **20**, 833.

***The Influence of Periodic Overstressing on the Creep Properties of Several Heat-Resistant [Cobalt-Base] Alloys.** G. J. Guarnieri and L. A. Yerkovich (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 934–946; discussion, 947–950).—See *M.A.*, **20**, 833.

***Appearance of Portions of Anomalous Values on the Logarithmic Curves of Dissociation Pressure of Cobalt Arsenides.** M. I. Kochnev (*Zhur. Priklad. Khim.*, 1948, **21**, (12), 1210–1227).—[In Russian]. K. determined the dissociation pressure, *P*, by the effusion method, using ~1 g. powdered alloy in a quartz glass ampoule; the ampoule orifice areas varied from $0 \cdot 6 \times 10^{-3}$ to $3 \cdot 12 \times 10^{-3}$ cm.^{2}. Curves showing the variation of log *P* with $1/T$ (where *T* is the abs. temp.) are given for the following arsenides at the ranges of temp. (°C.) shown: $CoAs_2$ (465°–660°), Co_2As_3 (550°–740°), CoAs (740°–1065°), Co_3As_2 (755°–1080°), Co_2As (768°–995°), and Co_5As_2 (768°–1060°). The curves are straight lines with discontinuities (either a sharp decrease followed by an increase, or an S-shaped kink resembling van der Waals curves) at the following temp. (°C.): $CoAs_2$, 505°–542°; Co_2As_3, 550°–601°; CoAs, 768°–785° and 850°–870°; Co_3As_2, 778°–798° and 837°–885°; Co_2As, 787°–805° and 844°–885°; and Co_5As_2, 798°–818°, 864°–885°, and 885°–900°. At any one temp., the value of *P* for $CoAs_2$ > that for Co_2As_3 by ~100×, and *P* for Co_2As_3 > that for CoAs by ~1000–10,000×; values of *P* for CoAs, Co_3As_2, Co_2As, and Co_5As_2 differ in magnitude by <10×. The temp. at which the anomalies occur correspond with the temp. at which the powders ignite in oxidizing atmospheres. This is explained by the hypothesis that changes in the crystal lattice occur at these temp.—G. V. E. T.

***The Thermodynamic Properties of the Cobalt Arsenides.** M. I. Kochnev (*Doklady Akad. Nauk S.S.S.R.*, 1950, **70**, (3), 433–435).—[In Russian]. The thermal dissociation of the Co arsenides was studied by measuring the pressure of the liberated As vapour by the method of flow. Synthetic $CoAs_2$, $CoAs_3$, CoAs, Co_2As, and Co_5As_2 were studied, and equations for their dissociation are given. Temp. of experiment ranging from 460° to 1095° C. were used, depending on the compn. of the arsenide. The mol. of gaseous arsenic

was assumed to be As_4, and as the dissociation pressure of the arsenides in the given temp. interval was very low, the ideal gas laws were assumed to be applicable. The dissociation pressures of the six Co arsenides at $>7°$ C. from their ignition temp. are given, and the equilibrium const. of the dissociation reactions are calculated from them. The heats of formation of the Co arsenides and their heats of dissociation are also calculated. Solubility of the dissociation products in the Co arsenides affects the results slightly. Empirical equations for the dependence of the equilibrium const. on temp. are given.—Z. S. B.

***Dissociation Pressure of Copper Arsenide.** M. I. Kochnev (*Doklady Akad. Nauk S.S.S.R.*, 1951, **79**, (3), 463–465).—[In Russian]. The dissociation pressure (P) of an alloy contg. 71·40% Cu, 28·60% As (Cu_3As contains 28·23% As) was measured over the range 505°–700° C. by the molecular-flow method used previously for cobalt arsenide (*Zhur. Priklad. Khim.*, 1948, **12**, 1210; preceding column). Over the range 505°–590° C., $\log P \propto 1/T$, where T is the abs. temp., but in the interval 590°–595° C. P drops sharply, and at 600° C. it could not be measured. Beginning at 605° C., however, P again increases with temp., so that at 665° C., it has reached the value it had at 590° C. By 700° C., P has begun to fall gradually. Comparison of the log P vs. $1/T$ curve with the equilibrium diagram shows that anomalies in the curve correspond to temp. of isothermal transformations in alloys with compn. near to Cu_3As. Over the temp. range 500°–590° C., the equilibrium const. K_p for the formation of Cu_3As from the elements was given by: $\log K_p = \frac{2490}{T} - 1{\cdot}25$. The free energy of formation at 590° C. $\Delta\Phi_{863} = -6472$ cal./g.-mol. For the interval 505°–590° C., the change in heat content $\Delta H = -11{,}395$ cal./g.-mol., and the change in entropy $\Delta S = -5{\cdot}7$ cal./g.-mol. The value of 25,600 cal./g.-mol. for the heat of formation obtained by Savelsberg (*Metall u. Erz*, 1936, **14**, 379) is criticized.

—G. V. E. T.

***Influence of the Gaseous Atmosphere on the Formation of Blisters in Beryllium Bronze.** A. K. Chertavskikh and Yu. A. Klyachko (*Zhur. Priklad. Khim.*, 1950, **23**, (10), 1032–1039).—[In Russian]. An investigation was made of blisters, dia. 0·5–1·0 mm. and wall thickness 0·1–0·25 mm., found in annealed sheet. Sheets 0·5 mm. thick were prepared from ingots cast from Be bronze melted in a H.F. furnace, with and without charcoal fluxes (calcined or moistened). Specimens were heated in various atmospheres and then quenched in water. With moist charcoal, the amount of scrap due to the presence of blisters was 2–3 times greater than with calcined or no charcoal. The greatest amount of scrap was obtained on annealing in steam or moist NH_3. With ingots vacuum-cast from remelted material, cracking and lamination occurred on rolling. However, the sheet produced did not give blisters when annealed in steam for 30 min. at 790° or 850° C. Annealing tests with cleaned strip showed that strip made from ingots vacuum-melted but cast in air (I) gave ~31 times as much scrap and ~100 times as many blisters as that made from ingots vacuum-melted and vacuum-cast (II). If the surface of strip (II) was not cleaned, blisters were not produced on annealing in steam or dissociated NH_3. Blisters were not observed when cleaned strip (II) was heated in air, but with (I) blistering occurred on heating at 810° C. and increased with increase in temp. Cleaned (II) heated in steam at 750°–850° C. was almost free from blisters, but with (I) blisters were formed even at 750° C. (The number of blisters produced remained almost const. up to 800° C., then increased with increase in temp.) Similar results were obtained with moist NH_3. Blister formation is attributed to the initiation at a critical temp. (800°–810° C.) of a self-accelerating chain reaction, the decompn. of adsorbed water vapour to give H. The gas content of the blisters was determined by heating to 1050° C. in a vacuum (2×10^{-4} mm. Hg). Be bronze cast in air had a gas content of 6·1 c.c./100 g. metal (the bronze contained 0·00145% O and 0·00037% H); with air-cast and quenched metal the corresponding figures were 5·3 c.c./100 g., 0·00108% and 0·00034%; and with vacuum-cast metal, 1·9 c.c./100 g., 0·00059% and 0·000097%.—G. V. E. T.

***Investigation of the Ordering Process in the Alloy Cu_3Au by Measurements of Electric Fluctuations.** E. Ya. Pumper (*Doklady Akad. Nauk S.S.S.R.*, 1950, **72**, (6), 1033–1036; *C. Abs.*, 1951, **45**, 9331).—[In Russian]. A new method of analysing the ordering process in a conductor by measuring the e.m.f. fluctuation-level is applied to Cu_3Au. The noise temp. t is measured at 330° and 370° C. for periods up to 30 hr. At both temp. t decreases during the first 4 hr., then increases to a max., and then falls. For 370° C. t is higher up to the max., which occurs sooner and has a larger value than for 330° C., but in the descending branch of the curves, t is lower for 370° C. The shift of the max. is connected with the approach to the critical point. Measurements at 395° and 415° C., i.e. for higher critical temp., show that the form of the curves characterizes the kinetics of the ordering process. Two stages of the ordering process are assumed: in the first stage a large number of small lattice-cells are ordered, the speed of the process and the resistance decreasing rapidly with time; in the second stage large ordered particles in the process of formation interact, but only at the boundary layers, so that the total resistance is little affected. This method permits more detailed study of the ordering process in Cu_3Au than does X-ray analysis or the method of measuring resistances.

***The Influence of Lead on the Modulus of Elasticity and the Damping of Copper, Silver, Brass, and Red Brass.** Werner Köster and Lothar Bangert (*Z. Metallkunde*, 1951, **42**, (12), 391–394).—The materials studied, at temp. up to 400° C., were: Cu and Ag, with and without Pb 20 and 11%, resp.; brass contg. Cu 58–64, Pb 3–1%, balance Zn; and alloys contg. Cu 92, 88·5, and 75·2, Zn 3·5, 4·3, and 4·1, Sn 4·2, 3·7, and 6·2, and Pb 0, 3·5, and 14·5%, resp. The results of the detn. show that while the modulus of elasticity of the leaded alloys corresponds to that expected from theoretical considerations, the damping capacity is higher. As a consequence of the viscosity of Pb increasing rapidly when approaching the m.p., relaxation phenomena occur, the outward signs of which are an increase in damping and a decrease in elastic modulus. At the m.p. of Pb, or of the eutectic, if formed, the viscosity of the low-m.p. constituent of the alloy falls sharply, leading to sudden decreases in damping and elastic modulus—which are proportional to the amount of Pb taking part in the transition and, therefore, in general, to the Pb content of the alloy. Other discontinuities in the curve showing temp.-dependence of the properties can be traced to the onset of solid → liq. transitions.—E. N.

***Some Studies on the Behaviour of Metals and Alloys [Brass] at Elevated Temperatures Under Vacuum.** W. Baukloh and G. P. Chatterjee (*Trans. Indian Inst. Metals*, 1950, **4**, 239–252; discussion, 252–254).—The apparatus and procedure for studying the behaviour of α/β brass when heated *in vacuo* are described. Vacuum etching occurred at 350° C. when specimens were heated for 1 hr. and at 200° C. after 8 hours' heating. The etching temp. was lowered by 40°–50° C. with 50% cold reduction. Above 350° C. the loss of weight/unit area for a given time due to volatilization is an exponential function of temp. up to ~750° C.; beyond this deviation occurs owing to the conversion to β-brass.—P. F. N.

***Diffusion of Zinc in Alpha Brass.** G. P. Chatterjee (*Trans. Indian Inst. Metals*, 1950, **4**, 255–268; discussion, 269).—C. presents the theory and method of evaluation of the diffusion coeff. of an element in a binary alloy by detn. of the rate of loss of that element when the alloy is heated at different temp. *in vacuo*. The results of an experimental series on brass (39·8% Zn) are discussed, and the conclusions are that the values of the diffusion coeff. of Zn in brass at temp. >700° C. are too high, but below 700° C. the values are comparable with those found by other methods. 13 ref.

—P. F. N.

On Various Diagrams of the Effect of Alloying Additions on the Strength of Binary Copper Alloys at Elevated Temperatures. M. V. Zakharov (*Doklady Akad. Nauk S.S.S.R.*, 1949, **65**, (3), 337–339).—[In Russian]. Three diagrams are

given showing the effect of certain alloying elements on the relative strength of binary Cu alloys at elevated temp. The first, examples of which are Cu–Cr at 400°–500° C. up to 5% Cr, Cu–Ca at 400°–500° C. up to 4% Ca, Cu–NiAl at 400°–500° C. up to 15% NiAl, shows that relative strength increases in every case with increase of alloying element. The second, examples of which are Cu–Zn at 350°–500° C. up to 48% Zn, Cu–Si at 400°–500° C. up to 7% Si, Cu–Sb at 400°–500° C. up to 15% Sb, Cu–Be at 400°–500° C. up to 5% Be, &c., shows that although a progressive increase of relative strength with increase in alloying element is maintained at 20° C., at 500° C., the curve rises to a max. at the optimum concentration of the α solid soln. and then decreases. The third, examples of which are Cu–Al at 500° C. up to 20% Al, Cu–Sn at 400°–500° C. up to 32·5 Sn, &c., shows that whereas the 20° C. curve is much the same as in the other two cases, the 500° C. curve takes on an S-form with a max. in the α solid soln. range followed by a min. and then another increase.—W. J. K.

The "Fictitious Value" in Special Binary [Copper] Alloys and Their [Industrial] Applications. J. Cournot (*Cuivre, Laitons, Alliages*, 1951, (1), 43–46).—A reminder of the indust. importance of the Guillet theory, first propounded in 1905, of the fictitious values in Cu–Zn (and similar binary Cu alloys such as Cu–Al) in which the addn. of small amounts of certain other metals capable of forming solid soln. was shown to displace the boundary lines between the phase fields α, α + β, and β, thereby exerting effects on the properties, particularly in the α + β range, similar to changes in the Zn content. The use of the "coeff. of equivalence" worked out by G. enables proportions of the added metals to be expressed in terms of Zn; thus 1% Al can replace 6% Zn, based upon the following "coeff. of equivalence": Si +10, Al +6, Sn +2, Fe +0·9, Cd +0·7, Mn +0·5, Co −1·0, Ni −1·2. A number of examples are given showing the appn. of the theory to brasses contg. addn. of Ni and Al, as well as some compound alloys contg. Ni, Mn, Fe, and Sn.—W. F. H.

***The More Accurate Determination of the Equilibrium Diagram of the System Iron–Chromium–Carbon.** B. G. Livshits and K. V. Popov (*Doklady Akad. Nauk S.S.S.R.*, 1950, **70**, (4), 633–635).—[In Russian]. The equilibrium diagram of the Fe–Cr–C system has been more accurately determined. Chem. and X-ray methods were applied to the carbides separated from the steels by an electrolytic method. The steels were melted in an induction furnace and annealed at 700° C.; those with high Cr content were very slowly cooled, especially in the region 600°–400° C. An isothermal cross-section of the diagram below the critical temp. is given.—Z. S. B.

***The Mechanism of Magnetic Jumps [in Iron–Nickel].** T. Hofbauer and K. M. Koch (*Z. Physik*, 1951, **130**, (4), 409–414).—The magnetization of rolled Fe–Ni alloy sheet specimens was investigated in the presence of an auxiliary field which was smaller and had a higher frequency than the main magnetizing field. The specimens had a preferred direction of magnetization. The auxiliary field was found to initiate and propagate magnetic discontinuities (Barkhausen jumps), and also to increase the saturation magnetization and the remanence. 3 ref.—J. W. C.

***Constitution of Iron–Nickel–Aluminium Alloys for Permanent Magnets.** Yu. Skakov (*Doklady Akad. Nauk S.S.S.R.*, 1951, **79**, (1), 77–80).—[In Russian]. S. studied alloys contg. 33–70 at.-% Fe in the quasi-binary system NiAl–Fe. The phase rich in NiAl (β′) was separated electrolytically from an alloy cooled at 15° C./hr. from 1250° C. Its compn. (~30 at.-% Fe) agreed well with the X-ray data of Bradley and Taylor (*Proc. Roy. Soc.*, 1938, [A], **166**, 353; *M.A.*, **5**, 474), and corresponded to equilibrium at 850° C. Heating for 800 hr. at 650° C. reduced the Fe content of the NiAl phase to 10 at.-%. The suggestions of Snoek (*Physica*, 1936, **6**, 321; *M.A.*, **6**, 506) and Ivanov (*Izvest. Sekt. Fiziko-Khim. Anal.*, 1949, **19**, 503) that at low temp. the (β + β′) region extends from the Fe corner to NiAl were confirmed. On slow cooling below 800°–850° C. the sepn. of Fe from ordered NiAl phase is sharply retarded. In all the alloys studied the transformations are similar: on cooling below 875°–900° C. the solid soln. breaks down into almost pure Fe and NiAl-base solid soln. In the 70 at.-% Fe alloy, the Fe-rich β phase predominated; in the other alloys, the NiAl phase (β′). Electron micrographs showed that in alloys contg. 50 at.-% Fe, the precipitate was in the form of thin plates, but in the 70 at.-% Fe alloy the precipitated NiAl particles were spheroidal. On continuous cooling from 1200° C. (at various speeds), alloys contg. >50% Fe attained high coercivity ($H_c \cong 500$ Oe.), but with the 70% alloy, $H_{c\ max.}$ was only ~70–80 Oe. S. concluded that the NiAl matrix was necessary for high coercivity. The effect of annealing at 850° and 750° C. on the structure of the 50% alloy quenched from the solid-soln. range was studied. Pptn. had already occurred after 10 min. at 750° C., when $H_c = 210$ Oe. (pptn. took place throughout the grains; only in alloys contg. <40 at.-% Fe was there a tendency for preferential pptn. of the Fe phase at the grain boundaries). The thickness of the precipitated plates on annealing at 850° C. was <200–300 Å. after 30 min. ($H_c = 140$ Oe.), ~500–600 Å. after 10 hr. ($H_c = 40$ Oe.), and 1000–1500 Å. after 200 hr. ($H_c = 30$ Oe.). The structure of the continuously cooled alloys was essentially similar to that of alloys annealed for max. H_c. The Fe-phase plates were ~0·1 μ long × ~0·01 μ broad × some tens of interatomic distances thick. This disproves the "diffusion hardening" hypothesis of Snoek ("Probleme der technischen Magnetisierungskurve", 1938, p. 73) and verifies that of Livshits (*Trudy Mosk. Inst. Stali*, 1941, (18)) concerning the heterogeneity of Fe–Ni–Al alloys in the high-coercivity condition. X-ray analysis showed that in alloys contg. 50 at.-% Fe the lattice spacing after 800 hours' annealing at 650° C. ($H_c = 106$ Oe.) was 15% less than that of the same phase after electrolytic sepn. This is equivalent to a stress of ~100 kg./mm.². After 100 hours' annealing at 850° C. ($H_c = 35$ Oe.), the difference is negligible. S. concludes that the high coercivity of Fe–Ni–Al alloys is due to the formation of isolated, uniformly-stressed, anisotropically-shaped, dispersed Fe-phase precipitate within the weakly magnetic NiAl matrix.—G. V. E. T.

***New Iron–Palladium and Nickel–Palladium Magnetostriction Alloys.** Z. I. Alizade (*Doklady Akad. Nauk S.S.S.R.*, 1950, **73**, (1), 79–81; *C. Abs.*, 1951, **45**, 6984).—[In Russian]. The alloys Fe–Pd and Ni–Pd were prepared by melting the components in a H.F. vacuum furnace, followed by long annealing in vacuum at 950° C., and they were rolled into strips at the same temp. A control sample of 99·985% pure Ni was also prepared. The samples were then annealed in vacuum at 1005° C. for 10 hr. and cooled to room temp. at the rate of 200°–210° C./min. The magnetostriction was measured by the method of wire tensometers; for the 60:40 Fe–Pd alloy the magnetostriction $\lambda_s = +70 \times 10^{-6}$. For pure Ni $\lambda_s = -34 \times 10^{-6}$, for the alloy contg. 62·25% Ni and 37·75% Pd, $\lambda_s = -63 \times 10^{-6}$. The saturation magnetization of these 2 alloys is given in graphs. The sp. resistance at 20° C. was found to be $\rho_{Fe-Pd} = 40$ μΩ-cm., $\rho_{Ni-Pd} = 26$ μΩ-cm.

***The System Iron–Phosphorus–Cobalt.** Josef Berak (*Arch. Eisenhüttenwesen*, 1951, **22**, (3/4), 131–135).—The portion of the ternary system Fe–P–Co bounded by the planes Fe–Fe_2P–Co_2P–Co was studied, and an equilibrium diagram was constructed. Armco Fe (0·01% C), granular Co (99·4% Co), and pure violet P were melted in 20-g. heats in Pythagoras crucibles. Master alloys with 26·4% P in Fe and 23·4% P in Co were made by melting the pure metal under purified N and adding compressed P lumps. In all heats, the temp. never exceeded 100° C. above the liquidus of the projected alloy. Rapid melting and mixing, as well as the above precautions, kept P losses to a min. Supercooling was prevented by stirring or inoculation. Thermal analysis was carried out at cooling rates of 0·5°–1·0° C./min.; metallographic and X-ray examinations were also performed to help to establish a reliable diagram. Fe_2P and Co_2P form two series of solid soln., separated by a narrow two-phase field. The compound Co_3P does not occur in this system; an equilibrium line from Fe_3P in the direction of the compn. Co_3P extends only as far as 33% Fe. The solid soln.

$(Fe,Co)_3P$ is stable between the solidus and 800° C.; below this temp. it decomposes to α and $(Fe,Co)_2P$. There is only a very slight difference in the affinities of Fe and Co for P.
—K. S.

***Contribution to the Study of the Lead–Oxygen System.** Théodore Katz (*Ann. Chim.*, 1950, [xii], **5**, (Jan./Feb.), 5–65).—A comprehensive investigation of the Pb–O system has been made by means of chem. analysis and X-ray diffraction, using a focusing camera. Full details are given of the main method of analysis used (reaction of the oxide with HCl and estn. of the Cl evolved—Bunsen's method), of others examined, and of the X-ray technique. The results show that the following oxides are formed: PbO in the forms PbO_β (yellow, orthorhombic) and PbO_α (red, orthorhombic, pseudo-tetragonal when formed from PbO_β and orthorhombic when formed directly from another oxide); Pb_3O_4 tetragonal; PbO_2; a series of pseudo-cubic solid soln. PbO_n ($1{\cdot}33 < n < 1{\cdot}57$); and $PbO_{1{\cdot}87}$. A theoretical study of the Debye–Scherrer pattern of an orthorhombic pseudo-cubic substance and a discussion on the structure and chem. nature of homogeneous pseudo-cubic solid soln. are given as appendices. 25 ref.—S. V. R.

***The Electrical Properties of the Intermetallic Compound Mg_2Sn.** B. I. Boltaks (*Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, (5), 653–656).—[In Russian]. B. determined the sp. elect. conductivity (σ) from −170° to +400° C., the Hall const. (E), and the thermo-e.m.f. against Cu (α) for a series of alloys in the region of the compound Mg_2Sn. At 20° C. σ is min. exactly at the stoichiometric compn., and increases with excess of either metal. The temp. coeff. of σ is positive in the immediate vicinity of Mg_2Sn, but negative for alloys deviating from this compn. From the temp. variation of E, it was found that the concentration of conductivity electrons varies from 3×10^{18} at −170° C. to 3×10^{19} at +400° C. α has the sign of an electronic conductor, decreasing with rising temp. On the basis of its elect. properties, Mg_2Sn is classed as an impurity semiconductor with a forbidden zone of ~0·2 eV. At compn. removed from the stoichiometric, the semi-conductivity is masked by the normal conductivity of the excess metal.
—N. B. V.

***Magnetic Susceptibility of the Intermetallic Compound Mg_2Sn.** B. I. Boltaks (*Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, (4), 487–490; *C. Abs.*, 1949, **43**, 4528).—[In Russian]. Theoretically, a mixture of Mg and Sn should show a temp.-independent paramagnetism, whereas a heteropolar compound Mg_2Sn should be temp.-independently diamagnetic. Measurements at 20° C. showed Mg–Sn alloys of a compn. very close to Mg_2Sn to be diamagnetic, $10^6\kappa = 0{\cdot}025$; with an excess of either Mg or Sn, the alloys are paramagnetic, κ decreasing slowly with rising temp. between −170° and +400° C. Samples close to the stoichiometric compn. also show decreasing paramagnetism at lower temp., but at 150°–200° C. and above, this changes to diamagnetism, increasing with the temp. The diamagnetism of stoichiometric or nearly stoichiometric Mg_2Sn increases with rising temp., from room temp. onwards. The results are thus incompatible with either of the simple models. The apparent rise of the diamagnetism with the temp. is the result of the simultaneous presence of a temp.-independent diamagnetism and of a paramagnetism that decreases with rising temp., and can be due only to ions with const. magnetic moments, such as Sn^+, Sn^{++}, Sn_2^+, &c.; such ions were detected by mass-spectrography of Mg_2Sn vapour. The bonding in Mg_2Sn is partly heteropolar, partly metallic.

***On the Equilibrium Diagram and Mechanical Properties of the Magnesium–Zinc System.** E. M. Savitsky and V. V. Baron (*Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, (5), 693–696).—[In Russian]. S. and B. determined the hardness of Zn–Mg alloys in the range 70–100% Zn: (*a*) at 20° C., as-cast; (*b*) at 20° C. after hot working and annealing for 20 days; (*c*) as (*b*), but at temp. corresponding for each alloy to 75% of its m.p. on the abs. scale; and (*d*) as (*b*), but at 325° C. for all alloys. Sharp min. in the hardness curves, particularly in curve (*c*), indicated the existence of the compounds MgZn, $MgZn_2$, and $MgZn_5$. Micro-examination confirmed single-phase fields in the regions of these compounds.
—N. B. V.

New Magnesium–Zirconium Casting Alloys. R. J. M. Payne, A. D. Michael, and R. W. Eade (*Magnesium Rev. and Abs.*, 1952, **8**, (4), 173–176).—Reprinted from *Metal Ind.*, 1952, **80**, (6), 103; *M.A.*, **20**, 14.—N. B. V.

Magnesium–Zirconium Casting Alloys Attain High Strength: Weight Ratios. H. J. Millward (*Magnesium Rev. and Abs.*, 1952, **8**, (4), 177–185).—Reprinted from *Amer. Foundryman*, 1951, **20**, (3), 44; *M.A.*, **19**, 615.—N. B. V.

***The Constitution of Manganese-Rich Manganese–Copper–Nickel Alloys.** Ulrich Zwicker (*Z. Metallkunde*, 1951, **42**, (11), 331–335).—Twenty alloys in the range of compn. Cu 0–30 and Ni 0–60% were prepared from electrolytic Mn, Cu, and Ni, by melting under H in a Tammann furnace, part of each melt being cast in a Fe mould and the remainder allowed to solidify in the crucible. After homogenization at temp. of 350°–1000° C., the specimens were studied by metallographic and X-ray techniques, and detn. were made of their hardness and relative workability. From the results equilibrium diagrams have been prepared in the form of isothermal sections at 1000°, 700°, and 500° C., which show: (1) that the heterogeneous region between the cubic and tetragonal form of γ-Mn solid soln. (γ_t) which is common in binary systems with Mn, is perpetuated in the ternary system, and (2) that the following phase fields exist: (*a*) at 1000° C., $\beta + \gamma_t$—in the Mn corner—followed by γ_t, $\gamma_t + \gamma$, and γ; (*b*) at 700° C., α and β—in the Mn corner—$\alpha + \beta + \gamma$, $\beta + \gamma + \gamma_t$, $\alpha + \gamma$, $\gamma + \beta$, an extensive γ region, $\delta + \gamma$, and δ; and (*c*) at 500° C., α, $\gamma + \alpha$, γ, $\gamma + \delta$, and δ. Mn-rich alloys consisting of $\gamma + \gamma_t$ crystals were ductile; the hardness increased with increasing amounts of precipitated β- and α-Mn, and δ(MnNi), and pptn.-hardening could be carried out by quenching from 900°–950° C. and ageing for several hr. at 500°–700° C. The deformation characteristics of specimens originally cast in Fe moulds showed evidence of N contamination resulting from contact with air. Photomicrographs show the typical structures encountered. 10 ref.
—E. N.

***Ferromagnetic Interactions in Manganese Alloys.** L. Castelliz and F. Halla (*Acta Phys. Austriaca*, 1949, **2**, 348–355; *C. Abs.*, 1949, **43**, 4911).—The magnetic susceptibility/g. (χ_g) was determined for ternary alloys prepared by replacing with Ti, Cr, Fe, Co, Ni, or Cu up to 9 at.-% of the Mn in the ferromagnetic ε phase of the system Mn–Sb. A fluxmeter method was used with a max. field of 1300 Oe. With increasing at.-% of replacing metal, at 1000 Oe., χ_g increases for Ni and Cu, remains const. for Cr, first decreases and then increases for Co, and decreases for Fe. A plot of χ_g against at. number for the alloys contg. 1·5 at.-% at 1000 Oe. gives a curve qual. similar to the curve obtained by plotting the at. moment against at. number in a given solvent such as Fe. χ_g decreases from 1·69 for Ti to 1·60 for Co, increases sharply to a max. of 1·82 for Ni, and then falls to 1·72 for Cu. The concentration limits of the ε phase in the system Mn–Sb were determined by X-ray analysis to be 53·3–57·9 at.-% Mn (cf. Honda and Ishiwara, *Sci. Rep. Tohoku Imp. Univ.*, 1917, [i], **6**, 9; *J. Inst. Metals* (Abstracts), 1918, **20**, 326). Susceptibility/concentration curves were determined in and about the ε phase. With decreasing concentration of Mn there is first a slow increase of χ_g to 57·9 at.-% Mn, then a sharp increase in χ_g in the ε phase to a pronounced max. at 53·3 at.-% Mn. Thus, the max. ferromagnetism occurs at the concentration corresponding to the smallest concentration of Mn consistent with the existence of a homogeneous ε phase.

***On the Nature of the β-Phase of the System Nickel–Aluminium.** L. N. Guseva (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (3), 415–418).—[In Russian]. Alloys contg. 43·3–62·7 at.-% Ni were prepared from 99·99% Al and electrolytic Ni in a H.F. furnace in a corundum crucible under a mixture of CaF_2 + NaF as flux. Because of the considerable amount of heat liberated during the formation of the compound NiAl, the furnace was switched off from the beginning of melting until the end of the reaction. Rods ~3 mm. in dia.

and 15–25 cm. long were cast in a porcelain tube, and homogenized by heating at 1100° C. for 4 hr. *in vacuo*. Rods free from surface defects were used for potentiometric measurement of the elect. resistivity (ρ) at 25° and 100° C., and were then broken to see whether cavities were present, were analysed chem., and their structure determined by X-ray analysis, using Co radiation. The lattice const. *a* was calculated from the doublet $(310)\alpha_1\alpha_2$, the powder being prepared in a mortar and then annealed at 600° C. for 30 min. *in vacuo*. Clear resolution of the doublet was obtained. The data obtained confirm Bradley and Taylor's conclusions (*Proc. Roy. Soc.*, 1937, [A], 159, 56; *M.A.*, 4, 241) concerning the boundaries of the β phase, but the max. on the *a*/compn. curve is not at 50 at.-% Ni but at a compn. richer in Al (~49% Ni). The max. on the temp. coeff. of resistivity/compn. curve, and the min. on the ρ/compn. curve, both occur at a similar place. Isaichev and Miretsky (*Zhur. Tehkn. Fiziki*, 1940, 10, 316) reported that at 600° C. the Al–50 at.-% Ni alloy undergoes partial disordering, two b.c.c. lattices with const. differing by 0·04 Å. being present; to determine these lattice const. more accurately, G. has made X-ray measurements on alloys contg. 49·4 and 50·5 at.-% Ni at room temp., 600°, and 900° C. All the photographs indicated the presence of an ordered cubic structure of CsCl type; lines not corresponding to this structure were not observed, and photometric measurement of the intensity of the (100) and (110) lines on photographs taken at 900° C. showed that the ordering had not changed on heating. The lattice const. of Al–49·4 at.-% Ni in the quenched condition was 2·878 Å. (compared with 2·880 Å. in the annealed state); the difference is within the experimental error, and could be connected with the appearance of lattice defects at high temp.—G. V. E. T.

***On the Change of Electrical Resistance and Thermoelectromotive Force in a Longitudinal Magnetic Field in the Alloy Ni_3Mn as a Function of the Amount of Ordered Phase.** R. G. Annaev (*Doklady Akad. Nauk S.S.S.R.*, 1948, 61, (6), 1009–1012).—[In Russian]. Electrolytic Ni and Mn were used to make up the alloy, which was melted in a corundum crucible in a H.F. furnace, homogenized by prolonged heating at 1000° C. in vacuum, and then reduced to wires 1–0·34 mm. in dia. by repeated drawing and annealing. The wires were then heated at 370° C. for 8 different times ranging from 20 min. to 30 hr. in order to produce various amounts of the ordered phase, and the elect. and magnetic measurements were made. From these, diagrams were drawn showing: (1) intensity of magnetization against magnetic field (up to 1500 Oe.); (2) longitudinal galvanomagnetic effect ($\Delta R/R$) against magnetic field; (3) $\Delta R/R$ against intensity of magnetization; and (4) Thomson thermomagnetic effect (change of thermo-e.m.f. in a magnetic field) against temp. difference, using a thermo-element consisting of Ni_3Mn and Cu with the cold junction at 0° C. and the hot junction at temp. up to 480° C., in a saturated magnetic field of 1500 Oe.—N. B. V.

***On the Effect of Plastic Deformation on the Change in Electrical Resistance of the Alloy Ni_3Mn in a Longitudinal Magnetic Field (Thomson Galvanomagnetic Effect).** R. G. Annaev (*Doklady Akad. Nauk S.S.S.R.*, 1949, 64, (1), 45–47).—[In Russian]. Wire specimens of Ni_3Mn (0·46 mm. in dia.) were first annealed *in vacuo* at 900° C. and water-quenched, and then heated at 466° C. for 11 or 20 hr. and rapidly cooled in air. Values of $\Delta R/R$ were determined at room temp. in longitudinal magnetic fields up to ~1100 Oe. on wires stressed by various amounts up to ~50 kg./mm.², which is beyond the elastic limit. At all stresses $\Delta R/R$ first rises very sharply as the magnetic field increases from zero; it reaches a max. at ~100 Oe. and then very gradually decreases with further increase in field strength. At low intensities of magnetization (I), $\Delta R/R \propto I^2$. In a given field, $\Delta R/R$ increases with stress in the elastic range, but begins to decrease once the elastic limit is passed. This is attributed to disordering of the ordered phase during plastic deformation.—N. B. V.

***On the Magnetostriction of Nickel–Manganese Alloys in Longitudinal and Transverse Magnetic Fields.** D. I. Volkov and V. V. Zubov (*Doklady Akad. Nauk S.S.S.R.*, 1950, 71, (5), 863–865).—[In Russian]. V. and Z. checked the second law of even effects as applied to the magnetostriction of Ni–Mn alloys. Electrolytic Ni of purity 99·9% and electrolytic Mn of purity 99·5% were used. Specimens in the form of plates of dia. ~15 mm. and thickness 0·8–1·0 mm., were annealed at 380° C. for 50 hr. and water-quenched. Curves showing the dependence of magnetostriction on the strength of the applied magnetic field for Ni–Mn alloys contg. 3, 6·5, 8·5, 12, 17, 19, and 21% Mn are given; also the nature of the magnetostriction of an alloy near to the compn. Ni_3Mn in longitudinal and transverse applied magnetic fields is discussed. The results showed that the second law of even effects in the usual form, $\lambda_{||} = -2\lambda_{\perp}$ can be applied to Ni–Mn alloys contg. 0–19% Mn, but, in the case of alloys near to Ni_3Mn, $\lambda_{||}$ and $\lambda_{\perp}$ are of the same sign and nearly equal in magnitude, i.e. $\lambda_{||} = \lambda_{\perp}$.—Z. S. B.

***The Equilibrium Diagram Nickel–Silicon.** N. F. Lashko (*Doklady Akad. Nauk S.S.S.R.*, 1951, 81, (4), 605–607).—[In Russian]. Alloys contg. 2, 4, and 7% Si were prepared in a H.F. furnace and cast. The 2% alloy was single-phase; the as-cast 4% alloy was two-phase, but became single-phase on annealing at 1000° C. The 7% alloy (1% impurities) had two phases up to the beginning of melting and had a typical eutectic structure; photomicrographs showed dendrites of inhomogeneous solid soln. surrounded by a white weakly-etched second phase. Heating to 600°–700° C. caused partial soln. inside the dendrites, so that their central bright portions broadened. At higher temp. this broadening increased and the amount of the second phase decreased, most sharply at 1150° C. Melting began at 1150° C. The max. solubility of Si in Ni is thus <7%. The second phase can be isolated by anodic etching; X-ray investigation showed that it has a face-centred lattice of the superlattice type (Cu_3Au), with parameter 3·50 ± 0·005 kX at all annealing temp. The data indicate that the second phase is Ni_3Si; its superlattice persists right up to the melting temp., and the properties do not change. Thus microhardness, measured with M. M. Khrushchov's apparatus, is ~400 H_B (independent of temp.). That of the solid soln. is ~ $222H_B$. On introducing Cr, Ni_3Si is replaced by $Ni_3(Si,Cr)$. The parameter of the alloy containing Si 7, Cr 14%, is 3·513 kX; there is no superlattice.—G. V. E. T.

***On the Dependence of the Magnetic Permeability of Permalloy-Type Alloys on Frequency.** K. A. Goronina (*Doklady Akad. Nauk S.S.S.R.*, 1948, 61, (3), 459–462).—[In Russian].—N. B. V.

***The Effect of Environment on the Stress-Rupture Properties of Metals [Steel and Hastelloy C] at Elevated Temperatures.** O. Cutler Shepard and Willis Schalliol ([*A.S.T.M.*] *Symposium on Corrosion of Materials at Elevated Temperatures*, 1951, 33–38; discussion, 39–41).—See *M.A.*, 18, 355.

***A Thermomagnetic Study of the Carbides of Iron and Nickel [and Nitrides of Nickel].** Roger Bernier (*Ann. Chim.*, 1951, [xii], 6, (Jan./Feb.), 104–161).—A comprehensive study has been made of the carbides of Fe and Ni, of the nitrides of Ni, and of the carbides of Fe–Ni alloys by means of a thermomagnetic technique supplemented by chem. and X-ray analysis. High-purity materials were used, and a detailed account is given of the prepn. of the compounds and their examination. The results show that the carbide of Ni first formed (h.c.p., paramagnetic, richest in C, corresponds to Ni_3C) becomes f.c.c. and ferromagnetic on heating *in vacuo* at 210° C., when the C atoms occupy the face-centre positions; the nitrides of Ni first formed (h.c.p., paramagnetic) become f.c.c. and ferromagnetic on heating *in vacuo* at 190° C.; cementite, both artificial and that present in steel, corresponds to Fe_3C and there is no evidence of the existence of Fe_2C; carburizing of Fe–Ni alloys gives rise to orthorhombic "cementite" type of carbide (0–40% Ni), two co-existing phases—orthorhombic and h.c.p. (40–70% Ni), and h.c.p. (70–100% Ni).—S. V. R.

***Plutonium Hydride and Deuteride.** I. B. Johns (*U.S. Atomic Energy Commission Publ.*, 1947, (**MDDC-717**), 8 pp.).—Measurements indicated that the hydride had the formula

PuH_3 at 26° C. when the H pressure was 350 mm. Hg. The ratio of H : Pu decreased as the pressure was reduced and was 2·892 at 2·4 mm. Hg. Isothermal molecular ratio (H : Pu)/pressure measurements indicated that the first stage of H adsorption was the formation of PuH_3; at higher molecular ratios than two, a solid soln. of PuH_3 in PuH_2 was formed. Heats of reaction are given for PuH_2 and the solid soln. of PuH_3 in PuH_2. Replacement of H by 99% D had little effect on the results.—J. W. T.

***The Internal Friction of Molten Potassium Amalgam.** J. Degenkolbe and F. Sauerwald (*Naturwiss.*, 1950, **37**, (23), 539).—The viscosity of molten K amalgam has been measured in a high-vacuum viscometer. The results show, possibly for the first time, a distinct max. in the viscosity/concentration isotherm. It is concluded from this and other evidence that melts of K amalgam have the character of intermetallic compounds.—S. V. R.

***The Reflecting Power of Certain Alloys of Silver in the Near Ultra-Violet.** M. M. Noskov and G. P. Skornyakov (*Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, (6), 809–811).—[In Russian]. Alloys of Ag with $\geq$5% Sb, Sn, or Pd were prepared, the first two in an arc furnace in C crucibles, and the Ag–Pd alloy in quartz under a steady vacuum in a resistance furnace. The alloys were annealed and polished, and samples taken for detn. of elect. conductivity. The min. in the reflecting power (cf. Al)/wave-length curve is shown to be at 320 μμ for pure Ag, but this is shifted to 310 μμ for Ag–Pd and 300 μμ for Ag–Sn alloys. Increase of alloying element causes the shift of the min. in the reflective power in approaching the region of shorter waves according to a linear law.

—W. J. K.

***Thermal Conductivity of Silver–Cadmium Alloys from 100° to 400° C.** H. W. Deem and H. R. Nelson (*U.S. Atomic Energy Commission Publ.*, 1951, (**BMI-77**), 12 pp.).—The thermal conductivities of Ag–Cd alloys contg. 5–36% Cd were measured by a steady-heat-flow method in the temp. range 100°–400° C. The values ranged from 0·85 to 0·95 cal./cm.²/cm./°C./sec. at 0% Cd to 0·3–0·35 cal./cm.²/cm./°C./sec. at 40% Cd. An alloy contg. 1·7% Cd was found to have a const. thermal conductivity over the temp. range 100°–400° C.—J. W. T.

***Quarterly Progress Report No. 8 on the Development of the Physical and Chemical Properties of the Sodium–Potassium Alloys.** C. T. Ewing, R. E. Seebold, J. A. Grand, and H. B. Atkinson, Jr. (*U.S. Atomic Energy Commission Publ.*, 1948, (**NRL-C/3330**), 8 pp.).—A comparative, steady-state method is described for the detn. of thermal conductivity of Na–K alloys, and a description of a modified calorimeter for sp. heat measurement is included. The surface tension of Na is given as 71 dynes/cm. at 102° C. and that of K as 30·7 dynes/cm. at 102° C., as measured by a max. bubble-pressure method.—J. W. T.

***A Study of the Paramagnetic Susceptibility of Alloys of the Transition Metals with Tellurium.** F. M. Gal'perin and T. M. Perekalina (*Doklady Akad. Nauk S.S.S.R.*, 1949, **69**, (1), 19–22).—[In Russian]. Alloys of Te with V, Cr, Co, and Ni were prepared by heating *in vacuo* the fine, well-mixed powders of the metals pressed into cylinders. Their paramagnetic susceptibilities were measured, using a modified Sucksmith apparatus. The alloys were also examined by X-ray and magnetic methods. CrTe, CoTe, and NiTe had the NiAs-structure. All Cr–Te alloys were ferromagnetic; those contg. <50% Te had a Curie point at 91° C. and were mixtures of Cr and CrTe; those with >50% Te were solid soln. and had Curie points varying with compn. Cr–Te alloys contg. 50, 52, 54, and 56% Te had the same paramagnetic susceptibility above the Curie point (345° C.), the dependence of susceptibility on temp. obeying the Curie–Weiss law; those contg. more Te follow this law, but have different Curie points. The experimental value of $\mu_{eff.}$ for the alloy contg. 50% Te agrees well with that expected from a compound formed by combination of two unequal *p*-electrons from Te with two *d*-electrons from Cr. A Ni–Te alloy contg. 50% Te had $\mu_{eff.}$ independent of temp., as would be expected if two *d*-electrons from Ni combine with two *p*-electrons from Te, the paramagnetism being due only to free electrons. The magnetization of VTe varied with temp., and the experimental curve was as expected from a compound with one unpaired electron. The magnetization of CoTe also varied with temp.; the alloy may be antiferromagnetic.—Z. S. B.

[Discussion on a Paper by H. R. Ogden, D. J. Maykuth, W. L. Finlay, and R. I. Jaffee:] Mechanical Properties of High-Purity Titanium–Aluminium Alloys. —— (*J. Metals*, 1953, **5**, (11), 1561–1562).—See *M.A.*, **20**, 759.

***Investigations into the System Titanium–Antimony.** H. Nowotny and J. Pesl (*Monatsh.*, 1951, **82**, 336–343; *C. Abs.*, 1951, **45**, 6984).—The system Ti–Sb has been studied up to 60 wt.-% Ti by X-rays and thermal analysis. It is found that Ti is virtually insoluble in Sb, and that homogeneous phases of compn. $TiSb_2$ and TiSb are formed. The crystal structures of these phases are given. At least one other solid phase richer in Ti is also formed. On the Sb side, the phase diagram resembles that of Cr–Sb.

[Discussion on a Paper by I. Cadoff and J. P. Nielsen:] Titanium–Carbon Phase Diagram. —— (*J. Metals*, 1953, **5**, (11), 1564–1565).—See *M.A.*, **20**, 759.

[Discussion on a Paper by J. L. Taylor and P. Duwez:] Constitution of Titanium-Rich Ti–Cr–Al Alloys at 1800° and 1400° F. [980° and 760° C.]. —— (*J. Metals*, 1953, **5**, (11), 1565–1566).—See *M.A.*, **20**, 840.

***Investigations into the System Titanium–Lead.** H. Nowotny and J. Pesl (*Monatsh.*, 1951, **82**, 344–347; *C. Abs.*, 1951, **45**, 6984).—An X-ray study of the system Ti–Pb shows the formation of only one compound, of compn. Ti_3Pb or Ti_5Pb. Its structure is discussed, with ref. to that of related compounds.

[Discussion on a Paper by D. J. Maykuth, H. R. Ogden, and R. I. Jaffee:] Titanium–Manganese System. —— (*J. Metals*, 1953, **5**, (11), 1566–1568).—See *M.A.*, **20**, 759.

***Electron-Emission Experiments on the Systems Tungsten–Carbon and Molybdenum–Carbon.** Enis Bas-Taymaz (*Z. angew. Math. Physik*, 1951, **2**, (1), 49–51).—A W filament was carburized at 2000° C., and resistance measurements showed it to be W_2C. Thermionic measurements gave a straight Richardson plot. The results with Mo are entirely different; the electron-emission curve, and to a lesser extent the resistance/temp. curve, show marked steps at certain temp. There is some temp. hysteresis, and the reproducibility of the observations suggests that the effects are due to phase changes. This may be a useful method of searching for new high-temp. phases in alloys of rare, high-m.p. metals, and in compounds.—W. M. L.

***Oxides of Transuranium Elements.** D. M. Gruen and J. J. Katz (*U.S. Atomic Energy Commission Publ.*, 1948, (**AECD-1892**), 5 pp.).—The prepn. and study of higher oxides than PuO_2 and NpO_2 were undertaken and, in view of interest in the actinide hypothesis, a comparison of the O systems of the heaviest metals and the rare earths was made. Oxidation was effected by NO_2 or by atomic O. The oxides PrO_2, Tb_4O_7 and TbO_2, Np_3O_8, and $UO_{2\cdot2}$–UO_3 were formed in the range 250°–450° C.; they were of comparable thermal stability, yielding, *in vacuo* at 450° C., Pr_2O_3, Tb_4O_7, U_3O_8, and NpO_2. The dioxides of Pr and Tb have a fluorite structure, while Np_3O_8 is isomorphous with the orthorhombic U_3O_8. Both methods of prepn. gave the same crystal modification of U_3O_8, whence it is suggested that both agents oxidize by a similar mechanism. A separate investigation confirmed the formula Np_3O_8.—J. W. T.

***On the Plasticity of Intermetallic Phases.** E. M. Savitsky (*Doklady Akad. Nauk S.S.S.R.*, 1948, **62**, (3), 349–351).—[In Russian]. Extrusion tests on MgZn, $MgZn_2$, and $MgZn_5$, compression tests at 400° C. on β and γ phases in the Mg–Al system, and microhardness tests at various temp. on Cu–Zn alloys contg. up to 40% Zn, show that all these materials are plastic at elevated temp. Phases of the β type soften more with increasing temp. than do those of the γ type. The rapid increase in plasticity with rise of temp. is thought to be greater than can be accounted for simply by the increasing amplitude of vibration of the atoms, and some change in the lattice of the intermetallic phases is presumed.—N. B. V.

The Fundamental Bases of the Alloying of Metals Having Strength at Elevated Temperatures. K. A. Osipov (*Doklady Akad. Nauk S.S.S.R.*, 1948, **60**, (9), 1535–1538).—[In Russian]. An explanation of the properties of solid soln. based on α- and γ-Fe is attempted in terms of the $N(E)$ curves. —N. B. V.

***On the Relation Between Melting Temperature and the Strength of Metallic Alloys at Elevated Temperatures.** K. A. Osipov (*Doklady Akad. Nauk S.S.S.R.*, 1948, **61**, (1), 71–74).—[In Russian]. Mech. tests carried out at 1100° C. on solid-soln. Fe–Cr, Fe–Ni, Co–Ni, and Mn–Ni alloys quenched from 1150° C. showed a correlation between strength at elevated temp. and the solidus curve in each case.—N. B. V.

***Magnetic Viscosity and the Part Played by the Displacement of Domain Boundaries in the Process of Remagnetization of High-Coercivity Alloys.** N. Bulgakov and E. Kondorsky (*Doklady Akad. Nauk S.S.S.R.*, 1949, **69**, (3), 325–328).—[In Russian]. The magnetic viscosity in the alloys (1) Ni 24, Al 72, Cu 1·5%, remainder Fe, after various thermal treatments causing different decompn. of the solid soln. and (2) Ni 13, Al 8, Cu 3, Co 24%, remainder Fe, cooled in a magnetic field and also given various thermal treatments, was studied. Experiments were carried out at various temp. The time interval, T, from the moment of appn. or change of the magnetic field to the moment of measurement of the change of magnetization of the specimen varied between the limits 2×10^{-3} to 81 sec. For $T = 15 \times 10^{-3}$ sec. a Helmholtz pendulum breaker with a ballistic galvanometer was used for the measurements; for $T = 0{\cdot}1$ sec., a manually operated fluxmeter. The measurements were taken on the downward branch of the hysteresis loop and also at the beginning of the magnetization curve. In the latter case the specimens were carefully demagnetized before the experiment. The influence of eddy currents and auto-induction was shown theoretically to be unimportant. The results indicate that the high viscosity which occurs in relatively magnetically soft materials also occurs in high-coercivity alloys. It is concluded that the movement of domain boundaries plays an important part in the remagnetization of such alloys, which is contrary to the views currently accepted. B. and K. also show theoretically that the growth of thermally nucleated domains of favourable orientation is possible at fields greater than the critical value. A purely rotational process can take place only in very fine powders.—Z. S. B.

***On the Constant of Magnetic Anisotropy of High-Coercivity Alloys.** N. V. Bulgakov (*Doklady Akad. Nauk S.S.S.R.*, 1949, **69**, (4), 521–522).—[In Russian]. B. determined the anisotropy const. of a spherical single crystal of an alloy contg. Al 8, Ni 12, Co 24, Cu 3%, remainder Fe. Although the alloy has a cubic structure, the crystal had two directions of easy magnetization at right angles to one another. Measurements were made of the mech. moments on the single crystal when the direction of easy magnetization was at various angles to the direction of the applied field. When the axis of rotation of the specimen was through a dia. at right angles to both directions of easy magnetization, the const. of anisotropy was $1{\cdot}63 \times 10^5$ ergs/c.c. When the axis of rotation was one of the directions of easy magnetization, the const. of anisotropy was $2{\cdot}3 \times 10^5$ ergs/c.c. The discrepancy in the two values is due to the approx. formulæ used. The coercive force calculated from the value $1{\cdot}63 \times 10^5$ ergs/c.c. was 295 Oe., the theoretical value being 225 Oe. The discrepancy in these values is due to movement in the domain boundaries which was not taken into account. —Z. S. B.

***On the Internal Demagnetization Factor of High-Coercivity Alloys.** N. V. Bulgakov (*Doklady Akad. Nauk S.S.S.R.*, 1950, **70**, (2), 205–206).—[In Russian]. The internal demagnetization factor of three high-coercivity alloys which had been given various heat-treatments were studied and values are given.—Z. S. B.

***Optical Properties of Metallic Alloys.** S. V. Vonsovsky, A. A. Smirnov, and A. V. Sokolov (*Doklady Akad. Nauk S.S.S.R.*, 1951, **80**, (3), 353–356).—[In Russian]. According to the Drude–Zener theory, the elect. conductivity σ and the dielect. const. ε are given by $\sigma = Ne^2\gamma/[2\pi m^*(\nu^2 + \gamma^2)]$ and $\varepsilon = 1 - (2\sigma/\gamma)$, where the free path (relaxation) time $\tau = 1/(2\pi\gamma)$ and m^* is the effective mass of the electron in the lattice. If this be extended to a binary disordered alloy in which the concentrations of the components are c and $1 - c$, $\gamma = c\gamma_1 + (1 - c)\gamma_2 + Dc(1 - c)$, where $\tau_1 = 1/(2\pi\gamma_1)$ and $\tau_2 = 1/(2\pi\gamma_2)$ are the relaxation times for the scattering of the electrons on the atoms of the first and second kinds, resp., and D corresponds to the relaxation time for the residual resistance. This gives $\sigma = \{Ne^2/2\pi m^*\} \cdot [Dc(1 - c) + c\gamma_1 + (1 - c)\gamma_2]/\{\nu^2 + [Dc(1 - c) + c\gamma_1 + (1 - c)\gamma_2]^2\}$ and $\varepsilon = 1 - \{2\sigma/[Dc(1 - c) + c\gamma_1 + (1 - c)\gamma_2]\}$. A reflectivity/compn. curve has been computed for low frequencies (infra-red region) using these formulæ and the following data: $\nu = 10^{14}$ sec.$^{-1}$, $\gamma_1 = 4 \times 10^{12}$ sec.$^{-1}$, $\gamma_2 = 5{\cdot}4 \times 10^{12}$ sec.$^{-1}$, and $D = 6 \times 10^{14}$ sec.$^{-1}$. The curve is a catenary with min. value (~89) at 50 at.-%. This cannot be compared with experimental results because of the lack of data, but Bergman and Guertler's work on Cu–Ni alloys (*Z. techn. Physik*, 1935, **16**, 235; *M.A.*, **3**, 3) indicates a tendency towards catenary curves as the wave-length is increased. Formulæ are also derived for partially ordered alloys with b.c.c. lattice (cf. Sergeev and Chernikhovsky, *Zhur. Eksper. Teoret. Fiziki*, 1934, **4**, 235; *M.A.*, **2**, 93; Sergeev, *ibid.*, 1938, **8**, 948; *M.A.*, **10**, 135). The formulæ for σ and ε in the vicinity of the order/disorder transformation temp. reduce to expressions which are almost analogous to corresponding formulæ for ferromagnetic metals with the long-range order parameter η replacing the relative magnetization y. It is thought that the opt. properties of ordered alloys in the visible part of the spectrum must exhibit anomalies at temp. below the transformation point.—G. V. E. T.

Solid Solutions of Metallic Compounds. I. I. Kornilov (*Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, (4), 597–600).—[In Russian]. Continuous solid soln. can be formed between metallic compounds in the following cases: (1) between compounds with ordered structures formed by transformations of continuous solid soln. of metals; (2) between daltonide compounds formed during the crystn. of mixtures of metals; (3) between berthollide compounds of variable compn.; and (4) between daltonide and berthollide compounds. Necessary conditions for the formation of continuous solid soln. are that: (1) the crystal lattices of the compounds are of the same type; (2) their chem. bonds are of the same type; (3) the atoms of the components from which the compounds are formed are similar; and (4) the compounds have a common constituent element, isomorphous structure, and the same stoichiometric compn. Many examples are given to illustrate these rules.—G. V. E. T.

***A Study of the Refractory Borides.** Leo Brewer, Dwight L. Sawyer, D. H. Templeton, and Carol H. Dauben (*J. Amer. Ceram. Soc.*, 1951, **34**, (6), 173–179).—The phases present in the binary systems of B with Cc, Ti, Zr, Nb, Ta, Mo, W, Th, and U were determined by X-ray examination of samples prepared by heating various mixtures of B and the resp. metal to elevated temp. in an atmosphere of A. The following phases are shown to exist: W_2B, $WB_{0{\cdot}92-1{\cdot}02}$, $WB_{2{\cdot}0-2{\cdot}12}$, Mo_2B, $MoB_{0{\cdot}95-1{\cdot}06}$, $MoB_{2{\cdot}33}$, TaB_m, Ta_2B, TaB, Ta_3B_4, $TaB_{1{\cdot}78-2{\cdot}57}$, NbB_m, NbB_n, NbB, Nb_3B_4, $NbB_{2\pm x}$, ZrB_2, TiB_2, CeB_4, CeB_6, ThB_4, UB_2, and UB_4. The isomorphism of these compounds is indicated. Mo and W borides have very high m.p., but are less stable towards reduction than the other borides. TaB and NbB, both melting at temp. >2000° C., appear to be the most promising refractory borides for highly reducing conditions.—N. B. V.

Crystal Chemistry of the Metal Carbides and Its Importance in Metallurgy. W. Epprecht (*Chimia*, 1951, **5**, (3), 49–60).—The influence of C, now recognized to be present as carbide, in Fe and steel is first discussed, followed by an investigation into the chem. and phys. properties of other metal carbides as revealed by X-ray-diffraction and back-reflection technique. Sections are devoted to the principal carbide-forming metals, Ti, Nb, Ta, V, W, Mo, Cr, Mn, Fe, Co, Ni, and Si, and their modes of formation and compn. in pure metals and various

alloys are discussed. It is suggested that the diffusion of the atoms of the individual constituents of an alloy is the determining factor in the formation of carbide crystals in solid metal and that the chem. behaviour of the metal towards C is of minor importance, the space requirements of the metal atoms being of greater weight. As diffusion itself is a product of temp. and time, both these factors must be taken into account in any study of carbide formation. 35 ref.
—W. F. H.

***Study of Metal-Ceramic Interactions at Elevated Temperatures.** F. H. Norton and W. D. Kingery (*U.S. Atomic Energy Commission Publ.*, 1951, (NYO-3136), 13 pp.).—The tendency for a reaction to occur was studied in pairs made up from the oxides Al_2O_3, ZrO_2, MgO, TiO_2, ThO_2, and BeO and the metals Zr, Ti, Ni, Mo, Si, Be, and Nb; the temp. studied were 1400°, 1600°, and 1800° C. The results are classified as no, slight, and pronounced reaction. A number of thermodynamic calculations of possible reactions in these systems were made, neglecting effects due to solid and liquid soln. Similar calculations have been carried out for metal–metal carbide, –metal nitride, and –metal sulphide systems. An apparatus is described for studying the surface tension and the wettability of liq. metals simultaneously. Fe and Ni are non-wetting on the oxides mentioned above; Si wets the oxides. Fe, Ni, and Si tend to wet the carbides. Wetting was generally accompanied by interfacial reaction. The surface tension of Fe–Ni alloys decreases gradually from 1580 ergs/cm.^{2} for Ni to a value of 1420 ergs/cm.^{2} for Fe in H.—J. W. T.

How To Evaluate High-Temperature Performance of Materials. L. B. Pfeil (*Materials and Methods*, 1953, **37**, (3), 79–84).—Condensed from *Schweiz. Archiv angew. Wiss. Techn.*, 1952, **18**, 88; *M.A.*, **20**, 471.—R. P. H. F.

***Surface Tension of Eutectic Alloys.** Yu. A. Klyachko and L. L. Kunin (*Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, (1), 85–86).—[In Russian]. The surface tensions of the pure metals Pb, Sn, and Bi, of their binary eutectics, and of alloys with compn. closely approximating to the eutectics, were determined at various temp. up to 340° C. The following conclusions were arrived at: (1) On considerably superheating above the crystn. temp. the eutectic point does not lie on the curve of surface tension versus compn. (2) At a superheat just above the crystn. point the surface tension of the eutectic and alloys adjacent falls sharply. The surface tension of eutectic alloys close to the crystn. temp. is less than that of each of the components of the alloy at the same superheat. (3) The surface tension of eutectic alloys in the region of, for example, 100° above the crystn. point possesses a positive temp. coeff. The theoretical implications of these results are discussed.—W. J. K.

The Quantitative Micrographic Analysis of Ternary Alloys. Salvatore Amari (*Met. Ital.*, 1951, **43**, (1), 6–12).—After a detailed theoretical investigation of the triangular constitutional diagrams of ternary alloys, A. considers the applicability of quant. micrographic analysis to this type of alloy.
—I. S. M.

Rate of Growth of the Nucleus of a New Phase During the Isothermal Decomposition of a Solid Solution. B. Ya. Lyubov (*Doklady Akad. Nauk S.S.S.R.*, 1950, **72**, (2), 273–275; *C. Abs.*, 1950, **44**, 10426).—[In Russian]. A theoretical expression was derived to account for a slower rate of growth of small nuclei than that given by the diffusion rate of the solute. This slow rate is especially noticeable in the pptn. of a new phase from a supercooled hypoeutectoid solid soln. having a different compn. and structure. Two processes are necessary for the growth of such nuclei: re-formation of the solute lattice and movement of solute atoms across the nucleus interface. In the initial stage of nucleus growth, when its size is just above the critical size, change in the solvent occurs slowly and the solute concentration at the surface of the nucleus is almost unchanged. However, the equilibrium concentration of such a nucleus is large. At this stage the rate of growth is wholly determined by the kinetics of lattice deformation. Beyond a critical nucleus size the rate of growth is determined by diffusion.

Mechanism of Diffusion in Substitutional Solid Solutions. T. A. Lebedev (*Doklady Akad. Nauk S.S.S.R.*, 1949, **65**, (2), 163–165; *C. Abs.*, 1950, **44**, 9760).—[In Russian]. A mechanism wherein the displacement of an element in a substitutional alloy is brought about in the act of rotation of a complex of atoms is used to account for the diffusion, in particular in the difficult instance of alloys of stoichiometric compn., e.g. $CuAl_2$, FeSi, &c. Calculations on a model show that the perturbation of the lattice produced by such a rotation is one-tenth or one-twelfth that caused by simple displacement of single atoms. The activation energy of rotation is lowered considerably if the complex involved is not one atomic layer thin, but represents a "packet" of several layers. That rotational can give rise to a unidirectional flow of a given atomic species is determined by the fact that a concentration gradient favours preferential rotation in a given sense. Rotations also account for back diffusion, which is brought about in the same way as the direct diffusion.

[Discussion on a Paper by L. C. C. da Silva and R. F. Mehl:] Interface and Marker Movements in Diffusion in Solid Solutions of Metals. —— (*J. Metals*, 1951, **3**, (11), 1060–1062).—See *M.A.*, **19**, 115.

Segregation in Regular Ternary Solutions.—II. J. L. Meijering (*Philips Research Rep.*, 1951, **6**, (3), 183–210).—Cf. *ibid.*, 1950, **5**, 333; *M.A.*, **19**, 184. Math. A method for the calculation of tie-lines is described. The solubility curves of a pure solid component and their interference with a miscibility gap are also treated, and some observations are made on multicomponent systems.—N. B. V.

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3 — STRUCTURE

(Metallography; Macrography; Crystal Structure.)

[For all abstracts on the constitution of alloy systems, including X-ray studies, see 2—Properties of Alloys.]

***A New Surface Structure on Strained Aluminium.** Heinz Wilsdorf and Doris Kuhlman-Wilsdorf (*Naturwiss.*, 1951, **38**, (21), 502).—The structure of slip lines in strained polycryst. and single-crystal 99·99% Al has been examined under the electron microscope. An improved replica technique has been developed, involving the sputtering of SiO_2, which has the advantage that the surface of strained specimens is faithfully reproduced. Extremely fine surface markings are revealed by shadow casting with W oxide. The existence of a fine structure within the slip bands has been confirmed, and in addn. a fine line or step structure has been found between slip bands. These line structures—termed "elementary structures"—are ‖ existing slip bands; they become clearer with increased strain, and have been observed in crystals contg. no slip bands. The elementary structure is considered to be an early stage of slip-band formation.
—S. V. R.

***An Electron-Microscope Study of the Development of Fatigue Failures [in Aluminium, Brass, and Iron].** W. J. Craig (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 877–889).—See *M.A.*, **20**, 765.

[Discussion on a Paper by H. C. Chang and N. J. Grant:] Grain-Boundary Sliding and Migration, and Intercrystalline Failure [of Aluminium] Under Creep Conditions. —— (*J. Metals*, 1953, **5**, (11), 1579–1581).—See *M.A.*, **20**, 763.

***Calculation of the Intensity of Diffuse Scattering of X-Rays for Ageing [Aluminium] Alloys.** Yu. A. Bagaryatsky (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (1), 45–48).—[In

Russian]. B. considers that during the natural ageing of Al alloys regions of atoms with a slightly distorted lattice are formed inside the lattice of the solid soln.; this leads to the appearance of a supplementary diffuse background in the X-ray scattering pictures (cf. *Zhur. Tekhn. Fiziki*, 1950, **20**, 424; 1948, **18**, 827; *M.A.*, **19**, 647, 648; also Elistratov *et al.*, *Doklady Akad. Nauk S.S.S.R.*, 1949, **68**, 1017; *M.A.*, **19**, 192). The proposed method for calculating the intensity of this diffuse scattering is explained by use of a particular example, a chain of atoms with a " fault " repeated along it according to some law. This example can be used to explain diffuse scattering observed with Al–Mg alloy. It is shown that in alloys contg. chem. different atoms of equal scattering ability it is not necessary to attribute the diffuse scattering to small regions with the lattice of the precipitating phase. The method can also be used to calculate the intensity of the diffuse background in substitutional solid soln.; B. shows that this will be a max. when the scattering angle, $\phi \approx \lambda/\gamma_{mean}$, where λ is the wave-length and γ_{mean} the mean, most probable distance between the dissolved atoms for an ideal solid soln. This is confirmed by the experimental data for Au–Ag alloys (Guinier, *Proc. Phys. Soc.*, 1945, **57**, 310; *M.A.*, **12**, 321). As an example of the use of the proposed method, B. gives curves for the distribution of the intensity of the diffuse scattering for Al–Cu alloy according to various hypotheses about the structure of the aged alloy: (i) that the principal feature is the displacement of neighbouring planes and not large local concentrations of Cu atoms (Jagodzinski and Laves, *Z. Metallkunde*, 1949, **40**, 296; *M.A.*, **17**, 639); (ii) that of Guinier (*Nature*, 1938, **142**, 569; *M.A.*, **5**, 589; *Mesures*, 1946, **11**, 305) and of Preston (*Proc. Roy. Soc.*, 1938, [A], **167**, 526; *M.A.*, **5**, 590) concerning the formation during natural ageing of layers of Cu atoms in 2–3 atomic layers (001) accompanied by some displacement of these atomic planes; and (iii) the appearance of a superstructure of period $2a$ in regions where the Cu atoms collect. Curves (ii) and (iii) agree with the experimental data. Certain assumptions were made in the calculations.—G. V. E. T.

***X-Ray Data on the Ageing of the Aluminium–[4%] Copper Alloy.** Yu. A. Bagaryatsky (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (2), 261–264).—[In Russian]. Data on the diffuse scattering of X-rays by Al–4% Cu alloy enable a number of questions to be answered. On a monochromatic photograph of the naturally aged alloy there are no two-dimensional diffraction spots with 30. and 03. indexes (in the co-ordinates of the reciprocal lattice of the solid soln.; the full stop replaces the non-integral third index κ_3), but spots with 11. indexes are present; hence the two-dimensional diffraction at this stage of the ageing is not produced by thin layers of the θ′-$CuAl_2$ phase. This agrees with Zakharova's conclusions (*ibid.*, 1950, **70**, 55; *M.A.*, **18**, 93) for Al–2% Cu alloy. The observed asymmetric distribution of the intensity of two-dimensional diffraction agrees well with B.'s calculations (*ibid.*, (1), 45; preceding abstract) based on the hypothesis that Cu atoms collect in regions contg. 2–3 atomic layers (001), with some change in interplanar distances. It does not support the suggestion that the displacement of neighbouring planes plays the predominant part. The apparent discrepancy between these conclusions and the results of Buinov and Lerinman (*ibid.*, 1950, **74**, 707, 929), who observed the same formations in both naturally and artificially aged alloys, is that regions of low Cu concentration were etched out, so that the parts contg. collections of Cu atoms and the strained regions of solid soln. around them appear isolated; the atoms in these regions rearrange themselves to form a stable phase, probably θ-$CuAl_2$. Guinier's explanation (*Mesures*, 1946, **11**, 305) for the formation of a superstructure at a certain stage of heat-treatment is not considered satisfactory; B. suggests that the regions with the superstructure consist of 12 atomic layers (001), and the concentration of Cu atoms in them corresponds to the compn. $CuAl_2$; layers Nos. 2, 6, and 10 consist wholly of Cu atoms, 0, 4, 8, and 12 only of Al atoms, and the odd layers contain an average of 1/6 Cu and 5/6 Al atoms. This structure easily rearranges to the θ′-phase, which forms in layers 4c thick interlinked with the lattice of the solid soln. During the growth of the θ′-phase nuclei, c falls from 6·06 to 5·8 Å. In the formation of θ or θ′ phase nuclei, a considerable increase in the elastic energy of the lattice is necessary, and the formation of the bonds at one lattice point causes strain in the surrounding regions, although this is reduced by directed diffusion of Cu atoms to this point. Hence as regards energy, structures in which the Cu atoms collect in 2–3 atomic layers are preferable to those with the max. number of Cu–Al bonds. At higher temp. the Cu–Al bond is weaker and the role of elastic energy is reduced, so that there are a large number of Cu–Al bonds and a more even distribution of Cu atoms throughout the lattice. The mechanism of natural ageing of Al–Cu alloy is thus determined by the large difference in sp. atomic vol. of the solid soln. and the precipitating phase. In Al–Cu–Mg and Al–Ag alloys the difference is small and the ageing mechanism is essentially different.—G. V. E. T.

***Metallography of Commercial Alloys of the Duralumin Type.—III.** Anand S. Sharma (*Trans. Indian Inst. Metals*, 1949, **3**, 279–307).—Cf. *ibid.*, 1948, **1**, (1), 39; 1949, **1**, (2), 11; *M.A.*, **17**, 15, 797. The previous investigations have been extended to the following quaternary systems: Al–Cu–Fe–Mn, Al–Cu–Fe–Si, Al–Cu–Mn–Si, Al–Cu–Mg–Si, Al–Cu–Mg–Fe, and Al–Cu–Mg–Mn. The microstructures of the alloys were examined in various conditions and correlated with hardness measurements made on samples immediately after quenching from the soln. temp. and at intervals during ageing at room temp. and at 160° C. Hardness curves and photomicrographs are presented. The constituents responsible for age-hardening, and effects of the various alloying elements, are discussed.—N. B. V.

***Investigations on Aluminium–Silicon Alloys: A Contribution on the Problem of [the Structure of] Silumin.** Roland Mitsche and Emma-Maria Onitsch-Modl (*Z. Metallkunde*, 1951, **42**, (11), 341–344).—The close relationship which exists between the structures of eutectic Al–Si and Fe–C alloys, and which has led to the development of M.'s " slag-cloud " theory of grain refinement (*Carnegie Schol. Mem., Iron Steel Inst.*, 1934, **23**, 65; *M.A.*, **2**, 220), has been extended to cover hypereutectic alloys. Binary Al alloys contg. 12, 15, and 24% Si were superheated to temp. of 700°–1600° C., and poured into C or cast-Fe moulds, at casting temp. of 700° C. and 800° C. for the 12 and 15% Si and the 24% Si alloys, resp. Observations of the grain structure of the resulting ingots lead to the conclusion that the structures encountered can be adequately interpreted only on the basis of M.'s hypothesis as to the grain-refining effects of the submicroscopic non-metallic particles which are present in such melts. —E. N.

Micrographic Measurement of Grain-Size in Copper and Copper Alloys. J. Hérenguel (*Cuivre, Laitons, Alliages*, 1951, (2), 51–54).—H. shows methods of preparing specimens and taking micrographs for the estn. of particle size in metals, with particular ref. to Cu and its alloys. Electrolytic polishing is followed by treatment with various reagents, chiefly HCl–$FeCl_3$ and HNO_3. Typical micrographs of 70 : 30 brass, treated with different reagents, are shown. A more recent method of chem. polishing in a bath of H_3PO_4 and HNO_3 at 70°–80° C. is also described.—W. F. H.

***The Cubic Texture of Face-Centred-Cubic Metals [Copper and 50 : 50 Nickel–Iron Alloys].** E. Schmid and H. Thomas (*Z. Physik*, 1951, **130**, (3), 293–303).—Experiments on the cold-rolling and annealing of Cu and 50 : 50 Ni–Fe alloy were made to determine the conditions necessary for the prodn. of the [100], (001) cubic recrystn. texture. After very large reductions, the cold-rolled plates showed a third deformation texture, [110], (001), in addn. to the normal textures [112], (1$\bar{1}$0) and [111], (11$\bar{2}$). For Cu, the sharpness of the recrystn. texture increased with increase in the amount of cold reduction from 95 to 99·9%, and then decreased again; the decrease corresponded to the formation of the third rolling texture. Similar results were found for Ni–Fe. Specimens annealed to give a sharp cubic texture and then cold rolled, approximated to the normal rolling texture, though the change was

incomplete even after 95% reduction. Despite the presence of a strong [100], (001) component, such specimens gave very imperfect cubic textures when re-annealed. Two conditions are necessary for the formation of the cubic recrystn. texture: (1) the presence of a considerable amount of the [111], (11$\bar{2}$) texture in the cold-rolled strip and (2) the material must be elastically very anisotropic.—J. W. C.

***The Formation of Facets on Copper Crystals at High Temperature.** Erich Menzel (*Naturwiss.*, 1950, **37**, (4), 166).—A continuation of previous work on the formation of facets—(111) and (001)—on spherical single-crystal specimens of Cu during heating *in vacuo*. Similar experiments on freshly cut specimens have not resulted in the formation of facets, and it is concluded that their presence is associated with preferential oxidation of the crystal surface and subsequent removal of the oxides. Heating in H causes the surface of the crystal to become glass-like, but the facet structure can be regained by repeated strong oxidation. Heating in A or CO_2 causes the (110) and (001) facets to appear; in the case of the CO_2 reflecting planes also appear at the octahedral and dodecahedral poles. The type of chemical used for pre-etching the crystals influences the final appearance. It is considered that the soln. of H in the crystal lattice of the Cu renders the O present inactive—CO_2 is less effective in altering the surface appearance, because of its lower solubility. Experiments on polycryst. Ag have revealed plane-like structures on heating in air which are not formed on heating *in vacuo*.—S. V. R.

[Discussion on a Paper by W. A. Backofen:] Torsion of Copper. —— (*J. Metals*, 1951, **3**, (11), 1062–1064).—See *M.A.*, **19**, 25.

Corrections [to "Crystal Structure of the Ternary Phase Cu_4MgSn"]. E. I. Gladyshevsky, P. I. Kripyakevich, and M. Yu. Teslyuk (*Doklady Akad. Nauk S.S.S.R.*, 1952, **87**, (4), 516).—[In Russian]. See *M.A.*, **20**, 697.—G. V. E. T.

[Discussion on a Paper by L. Guttman:] Crystal Structures and Transformations in Indium–Thallium Solid Solutions. —— (*J. Metals*, 1951, **3**, (11), 1056–1057).—See *M.A.*, **19**, 27.

[Discussion on a Paper by J. S. Bowles, C. S. Barrett, and L. Guttman:] Crystallography of Cubic–Tetragonal Transformations in the Indium–Thallium System. —— (*J. Metals*, 1951, **3**, (11), 1057–1060).—See *M.A.*, **19**, 27.

***An Electron-Diffraction Investigation of the Structure of Electrodeposited Coatings on Iron Single Crystals.** D. J. Evans and M. R. Hopkins (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 229–238; discussion, 245–251).—See *M.A.*, **20**, 408.

[Discussion on a Paper by J. S. Bowles:] Metallographic Study of the Martensite Transformation in Lithium. —— (*J. Metals*, 1951, **3**, (11), 1056).—See *M.A.*, **19**, 28.

[Discussion on a Paper by R. S. Busk:] Lattice Parameters of Magnesium Alloys. —— (*J. Metals*, 1951, **3**, (11), 1067).—See *M.A.*, **19**, 29.

***The Gamma Phase of Manganese. II.—High-Temperature Observations in the Gamma Region [of Binary Alloys with Copper, Gallium, and Germanium].** Ulrich Zwicker (*Z. Metallkunde*, 1951, **42**, (11), 327–330).—Cf. *ibid.*, (8), 246; *M.A.*, **20**, 690. A study of the Mn-rich side of the system Mn–Ge shows that addn. of Ge lower the $\gamma \rightarrow \beta$ transformation temp. of Mn, while raising that of the $\delta \rightarrow \gamma$ transformation from 1148° to 1154° C. (at ~3% Ge), at which temp. a peritectic reaction occurs between the δ phase and the melt contg. 7·75% Ge, to form γ-Mn solid soln., the homogeneity range of which has been determined down to 500° C. With further addn. of Ge, the liquidus decreases to 900° C., the temp. of the peritectic reaction, γ (solid soln.) + melt = $Mn_{3.25}Ge$. When wires of binary Mn alloys, contg. Ge 10·9 and 12·5, Ga 17·6 and 19·2, and Cd 13·3%, were annealed for long periods at 630°–890° C., and examined by high-temp. X-ray-diffraction methods, a f.c.c. structure was always found, thus implying that in the temp. range where it is stable, γ-Mn solid soln. has this type of lattice—and is designated γ_c. The tetragonal form of the γ phase—γ_t—was found only after quenching at rates which exceed the critical rate of cooling for formation of the stable β phase. The $\gamma_t \rightarrow \gamma_c$ transformation is reversible, and γ_t, therefore, can be considered as an unstable modification of Mn. The lattice parameters of the γ_c phase of all the alloys studied had the same temp. coeff. This leads to a calculated value of $a = 3{\cdot}83$ Å. at 1100° C. for the unit cell of the γ_c phase of pure Mn; the corresponding value at room temp.—obtained by extrapolation—is $a = 3{\cdot}69_4$ Å., which gives a cubic cell of vol. equal to that of the tetragonal cell of the γ_t phase. All compn. are in at.-%. 8 ref.—E. N.

[Discussion on a Paper by N. K. Chen and R. Maddin:] Cold-Rolling and Annealing Textures of Molybdenum Single Crystals. —— (*J. Metals*, 1953, **5**, (11), 1569).—See *M.A.*, **20**, 766.

***Structure of Alloys of Nickel with Aluminium in the β-Phase Region at High Temperatures.** L. N. Guseva and E. S. Makarov (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (4), 615–616).—[In Russian]. Alloys contg. 60–66 at.-% Ni quenched from 1340° C. are single-phase and have a tetragonal structure. X-ray analysis of these alloys in the annealed state shows the presence of two phases, $\beta + \alpha'$ (Ni_3Al), in agreement with the equilibrium diagram of Bradley and Taylor (*Proc. Roy. Soc.*, 1937, [A], **159**, 56; *M.A.*, **4**, 241). The quenched alloys have a partially ordered body-centred structure. For the alloy with 60·6 at.-% Ni (Ni_3Al_2), $a = 2{\cdot}663$, $c = 3{\cdot}237$ kX, $c/a = 1{\cdot}125$; $d = 6{\cdot}66$; number of atoms in unit cell = 1·96. For the alloy with 66·6 at.-% Ni (Ni_2Al), number of atoms in unit cell = 2·01. The observed intensities of the reflections in an X-ray photograph of an alloy contg. 60·6 at.-% Ni, quenched from 1340° C., agree satisfactorily with the values calculated for Ni_3Al_2.

—G. V. E. T.

***Crystal-Structure Studies of Plutonium and Neptunium Compounds.** W. H. Zachariasen (*U.S. Atomic Energy Commission Publ.*, 1946, (**MDDC-67**), 6 pp.).—In the hexavalent state U, Np, and Pu are crystal-chem. similar, with a decreasing at. size accompanying increasing at. number. This suggests the presence of at least one 5*f* electron in Np and two in Pu. In addition, a close similarity is found in the tetravalent state between these three metals and Th, Ce, Pr, suggesting the previous electronic structure. Near identity exists between Np^{4+}, Pu^{4+}, Ce^{4+}, and Pr^{4+}. In the trivalent state, the three are again similar, but a striking similarity exists with the series La–Sm. In metallic-type compounds, the size of Pr, Np, and Pu is nearly the same; Th and Ce are larger in these compounds. The available evidence is not sufficiently clear-cut to decide between an actinide and a thoride series.—J. W. T.

***The Crystal Structure of Electrodeposited Silver.** D. N. Layton (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 239–244; discussion, 245–251).—See *M.A.*, **20**, 409.

***Two-Dimensional X-Ray Diffraction Effects in Aged Polycrystalline Silver–Copper Alloys.** A. I. Pashilov (*Doklady Akad. Nauk S.S.S.R.*, 1950, **72**, (2), 281–283; *C. Abs.*, 1950, **44**, 10489).—[In Russian]. Cf. *ibid.*, 1949, **68**, 1017; *M.A.*, **19**, 192. Flat-film X-ray studies with unfiltered Cu radiation were made on 0·5–1·0-mm.-dia. wire specimens of coarse-grained Ag–6·5% Cu alloy aged to various degrees. Specimens were placed in C for soln.-treatment, and quenching was carried out in a vacuum. Ageing at temp. to 350° C. was done in an open furnace. Even in quenched specimens the first type of two-dimensional diffraction effect was observed, consisting of faint streaks from the white radiation and intense spots from the characteristic radiation. This effect became stronger during ageing up to 20 min. at 250° C., but the Laue spots were not blurred. In the rare cases that two streaks went through a Laue spot, the angles between the cylindrical diffracting regions in reciprocal space were determined and were found to be 55° 44′, 45°, and 35° 16′. Thus, the two-dimensional effect was associated with the (111), (100), and (110) planes. However, it was not possible to assume that Guinier–Preston zones || these planes were causing the effect. Ageing for >25 min. at 250° C. caused a second effect, viz. narrow streaks due to white radiation and occurring chiefly at small diffraction angles. The associated Laue spots became weaker but not blurred, and

they almost disappeared after 1·5 hours' ageing. At small diffraction angles, streaks occurred at places where no Laue spots appeared in films from the quenched specimen. Ageing for short times at higher temp. caused the same effects, and these times were about the same as those reported by Ageev for the appearance of blurred lines of the new phase and the disappearance of lines of the supersaturated solid soln. Like the first effect, this second one was associated with two-dimensional diffraction from the (111), (100), and (110) planes. The effect may be the result of non-coherent lattice displacements during non-homogeneous pptn. caused by the influence of grain boundaries. Other alloys with a large vol. change during pptn. should also show two-dimensional diffraction effects caused by plastic deformation. Thus, an effect of the first type has been observed in polycryst. Cu–Be alloy associated with the (111) and (100) planes, although only (100) plane effects have been found in single crystals of this alloy, perhaps because of poorer sensitivity of the method used.

[Discussion on a Paper by C. J. McHargue and J. P. Hammond:] Preferred Orientation in Iodide Titanium. —— (*J. Metals*, 1953, **5**, (11), 1563).—See *M.A.*, **20**, 700.

A Correction and Note on the Structure of $TiBe_{12}$. Richard F. Raeuchle and R. E. Rundle (*Acta Cryst.*, 1953, **6**, (1), 107).—Cf. *ibid.*, 1952, **5**, 85; *M.A.*, **20**, 23. An equation is corrected; the structure previously proposed is not affected. —N. B. V.

***Fractographic Study of Zinc-Rich Zinc–Aluminium Alloys.** C. A. Zapffe, C. O. Worden, and F. K. Landgraf (*Met. Ital.*, 1951, **43**, (3/4), 97–109).—After briefly dealing with fundamental fractographic principles, the fractographic properties of pure Zn are examined in relation to the mechanism of deformation of the metal. For some phenomena, such as rumpling and kink-band and rifle-mark formation, theories are advanced, particularly Z.'s "micellar" theory of the solid state (*Trans. Amer. Soc. Metals*, 1950, **42**, 387; *M.A.*, **18**, 31). Then the influence on the fractographic structure of Zn of hypo- and hyper-eutectic Al addn. of up to 25% is discussed. 35 ref.—I. S. M.

[Discussion on a Paper by R. K. McGeary and B. Lustman:] Kinetics of Thermal Re-Orientation in Cold-Rolled Zirconium. —— (*J. Metals*, 1953, **5**, (11), 1573–1577).—See *M.A.*, **20**, 768.

***Transformation Mechanism of Zirconium.** E. E. Hayes (*U.S. Atomic Energy Commission Publ.*, 1951, **(AECU-1960)**, 66 pp.).—Pertinent information available regarding the transformation of Zr is reviewed and brief consideration is given to the two possible transformation processes, viz. nucleation and growth, and diffusionless processes. To establish the type of process in Zr, the following methods of investigation were employed: (i) investigation of retained β-Zr, (ii) high-speed thermal analysis of the transformation temp. as a function of cooling rate, (iii) investigation of resistivity changes during cooling, (iv) investigation of the habit plane for the $\alpha \rightarrow \beta$ transformation, and (v) microstructure of single crystals of β-Zr when cooled in a preferred direction. Experimental details are given for each of these studies. The following results were obtained, viz. (*a*) No β-Zr was found to be retained even with cooling rates of 3000° C./sec. (*b*) An increased cooling rate was found to lower the transformation temp., e.g. 65° C. lower for a rate of 1000° C./sec. Greater amounts of O and N in the Zr lower the transformation temp. with faster cooling rates. A single transformation arrest was detected. (*c*) Sharp discontinuities in the resistivity curves were sometimes present, but never in a fresh Zr sample. No significant effect was found on the resistivity curves of altering the quenching temp. From these measurements an *Umklapp*-time lapse of $2–8 \times 10^{-4}$ sec. was deduced; this agrees with a value found by Förster and Scheil (*Z. Metallkunde*, 1940, **32**, 165; *M.A.*, **8**, 290). (*d*) In four- and six-sided crystals of β-Zr crystal bar, it was confirmed that the boundary faces are the (110) planes with the [100] and [111] directions along the axes, resp. Certain features were observed in the crystal bar which were characteristic of a martensitic type of reaction, but the evidence was not entirely conclusive. In water-quenched crystal-bar specimens, it appeared that the transformation occurred as a normal nucleation and growth process; when small amounts of impurity, such as O and N, are introduced, this results in features common to the martensitic type of process. In the latter case the habit plane is possibly the (223) plane. (*e*) Increasing cooling rates resulted in a finer crystal structure. Growth of an α crystal did not extend beyond the original β-crystal boundary. The latter suggests the oriented relationship of the α with the original β crystal. It is concluded that impure Zr transforms by a martensitic type of reaction, but it is not clear how this alters when the purity of material increases; several factors, e.g. high temp., allowing ready relaxation of stress, favour the alternative type of process in high-purity Zr. 22 ref.—J. W. T.

***On the Crystal Structure of Disilicides of Lanthanides [Rare-Earth Metals].** Georg Brauer and Heinz Haag (*Naturwiss.*, 1950, **37**, (9), 210–211).—A study of the ability of the rare-earth metals to form disilicides. The existence of $CeSi_2$ and $LaSi_2$ was confirmed, and these and other rare-earth metal disilicides were formed in a very pure state by reactions of the type: $Me_2O_3 + 7Si = 2MeSi_2 + 3SiO$; $MeO_2 + 4Si = MeSi_2 + 2SiO$. The crystal structure of these compounds was found to be similar to that of $ThSi_2$, e.g. $LaSi_2$ $a = 4·27$, $c = 13·74$ kX. Detn. of *d* gave the values expected from the constitution of these compounds.—S. V. R.

Report of [A.S.T.M.] Committee E-4 on Metallography. —— (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 540–542).—See *M.A.*, **20**, 849.

***Electrolytic Brightening of Metals.—II.** Roberto Piontelli (*Met. Ital.*, 1950, **42**, (6), 205–224).—Cf. *M.A.*, **20**, 850. After a review of existing theories, P. advances a comprehensive theoretical thesis on the mechanism of electrolytic brightening. The concepts introduced and discussed at length include levelling power, micro-planing power, brightening action, and selective attack. The influence of bath compn. and of the anodes is also considered. 20 ref.—I. S. M.

***An Experimental Study of Electropolishing.** J. Edwards (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 133–148; discussion, 149–154).—See *M.A.*, **20**, 409.

The Physical and Chemical Changes Which Accompany the Polishing of Metals. A. J. W. Moore (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 117–124; discussion, 125–131).—See *M.A.*, **20**, 409.

[Discussion on a Paper by C. S. Smith and L. Guttman: Measurement of Internal Boundaries in Three-Dimensional Structures by Random Sectioning.] —— (*J. Metals*, 1953, **5**, (11), 1561).—See *M.A.*, **20**, 702.

On the Nature of Eutectic Alloys. S. V. Avakyan and N. F. Lashko (*Doklady Akad. Nauk S.S.S.R.*, 1949, **65**, (1), 29–32).—[In Russian]. See *M.A.*, **20**, 574.

***On Eutectic Crystallization in the Presence of Surface-Active Substances.** S. V. Avakyan and N. F. Lashko (*Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, (6), 827–830).—[In Russian]. See *M.A.*, **20**, 574.

On the Solidification of Molten Metals. E. Scheil (*Giesserei (Techn.-wiss. Beihefte)*, 1951, (5), 201–210).—S. gives an up-to-date review of experimental and theoretical work on nucleation and rate of solidification. Spontaneous nucleation is considered in relation to the theories of Turnbull and of Becker and Döring. However, in casting, nucleation is generally heterogeneous. A comparison is made between inoculation of melts with foreign nuclei and heterogeneous catalysis. De-activation by adsorption of other substances on the surfaces of nuclei is seen to be the same effect as "poisoning" in catalysis. S. concludes with a description of the formation of cast structures.—J. M. C.

***Lamellar Growth of Crystals. I.—Experimental. II.—Mechanism of Growth of Crystals Far from Phase Equilibrium.** Ludwig Graf (*Z. Metallkunde*, 1951, **42**, (11), 336–340; (12), 401–409).—[I.—] After a review of previous observations on lamellar structures in metals and salts, and the conditions under which they are formed, G. describes his own studies on rapidly solidified—by placing a drop of the melt on a cold polished inert-metal plate—e.g. Cr-plated Fe—metals and salts, and on dendrites which have grown in the melt. Opt.

and electron photomicrographs show the structures encountered when Au, Cd, Cu, NaCl, Pb, W, and Zn are solidified under each condition. [II.—] From the results, which are described in detail, and from considerations of the interfacial energy, it is concluded that the lamellar structure found in dendrites grown in the melt originates from spherical nuclei and not, as has previously been thought, from minute plate-like structures of low crystallographic indices. It is only later, when various forces, including surface tension, come into play, that crystal boundaries and faces develop. The manner in which further development of the crystal takes place depends on whether growth occurs (1) near to equilibrium conditions, i.e. low supersaturation, and, therefore, extremely slowly, or (2) far removed from equilibrium, i.e. high supersaturation, and, therefore, extremely rapidly—a mechanism for which is described at length, and applied to the development of lamellar and dendritic structures. Reasons are given for assuming that "mosaic structures" or "block structures" are similar in type to lamellar structures. 32 ref.

—E. N.

Contribution to the Theory of Nucleus Formation. O. Knacke (*Z. Physik*, 1951, **130**, (3), 259–268).—The classical theory of nucleation as derived by Volmer, Becker and Döring, and others is described, and the possibility of both thermal and athermal nuclei is emphasized. K. gives the expression for the steady-state nucleation current as $J = w_K \cdot \eta_1 \exp(-A_K/kT)$, where A_K is the free energy of nucleus formation, η_1 the number of mol. in the original phase, and w_K the probability that a mol. will pass from the original phase into a nucleus in unit time. This is the same as V.'s expression, but the possible importance of a condensation coeff. contributing to w_K is mentioned. Heterogeneous nucleation round imperfections is also considered, and Frank's theory of dislocation-catalysed crystal growth is described. [Note by Abstractor: The paper appears to contain no *new* contribution to the theory.]—J. W. C.

On the Statistical Theory of First-Order Phase Changes. B. T. Geilikman (*Doklady Akad. Nauk S.S.S.R.*, 1949, **69**, (3), 329–332).—[In Russian]. Math.—Z. S. B.

***Thermodynamics of Phase Transitions of the Second Order.** V. A. Sokolov (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (5), 843–846).—[In Russian]. The theory of phase transitions of the second order is characterized by the introduction into the equation for thermodynamic potential (ζ) of an additional parameter κ, whose magnitude is determined by the additional internal energy A_{ad} (zero or very small for one phase), heat capacity, expansion, &c. Then $A_{ad} = a\kappa^2$ and the internal energy $E = U(T, v, \kappa) + a\kappa^2$, where $U(T, v, \kappa)$ is the vibrational part, whilst $\zeta = E - TS - a\kappa^2 = \psi - a\kappa^2$ and $d\zeta = -SdT - pdv - 2a\kappa d\kappa$. At equilibrium (min. ζ) and const. v, $2a\kappa$ will be a function only of temp. Hence the additional heat-capacity $c_{ad} = 2aT(\partial L/\partial T)_v$, and in the ideal case $c_{ad\,(Ideal)} = 2aLdL/dT$. Expressions are also given for the additional heat-capacity at const. pressure: $c_{p,ad} = T\left(\frac{\partial L}{\partial T}\right)^2 - p\left(\frac{\partial L}{\partial p}\right)_T\left(\frac{\partial L}{\partial T}\right)_p$, the additional pressure-coeff.: $\left(\frac{\partial p}{\partial T}\right)_{v,ad} = 2a\left(\frac{\partial L}{\partial v}\right)_p\left(\frac{\partial L}{\partial T}\right)_v$ and the additional compressibility: $\left(\frac{\partial p}{\partial v}\right)_{T,ad} = -2a\left(\frac{\partial L}{\partial v}\right)_T^2$. According to Bragg and Williams' theory of disordering (*Proc. Roy. Soc.*, 1934, [A], **145**, 699; *M.A.*, **1**, 348), $A_{ad} = \frac{1}{4}NW(1 - \xi_L^2)$, where N is Avogadro's number, W the work for two atoms changing place, and ξ the degree of disorder. Hence for the general case $c_{ad} = T\frac{NW}{2}\frac{\xi^2}{1-\xi^2}\left(\frac{d\xi}{dT}\right)^2$ and for the ideal case $c_{ad} = -\frac{NW}{2}\xi\frac{d\xi}{dT}$ (the equation obtained by B. and W.). By means of the approximation $\tanh^{-1}\xi \approx \xi$ (as in obtaining Curie's law for paramagnetics from Langevin's equation), S. derives the expression $-\xi = \tanh\left(\frac{W}{2kT}T\frac{\xi^2}{1-\xi^2}\cdot\frac{d\xi}{dT}\right)$, which in the ideal case reduces to B. and W.'s equation. Whereas B. and W. obtained the value $\frac{3}{2}R$ (R being the gas const.) for the limiting c_{ad} at the Curie point, S. shows that it is ∞, i.e. in the case of non-ideal disordering c_{ad} increases rapidly near the Curie point, as observed experimentally. If the parameter $\xi = -\alpha/\beta$ (where α and β are the coeff. in the resolution of the thermodynamic potential into a series: $\Phi(\xi, p, T) = \Phi_0(p, T) + \alpha(p, T)\xi + \frac{1}{2}\beta(p, T)\xi^2$) introduced by Landau and Lifshits ("Statisticheskaya Fizika", 1940) be used, then the equation for c_{ad} becomes $c_{ad} = \frac{T}{\beta}\left(\frac{\partial\alpha}{\partial T}\right)^2$ as obtained by L. and L. An expression for the heat capacity near the Curie point similar to that obtained by L. and L. can also be deduced. This scheme of reasoning can be applied to orientation melting and to the consideration of anomalous heat-capacity in pseudo-binary systems. The explanation of Smits' phase transitions of the second order is obtained as a special case; they may be divided into two classes (cf. also S., *Doklady Akad. Nauk S.S.S.R.*, 1949, **65**, 883): (1) non-variant, which take place at the transition point, after the state of one of the phases had gradually changed on approaching the point, consequent upon changes in κ, and (2) monovariant. The first represents Semenchenko's false Curie point (*Zhur. Fiz. Khim.*, 1947, **21**, 1461); the second, the true Curie point.

—G. V. E. T.

The Classical Picture of Recrystallization After Work-Hardening. D. I. Cameron and A. Stein (*Proc. Australasian Inst. Min. Met.*, 1947, [N.S.], (**145**), 15–30).—Deals specifically with the recrystn. of low-C steel. 12 ref.—N. B. V.

***Application of Fluorescence X-Rays to Metallurgical Microradiography.** H. R. Splettstosser and H. E. Seemann (*Non-Destructive Testing*, 1953, **11**, (5), 34–39).—Reprinted from *J. Appl. Physics*, 1952, **23**, 1217; *M.A.*, **20**, 634.

—L. M.

[Discussion on a Paper by J. E. Burke:] Formation of Annealing Twins. —— (*J. Metals*, 1951, **3**, (11), 1068–1070).—See *M.A.*, **18**, 764.

[Discussion on a Paper by W. C. Ellis and R. G. Treuting:] Atomic Relationships in the Cubic Twinned State. —— (*J. Metals*, 1951, **3**, (11), 1070–1074).—See *M.A.*, **19**, 31.

***A New Method for the Determination of "Thermal-Vibration-Like" Lattice Disturbances.** F. Hund and R. Fricke (*Naturwiss.*, 1950, **37**, (18), 424–425).—An X-ray method using the Geiger-Müller counter has been developed for the detn. of "thermal-vibration-like" disturbances which does not require a standard specimen for the purpose of comparison. From experimental results on one specimen, the value of B in the derived equation

$$B = \frac{\lambda^2}{2(\sin^2\theta_2 - \sin^2\theta_1)} \cdot \ln\frac{F_1 J_2}{F_2 J_1}$$

is calculated and hence $\sqrt{\mu_x^2}$ from the Debye equation $B = 8\pi^2\sqrt{\mu_x^2}$. The appn. of the method to active Ni is described, and the results compared with those obtained by other methods.—S. V. R.

***Distributions of Dislocations in Static Equilibrium.** G. Leibfried (*Z. Physik*, 1951, **130**, (2), 214–226).—Math. The distribution of dislocations in a glide plane under an external shear stress is considered. If the number of dislocations is large, all problems reduce to a type of integral equation for which the general soln. is known. Dislocations of like sign confined to a fixed region of the glide plane (anchored at both ends of the distribution), and to a semi-infinite region (anchored at one end only) are first considered, and soln. given for the problems previously treated by Eshelby, Frank, and Nabarro (*Phil. Mag.*, 1951, [vii], **42**, 351; *M.A.*, **19**, 837). Soln. are also obtained for distributions of positive and negative dislocations in two separated regions, and for a periodic arrangement of positive and negative dislocations.

—J. W. C.

***Theory of Dislocations in One-Dimensional Atom Rows. II.—Arbitrary, Arranged, and Accelerated Dislocations.** Alfred Seeger and Albert Kochendörfer (*Z. Physik*, 1951, **130**, (3), 321–336).—Cf. *ibid.*, 1950, **127**, 533; *M.A.*, **19**, 193. Math. Further work on the Frenkel one-dimensional

model is described. Soln. for the static interaction of dislocations are obtained in closed form by a perturbation method, and interaction with a surface is also considered. Soln. are also found for accelerated motion, and for the effect of a time-dependent force; this is used to discuss the damping of dislocations by thermal waves. The relation of the method of soln. to the Peierls integral equation, used in three-dimensional problems, is briefly considered.
—J. W. C.

***Theory of Dislocations in One-Dimensional Atom Rows. III.—Dislocations, Eigen-Motions, and Their Interaction.** Alfred Seeger, Hans Donth, and Albert Kochendörfer (*Z. Physik*, 1952–53, **134**, (2), 173–193).—Cf. *ibid.*, 1951, **130**, 321; preceding abstract. Math. An analysis is made of the interaction between dislocations and sound waves in the one-dimensional Frenkel model. Dislocations are desirable as translational eigen-motions. The relation of the results to the still largely unsolved problem of the energy dissipated by a moving dislocation and its limiting velocity is briefly discussed.—J. W. C.

The Application of the Group Theory to the Analysis of the Anisotropy of Crystals. N. S. Akulov and Ya. I. Fel'dstein (*Doklady Akad. Nauk S.S.S.R.*, 1950, **70**, (4), 593–596).—[In Russian]. Math.—Z. S. B.

***On the Use of Energy Band Models in the Crystal Chemistry of Alloys.** Konrad Schubert (*Naturwiss.*, 1950, **37**, (24), 561–562).—Calculation of the valence-electron concentration of a tetragonal A_1 phase in which the Fermi sphere touches the Brillouin zone boundary (111) shows that the concentration is a min. when the ratio $c/a = 1$. This phenomenon provides a structural argument for tetragonally shortened phases—NiZn, &c.—and tetragonally elongated phases, Au_3Zn, &c. The argument is extended to provide an explanation of peculiarities of Zn–Al alloys and other alloy phases.
—S. V. R.

***Space-Group Symmetry and Methods of Calculating Crystal Structure Factors.—I.–II.** Alfred Niggli and Paul Niggli (*Z. angew. Math. Physik*, 1951, **2**, (4), 217–232; (5), 311–336).—A method is developed in which the computation of summations over reciprocal lattice points or over crystal planes is simplified as far as possible by direct use of the space-group symmetries, and tables of characters of the various operations for all crystal classes are given. The effects of the space-group symmetry in the Patterson space is also discussed in some detail.—W. M. L.

Crystallographic Research in the Cavendish Laboratory. (Sir) Lawrence Bragg (*Proc. Roy. Inst.*, 1951, **35**, [i], (158), 103–113).—A short account of the early work in X-ray crystallography and a comparison with the modern techniques in use at the Cavendish laboratory. A number of examples are given of the investigation of the structure of complex organic crystals and of metals and alloys by the use of the Fourier synthesis for the detn. of electron *d*. The microbeam technique for investigating the shape, size, and strain of the crystallites in cold-worked metals is briefly described.
—S. V. R.

5 — POWDER METALLURGY

***Investigations on Sintered Aluminium Powder [S.A.P.].** Edith Boenisch and Wilhelm Wiederholt (*Z. Metallkunde*, 1951, **42**, (11), 344–348).—Cf. v. Zeerleder, *ibid.*, 1950, **41**, 228; *M.A.*, **19**, 293. A report of a study of the phys., mech., and corrosion-resisting properties of a rod of S.A.P. of the compn., S 0·16, Fe 0·50, Ti 0·02, Cu 0·01, Zn 0·00, Al_2O_3 10·49% (~5% combined O), balance Al (88·82%, by difference), and of sp. gr. 2·717 g./c.c., sp. elect. resistance 0·0364 Ω-mm.²/m., and elect. conductivity 27·5 m./Ω/mm.². Metallographic observations showed the material to be porous, and to contain inclusions (probably Al_2O_3) in a fine-grained matrix of sintered Al particles; no appreciable directional properties were evident. Mech. tests at temp. of −50° to +500° C. indicated that in traversing this temp. range the U.T.S. decreases steadily from 35 to 10 kg./mm.², while the elongation and redn. of area decrease only slightly. Corrosion tests were carried out, (1) in a humidity chamber (100% humidity at 40° C.) for 4 weeks, (2) by alternate immersion in distilled water and in 3% NaCl soln., (3) in a 3% NaCl spray, and (4) in 1*N*-NaOH and in 1*N*-HCl. They showed that S.A.P. is almost as resistant to weakly corrosive media, e.g., distilled water, and condensate, as is sheet Al contg. Si 0·02, Fe 0·53, and Mn 1·14%; S.A.P., however, (i) corrodes more rapidly in the presence of Cl ions, which penetrate through weak spots in the surface layer of oxide, and (2) is extremely susceptible to attack by NaOH and HCl, which dissolve the oxide surface and penetrate to the interior of the material via the fine pores and oxide inclusions. Photomicrographs show the typical structures encountered. 5 ref.—E. N.

[Discussion on a Paper by F. N. Rhines and H. S. Cannon:] Rate of Sintering of Copper [Powder] Under a Dead Load. —— (*J. Metals*, 1951, **3**, (11), 1076).—See *M.A.*, **19**, 193; **20**, 108.

***A Metallographic Study of the Sintering of Brass Powders.** C. J. Bier (*Proc. Metal Powder Assoc.*, 1951, 49–56; discussion, 56–58).—An account of some experimental work on the effect of sintering time, sintering temp., and briquetting pressure on the microstructure of sintered brass. Several photomicrographs are reproduced to illustrate the experimental results. 5 ref.—W. A. M. P.

Heat-Resistant Materials Produced by Powder Metallurgy. W. D. Jones (*Met. Ital.*, 1951, **43**, (10), 425–431).—J. discusses the prodn. by powder metallurgy and the properties of Ni, Co, Fe, Zr, V, Pt, Cr, Ti, Mo, and W bodies and of those of their oxides and alloys, with special ref. to high-temp. properties. Sintered carbides and Cermets are also dealt with in some detail. 10 ref.—I. S. M.

***The Influence of Surface-Active Lubricants on the Processes of Pressing and Sintering of Powdered Metals.** V. I. Likhtman and P. A. Rehbinder (*Doklady Akad. Nauk S.S.S.R.*, 1950, **70**, (5), 851–853).—[In Russian]. The influence of surface-active media on the processes of pressing and sintering of metal powders was studied. The surface-active medium employed was a soln. of oleic acid in either benzene or Vaseline grease, and the metal powders studied were Fe, Cu, and Sn. 5–10 mg. oleic acid in soln. to 1 g. of the metal powder ensured a monomolecular adsorbed layer. Powder treated with the benzene soln. had improved flow properties after evaporation of the benzene. The powders were pressed in cylinders of 12 mm. dia. The pressure necessary to obtain a given *d* was decreased by 10–20% by the presence of the adsorbed layer. This lowering is too great to be accounted for merely by the prevention of friction against the walls of the cylinder, and must be due to the facilitation of plastic deformation of the particles. The presence of surface-active media also influences the magnitude of the elastic expansion of compacts after pressing out of the cylinder. For Cu compressed at 20–40 kg./mm.², the elastic expansion was decreased 2–3 times, and for Sn made at 5–10 kg./mm.² it was decreased by 5–8 times. The presence of surface-active media increases resistance to corrosion. During sintering the surface-active medium is completely burnt away, but the physico-mech. properties of the product are better in comparison with those of the dry compacts prepared at the same pressure. Even at the same porosity, the quality of the compact made in the presence of surface-active media is somewhat better, as a result of the more even distribution of internal stresses introduced during pressing.
—Z. S. B.

Theory and Practice of Powder Pressing. Carl Ballhausen (*Arch. Eisenhüttenwesen*, 1951, **22**, (5/6), 185–196).—The apparent *d* in different parts of a compact varies as a result of non-uniform distribution of pressure, particularly in the direction in which the pressure is applied. The local variation in pressure depends largely on the friction at the walls of the

die. It has been found that the mutual interrelation of the local pressures follows an equation analogous to the friction of a rope running on a pulley: $P_1/P_2 = \exp\left(4\frac{H}{D}\tan\alpha\mu\right)$, where H is the height and D the dia. of the compact, α the angle of repose, and μ the coeff. of friction. An equation for annular and conical dies is developed, and the accuracy of the equation is confirmed by experimental detn. on rubber, Pb, Fe, and Cu. This equation makes it possible to eliminate the effect of the variation in pressure distribution in calculating the relation between pressure and movement of the plunger. The following equation is found to be valid under the most varied conditions: $P = \frac{F_i}{h_f} \cdot k_d$, where F_i is the area under pressure, h_f the free height of the powder in the die, and k_d the compressive strength; the variation of these factors with plunger movement is illustrated. The results are shown to agree with earlier work by Konopicki.—K. S.

Relationship Between Properties and Structure of Sintered Compacts. G. F. Hüttig and K. Torkar (*Kolloid Z.*, 1949, **115**, (1/3), 24–35; discussion, 35–36).—Math. The subject is considered under three main headings: (1) thermodynamics and energy levels, (2) kinetics of sintering and diffusion phenomena, and (3) properties as influenced by structure. H. and T. propound a number of questions regarding the limits within which properties are influenced by different variables and put forward a number of formulæ, based upon experimental and theoretical considerations, in an attempt to answer these questions. Finally, diagrams and curves are presented connecting the principal variables with properties. 20 ref.—W. F. H.

***The "Flywheel" Effect in Infiltrated Metal-Powder Parts.** George Stern (*Proc. Metal Powder Assoc.*, 1951, 14–18; discussion, 18–21).—S. gives an account of some experimental work to determine the effect of the complete and incomplete infiltration of a Cu alloy in bodies having various uniform Fe skeleton *d*. Mech.-test data are given.
—W. A. M. P.

Powder Metallurgy vs. Drawn-Wire Method of Producing Gears. John Rigby (*Proc. Metal Powder Assoc.*, 1951, 59–66; discussion, 66–67).—A general review.—W. A. M. P.

Metal Powders in Some Small-Arms Ammunition Applications. G. A. Miller, Jr. (*Proc. Metal Powder Assoc.*, 1951, 30–38; discussion, 38–40).—A comprehensive review.
—W. A. M. P.

Metal-Powder Applications in the Home-Appliance Field. J. D. Carey (*Proc. Metal Powder Assoc.*, 1951, 68–76; discussion, 76–77).—A general review.—W. A. M. P.

Considerations in Designing Tools for Powder Metallurgy. Irving J. Donahue (*Mech. Eng.*, 1950, **72**, (11), 886–889).—D. reviews some of the factors involved in die design, with special ref. to the dies required for pressing a simple bushing and a flanged bushing.—E. J. E.

Some Design Aspects of Metal-Powder Parts. D. C. Bradley (*Mech. Eng.*, 1951, **73**, (2), 123–127; also *Machine Design*, 1951, **23**, (3), 167, 206).—B. describes briefly the process of making small parts by powder metallurgy, and indicates, by ref. to practical examples, considerations that must be borne in mind in designing products for manufacture in this way.—N. B. V.

Report of [A.S.T.M.] Committee B-9 on Metal Powders and Metal-Powder Products. —— (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 210–211).—See *M.A.*, **20**, 778.

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6 — CORROSION AND RELATED PHENOMENA

***The Initial Oxidation Rate of Aluminium at Low Pressures and at Room Temperature.** N. K. Andrushchenko and P. D. Dankov (*Doklady Akad. Nauk S.S.S.R.*, 1948, **62**, (3), 353–356).—[In Russian]. The first stages in the oxidation of Al were studied by admitting O at a controlled rate ($3{\cdot}5 \times 10^{14}$ mol./sec.) into an evacuated vessel contg. a 1000-Å. layer of freshly deposited Al and comparing the changes of pressure with time with those observed in an identical vessel contg. no Al layer. Absorption was very rapid during the first 10–15 min., but then became increasingly slower until after ~30 min. it practically stopped. During the first 8–9 min. the amount of O absorbed was approx. $2{\cdot}83 \times 10^{12}$ mol./sec./cm.^{2} of fresh Al surface. At 18° C. absorption stopped when a total of $\sim 31 \times 10^{14}$ mol. O/cm.^{2} Al surface had been absorbed, corresponding to ~5 atomic layers of O if the true surface area = apparent surface area. It was likely that in fact the true area = 5 times apparent area, so that coverage would be approx. one layer thick, in contrast to the results of Vernon (*Trans. Faraday Soc.*, 1927, **23**, 113; *J. Inst. Metals* (Abstracts), 1927, **38**, 443), whose experiments were carried out with Al already covered with oxide. The results do, however, confirm other work on Fe, which tends to show that initial absorption of O on a virgin metal surface ceases after a layer a few atoms thick has been formed. Thicker films formed at higher O pressures are built up by a different mechanism.
—N. B. V.

[Discussion on a Paper by M. Stern and H. H. Uhlig:] Corrosion of Aluminium by Carbon Tetrachloride. —— (*J. Electrochem. Soc.*, 1953, **100**, (6), 292).—See *M.A.*, **20**, 415.

***The Relation Between the Deformation Textures of an Aluminium-Magnesium Alloy and Its Behaviour in the Presence of Mercury.** P. A. Jacquet and A. R. Weill (*Met. Ital.*, 1951, **43**, (2), 51–65).—[In French]. Cf. *Rev. Aluminium*, 1950, (172), 442; 1951, (173), 4; *M.A.*, **19**, 389. In the course of investigations on the cause of occasional explosions in marine service of compressed-air cylinders made of Al–7% Mg alloy, a relation was found between the rupture in contact with Hg, the microstructure, and the crystallographic texture. The present study was carried out on six cylinders, two of which had exploded in service. Micrographic and X-ray examinations, as well as tests in Hg salt soln., were carried out. Examination of the fracture showed that rupture was due to stress-corrosion probably caused by the pptn. of a high-Mg (β) phase. Internal stresses were thought to have played a secondary role. X-ray examination and a series of Hg corrosion tests, however, indicated that internal stresses played an important part in the rupture mechanism with Hg. 11 ref.—I. S. M.

***Stabilization of Powdered Copper as Regards Corrosion.** A. I. Levin and A. V. Pomosov (*Zhur. Priklad. Khim.*, 1950, **23**, (9), 949–957).—[In Russian]. Cu powders electrodeposited from acid $CuSO_4$ were washed with distilled water to which a stabilizer had been added, then dried in a vacuum (15–20 mm. Hg) at 110°–120° C. Corrosion tests were made in CO_2 saturated with water vapour for 24 hr. at 40° ± 1° C. The gains in weight with stabilizers of the high-molecular, hydrophobic type were (%): no addn., 1·45; benzoic acid, 0·03; hydroxybenzoic acid, 0·27; anthranilic acid, 0·16; oleic acid, 0·08; Na oleate, 0·10; Na oleate with ceresin, 0·10; Na oleate with rosin, 0·06; soda soap, 0·02; liq. soap, 0·09; soln. of Vaseline in benzene, 0·12 (powder washed in benzene alone, 2·3%); soln. of thiocresol in alcohol, 0·31 (powder washed in alcohol alone, 0·81%); soln. of thiocresol in 0·1*M*-NaOH, 0·07. With 0·5, 0·1, 0·01, 0·001, and 0·0001% soda soap in the wash water, the % gains in weight were, resp., 0·04, 0·02, 0·03, 0·35, and 0·54; with 0·5 and 0·1% oleic acid, 0·53 and 0·03; with 0·1, 0·01, and 0·001% Na oleate, 0·08, 0·10, and 0·22; and with 0·5 and 0·1% thiocresol/NaOH, 0·56 and 0·07. Using various proportions of flotation agents, the % gains in weight were as follows: 0·01 and 0·001% aeroflot, 0·10 and 0·51; 0·1, 0·01, and 0·001% amyl xanthogenate, 0·98, 1·12, and 0·09; 0·5, 0·1, 0·01, and 0·001% of a soln. of toluene sulphochloride in alcohol, 0·29, 0·32, 0·28, and 0·33. Finally, the stabilizing

action of hydrophilic substances was investigated, the % gains in weight being: 0·5% glucose, 0·18; 0·5% pyrogallol, 1·10; 0·5% gallic acid, 1·10; 0·5 and 0·1% tannin, 0·49, and 0·58; 0·5 and 0·01% hide glue, 0·25, and 0·22; 0·5, 0·1, 0·01, 0·001, and 0·0001% gelatin, 0·50, 0·40, 0·24, 0·69, 0·34, and 0·46; 0·5, 0·1, and 0·01% alkali sulphite, 0·11, 0·30, and 0·61. It was also found that stabilized powders having good corrosion-resistance were not easily wetted by water, 10% H_2SO_4, or 10% NaOH. L. and P. concluded that the best stabilizers were the hydrophobic substances, especially soda soap.—G. V. E. T.

[Discussion on a Paper by E. A. Gulbransen and W. R. McMillan:] Electron-Diffraction Studies on the Oxidation of Pure Copper and Pure Zinc Between 200° and 500° C. —— (*J. Electrochem. Soc.*, 1953, **100**, (6), 292–293).—See *M.A.*, **20**, 418.

***Black Marks on Brass.** Paul Ducommun (*Pro-Metal*, 1951, **4**, (24), 924–927).—[In French and German]. Although brass does not normally corrode in water, a galvanic couple may arise as a result of differential aeration, if the anodic and cathodic zones are close together. This may occur near the edge of a drop of water on a free surface or of a film of water entrapped between two sheets; in the latter case corrosion occurs along a line which moves relatively slowly because the rate of evaporation is slow, and black bands of Cu oxide and white ones of ZnO are formed; interference colours may also be observed. Experiments have shown that the phenomenon does not occur in the absence of O, that the condition of the surface and the purity of the water have no significant influence, and that alloys with $>\sim$20% Zn, including nickel silvers, are subject to severe corrosion, while Cu-rich alloys are comparatively immune.—K. S.

***Stress-Corrosion in Special Copper Alloys.** O. Lissner (*Sheet Metal Ind.*, 1953, **30**, (309), 45–55).—See *M.A.*, **20**, 264.—R. J.

***The Role of Peroxides in the Corrosion of Lead by Lubricating Oils.** B. S. Wilson and F. H. Garner (*J. Inst. Petroleum*, 1951, **37**, (329), 225–238).—The corrosion of Pb by lubricating oils undergoing oxidation at $\sim$150° C. has been studied. Methods have been devised for the estn. of acidity, peroxide content of the oil, and rate of corrosion of Pb. For white oils, the experiments showed a similarity between the slopes of the curves obtained for peroxide content and rate of corrosion, but a dissimilarity between these and the curve for acidity. The peroxides generated in white oils can cause corrosion in the absence of air, provided that acids are present. Though O is necessary for max. corrosion, peroxides still have a controlling influence on the rate of corrosion. For engine oils, the curves for peroxide content and rate of corrosion showed some similarity during continuous-oxidation tests, but there was no similarity between either of these sets of curves and the curves for acidity. After a period of oxidation in the absence of Pb, the engine oils proved extremely corrosive to Pb, but this heavy rate of attack decreased quickly if the oils remained in contact with the metal. With these oils the peroxides generated were capable of producing only very slight corrosion in the absence of air. A theory is put forward to explain the effect of atmospheric O on the rate of corrosion by engine oils which have been previously oxidized for several hr. in the absence of Pb.—Authors.

[Discussion on a Paper by J. J. Lander:] Effect of Corrosion and Growth on the Life of Positive Grids in the Lead-Acid Cell. —— (*J. Electrochem. Soc.*, 1953, **100**, (6), 294).—See *M.A.*, **20**, 491.

***Electrodeposited Tin–Nickel Alloy Coatings [and Their Corrosion-Resistance].** (Parkinson, Britton, and Angles). See col. 1026.

***Weathering Tests of Tin–Zinc Alloy Coatings on Steel.** S. C. Britton and R. M. Angles (*Metallurgia*, 1951, **44**, (264), 185–191).—The results of outdoor exposure tests of electrodeposited Sn–Zn alloy coatings on steel in (*a*) urban, (*b*) suburban, and (*c*) marine atmospheres are reported. In (*a*) and (*b*) the protection afforded by coatings of equal thickness diminished in the order: Zn, 50:50 Sn–Zn alloy, 80:20 Sn–Zn alloy, Cd. In (*c*), an alloy with 50% Sn was rather better than Zn and Cd, but an 80% Sn alloy was inferior to Zn and no better than Cd. In tests involving more continuously humid conditions, Sn–Zn alloy was superior to Zn. Conclusions drawn from visual observation of panels exposed to the weather were confirmed by cupping tests on corroded specimens. It is considered that although Sn–Zn alloy coatings cannot challenge Zn coatings for use solely as a protection against the weather, they have advantages for use in situations of prolonged high humidity and when a coating easily solderable with a non-corrosive flux is required.—N. B. V.

Report of [A.S.T.M.] Committee A-5 on Corrosion of [Galvanized] Iron and Steel. —— (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 103–122).—See *M.A.*, **20**, 778.

***The Process of Scaling and Short-Time Life-Tests in Resistance-Heating Alloys.** Helmut Krainer, Leopold Wetternik, and Carl Carius (*Arch. Eisenhüttenwesen*, 1951, **22**, (3/4), 103–110).—The scaling of metals and alloys is briefly reviewed, and ref. is made to various methods for increasing the life of high-temp. alloys by the addn. of very small amounts of Ce, Zr, Ca, or Th, or by surface treatments, such as dipping in $Th(NO_3)_4$. The authors' own experiments were carried out on alloys representative of those whose scale consists of Cr-bearing spinels (Cr 25, Ni 20%, balance Fe), of Cr_2O_3 (Ni 80, Cr 20%), and of Al_2O_3 (Cr 24, Al 55%, balance Fe). Cylindrical specimens were scaled in freely circulating air at 1200° C. After a given time the scale was removed in a NaH bath, and the remaining metal was weighed. The 80:20 Ni–Cr alloy followed approx. a parabolic law; the others oxidized more slowly. Similar tests with intermediate cooling, and life-tests on wires indicate that the 80:20 Ni–Cr alloy is able to withstand rapid temp. fluctuations better than the others, and that the scale rich in Al_2O_3 is particularly susceptible to flaking. It is shown that there is no clear-cut relation between the rate of scaling and the life of wires and the type of short-time life-test which is most representative of actual service conditions is discussed. A method of calculating the temp. of the wire in resistance-heater coils is described. In the discussion, *L. Horn* describes experiments on the effect of small addn. of elements with large atomic radii to 80:20 Ni–Cr alloys and concludes that they speed up initial oxidation and probably favour the formation, at a very early stage, of a scale consisting predominantly of Cr_2O_3.—K. S.

***The Corrosion of Metals by Solutions of Iodine in Hydrocarbons.** L. G. Gindin and M. V. Pavlova (*Doklady Akad. Nauk S.S.S.R.*, 1949, **69**, (3), 377–380).—[In Russian]. The corrosion of Cu, Pb, and Fe by soln. of I in benzene and *iso*-octane was studied. The required weight of I, many times resublimed, was put into a glass vessel, and the hydrocarbon was distilled, dried with Na, and added to the I. The strength of the I soln. was determined by titration. A strip of the metal of dimensions 2 × 20 × 60 mm. was left in contact with the soln. and the I and metal losses were determined. The nature of the corrosion products was also investigated. The rate of corrosion of Cu by a benzene soln. of I was up to 1 g./cm.^{2}/hr., the corrosion product being CuI. In all experiments the actual loss of I from the soln. was less than it would have been if all the Cu lost from the strip had been converted into CuI; the same discrepancy was observed in the case of Pb. It was concluded that some of the Cu had combined with O. The corrosion products took the form of thin layers on the specimen, which separated and deformed when dried. Soln. of I in *iso*-octane acted similarly on Cu, but as the solubility of I in *iso*-octane is small, only dil. soln. could be used. The corrosion product of the benzene soln. on Pb was PbI_2; the *iso*-octane soln. acted more vigorously, giving the same corrosion product. The results for Fe were explained by assuming that the primary corrosion product decomposed with time into I and Fe_2O_3. Analytical and X-ray methods showed that only 3–7% of the corrosion product was FeI_2. When Fe was sealed in a tube contg. de-oxygenated I soln. under an inert-gas atmosphere, the corrosion product after 20 months

was pure FeI_2. Only in the presence of soln. contg. O did the corrosion product on Fe form a layer structure; this indicated that the layer structure was connected with the process $FeI_2 \rightarrow Fe_2O_3$.—Z. S. B.

***Corrosion of Metals by Cracked Petroleum and Some Other Unsaturated Fuel Oils.** L. G. Gindin (*Doklady Akad. Nauk S.S.S.R.*, 1950, **71**, (2), 361–363).—[In Russian]. The corrosion of metals by cracked petroleum is due mainly to attack by acids formed by the atmospheric oxidation of the unsaturated organic compounds contained in it. The influence of the corrosion products on auto-oxidation processes is also discussed.—Z. S. B.

***Corrosion of Metals by Hydrocarbon Solutions of Fatty Acids.** L. G. Gindin and V. A. Kazakova (*Doklady Akad. Nauk S.S.S.R.*, 1951, **80**, (3), 389–392).—[In Russian]. The corrosion of Mg, Fe, and Pb in soln. in benzene, *iso*-octane, and petroleum ether, of acetic (**I**), propionic (**II**), butyric (**III**), valeric (**IV**), caproic (**V**), and lauric (**VI**) acids was studied at room temp., by immersing specimens 2 × 20 × 60 mm. in 50 ml. of soln. in diffuse light for ~40 days. The hydrocarbons were dried with Na. The aggressivity of the acid increases with its mol. weight. Thus, in one experiment with Mg in 0·5*N*-*iso*-octane soln. of **I**–**V**, the losses in weight after 66 hr. were 0·0098, 0·0220, 0·0900, 0·0880, 0·0896 g., resp., whilst with Pb in 70 ml. of 0·1*N*-soln. in *iso*-octane of **I**–**VI** they were 0·0452, 0·1795, 0·4690, 0·4266, 0·4965, and 0·1502 g., resp. If the dependence of the rate of corrosion (ρ) on the acid concentration (c) of *iso*-octane soln. be represented by $\rho = Kc^n$, then for Pb with **II** and Mg with **V**, $n < 1$, but for Fe with **I**, Mg with **I**, and Mg with **II**, $n > 1$. With Pb in **V**, ρ is the same for both the 0·5*N* and 1·4*N* soln. With Mg in benzene soln. of **I**, the neutral acetate is obtained, but in *iso*-octane soln. the product is $(CH_3COO)_2Mg.2CH_3COOH$; over the range 0·1–2·0*N* the acid concentration does not affect the compn. of the corrosion product. In 0·5*N* soln. of **II** and 0·1*N* soln. of **V** in *iso*-octane the neutral salts are produced, but in the *N* soln. of **II** and 0·5*N*-soln. of **V** the acid salts are obtained, the solubility of these salts in *iso*-octane increasing with increasing mol. weight of the acid. The corrosion product of Fe in *iso*-octane soln. of **I** is the neutral ferrous acetate, which is oxidized by the air to ferric acetate. The corrosion of Mg in ~1·5*N* soln. of **I** in petroleum ether is twice that in a similar soln. in benzene. Saturating the solvents with water did not affect the corrosion of Mg. The mean rates of corrosion in *iso*-octane soln. are (g./m.²/hr.) as follows: Fe in 0·26*N*, 0·50*N*, 1·00*N* soln. of **I**, 0·049, 0·166, 0·431; Mg in 0·25*N*, 0·54*N*, 1·00*N* soln. of **II**, 0·008, 0·027, 0·075; Pb in **II** at same concentrations, 0·489, 0·879, 1·320; Mg in 0·54*N*, 1·44*N* soln. of **V**, 0·111, 0·157; Pb in **V** at same concentrations, 0·420, 0·421, resp. The initial corrosion rates are much greater. In spite of the dielectric nature of these soln., the corrosion process is electrochem. (cf. G., *ibid.*, 1950, 73, 515; *M.A.*, 20, 420; *ibid.*, 1950, 74, 311; 1950, 71, 361). Mg corrodes with evolution of H; Pb, with O depolarization; Fe, with mixed H_2/O_2 depolarization. The practical significance of the results is discussed.

—G. V. E. T.

***Stress-Corrosion Tests on Turbo-Supercharger Materials in the Products of Combustion of Leaded Gasoline.** G. B. Wilkes, Jr. ([*A.S.T.M.*] *Symposium on Corrosion of Materials at Elevated Temperatures*, **1951**, 11–23; discussion, 24–25).—See *M.A.*, **18**, 533.

***Coal-Ash Corrosion of Metals at Elevated Temperatures.** C. T. Evans, Jr. ([*A.S.T.M.*] *Symposium on Corrosion of Materials at Elevated Temperatures*, **1951**, 3–8; discussion, 9–10).—See *M.A.*, **18**, 273.

High-Temperature Reactions Between Gas and Metals. Andrew Dravnieks and Hugh J. MacDonald (*Met. Ital.*, 1950, **42**, (4), 113–120; (5), 167–172).—The factors playing a part in gas–metal reactions are analysed, and the laws governing them are examined in this detailed study. Subjects dealt with include the mechanism of scale formation, the influence of impurities on the rate of reaction, variation in phase compn., and the structure of the transition zone. A good deal of research was carried out in connection with the study, and descriptions are given of methods and apparatus used. 71 ref.—I. S. M.

***Corrosion Experiments with Gaseous Boron Fluoride.** F. Hudswell, J. S. Nairn, and K. L. Wilkinson (*J. Appl. Chem.*, 1951, **1**, (8), 333–336).—Experiments carried out at temp. up to 200° C. showed that a wide range of metals and alloys suffered no apparent attack by gaseous BF_3.

—N. B. V.

***The Vertical Distribution of Photographically Active Particles Emitted by Metals During Atmospheric Corrosion.** I. L. Roikh (*Doklady Akad. Nauk S.S.S.R.*, 1950, **70**, (2), 253–256).—[In Russian]. The range of photoactive particles produced during atmospheric corrosion of some metals was studied. The air-wedge method was used, a foil of the metal being placed horizontally with a photographic plate at an angle to it varying from 16° to 90°. The experiments were carried out at temp. between 25° and 80° C. and controlled to 1°–2° C. The influence of the working of the surface of the metal was studied for four Zn specimens prepared by: (*a*) filing, (*b*) rubbing with fine emery, (*c*) rubbing with coarse emery, and (*d*) attack by 10% H_2SO_4. The photoactive particles from the four specimens were recorded on the same plate and the blackening was measured photometrically. The specimen–plate distances were plotted against this opt. *d*, and the relation was found to be linear. The slope did not depend on the prepn. of the surfaces. Analogous experiments on Zn, Al, and Mg gave lines having the same slope but different positions. This indicated that the number of particles from each metal is different, but that they are of the same type. The blackening for these three metals was in the order Zn > Al > Mg, which is different from the order of their electrochem. potentials. The number of particles coming from the surface increases exponentially with temp. R. also shows that the number of particles falling on the plate is given by $n = n_0^{-(D_0/\gamma h_0)h}$, where n is the number of particles falling on the plate at $h = 0$, γ = contrast factor, D_0 = max. opt. *d*, and h_0 = max. range of particles.

—Z. S. B.

Corrosion-Fatigue of Metals: A Critical Survey. A. J. Gould (*Iron and Steel*, 1951, **24**, (1), 7–10).—20 ref.

—N. B. V.

***Influence of Wetting Agents on Corrosion.** Luigi Piatti (*Chimia*, 1951, **5**, (1), 9–10).—An investigation into the influence of small amounts of surface-active agents contained in synthetic detergents on aq. corrosion. Steel plates were agitated at 50° C. for 1–40 days in ordinary tap water of 15·7° total hardness, and in the same water contg. 4% Teepol. The latter showed greater loss of weight, but were clean and free from corrosion products, while the former had adhering corrosion products and much pitting. This is shown in photomicrographs of sections. Conclusions are that the presence of the detergent is on the whole beneficial in preventing pitting. 7 ref.—W. F. H.

7 — PROTECTION

(Other than by Electrodeposition)

***The Anodic Oxidation of Aluminium in Oxalic Acid Baths.** A. von Zeerleder and W. Hübner (*Chimia*, 1949, **3**, (4), 77–84).—Most anodic films are transparent and colourless, but by incorporating Ti salts in the bath opaque films can be produced, as TiO_2 has a refractive index of 2·61–2·90, against 1·5–1·7 for Al_2O_3. This is the basis of the Ematal process, and v. Z. and H. present results of researches into the operating conditions to give optimum properties. The bath contains Ti–Na oxalate, and is operated at 50° C. for 40 min. at a c.d. of 2 amp./dm.^{2} D.C.—W. F. H.

***Vitreous Enamel for Aluminium.** William F. Carroll (*Bull. Amer. Ceram. Soc.*, 1951, **30**, (7), 232–233).—A low-m.p. enamel for use on Al has been developed, based on a phosphate glass. The enamel was attacked by strong acids and alkalies, but was unaffected by extended exposure to boiling water. Some protective layer was found to be necessary to prevent reaction between Al and the enamel, Cu being found the most successful in this respect. A good white colour was obtained by using TiO_2 as an opacifier, and there was some evidence that other colours could be satisfactorily produced.—N. B. V.

***Mechanism and Kinetics of the Chromizing of Mild Steel in Atmospheres Containing Chromous Chloride.** T. P. Hoar and E. A. G. Croom (*J. Iron Steel Inst.*, 1951, **169**, (2), 101–107).—It is shown experimentally that 0·1% C steel exposed to atmospheres contg. $CrCl_2$ at 950°–1100° C. becomes coated with a Cr-rich layer, owing to the reactions $CrCl_2 + Fe \rightarrow Cr + FeCl_2$ and, if the atmosphere contains H, $CrCl_2 + H_2 \rightarrow Cr + 2HCl$. The latter reaction proceeds catalytically on the growing surface. The overall rate of chromizing is limited, in the early stages, by the rates of the reactions (both of which are increased by increase of partial pressure of $CrCl_2$) and, in the later stages, by the rate of metallic interdiffusion in the growing alloy layer; the overall rate is at first const., and later falls off parabolically, with time. The apparent energy of activation of the diffusion process is 57 kg.-cal. Various practical chromizing processes are discussed in the light of the experimental results.—AUTHORS.

The Use of Magnesium Anodes for the Protection of Pipe Lines. W. F. Higgins (*Magnesium Rev. and Abs.*, 1949, **8**, (2), 99–119).—Reprinted from *Civil Eng.*, 1949, **44**, 712; 1950, **45**, 43; *M.A.*, **17**, 941.—N. B. V.

The Hot Tinning of Cast Iron. —— (*Metalloberfläche*, 1951, [B], **3**, (2), 19–21).—An account, largely based on "Hot Tinning", published by the Tin Research Institute. —E. J. E.

Calculation of Costs and Wages for Zinc Coating. K. Grimm (*Metall*, 1951, **5**, (13/14), 307–308).—A brief outline of costing methods and of some of the factors involved in galvanizing and Zn plating.—E. J. E.

Sherardizing: Modern Developments and Applications. A. E. Williams (*Iron and Steel*, 1951, **24**, (13), 529–533). —N. B. V.

***Mechanism of Protection of Iron Apparatus from Corrosion with the Aid of Inhibitors and Protective Coatings.** I. L. Rozenfel'd (*Doklady Akad. Nauk S.S.S.R.*, 1951, **79**, (3), 471–474).—[In Russian]. An investigation was made of the relation between ohmic and polarization resistances for flat specimens protected by both inhibitors and protective coatings. A micrometer apparatus was used to measure the potential (ε) distribution on an Fe specimen 14 cm. long, coated with Zn for 4 cm. at one end. From the experimental polarization curves for Zn and Fe, the distribution of c.d. on the specimen was determined, and hence the relation between the resistances could be calculated (cf. Tomashov and Timonova, *Zhur. Fiz. Khim.*, 1948, **23**, 221). The electrolytes used had the following compn. (g./l.): (I) NaCl 0·030, Na_2SO_4 0·070; (II) NaCl 0·030, Na_2SO_4 0·070, $ZnSO_4$ 5, $Ca(NO_3)_2$ 1; (III) NaCl 0·030, Na_2SO_4 0·070, $K_2Cr_2O_7$ 1. The introduction of the inhibitors into the electrolyte caused the values of ε for the Zn and Fe to approach one another, so that the curves showing the distribution of ε and c.d. along the specimens became more sloping; thus in II, $\varepsilon_{Fe} \simeq \varepsilon_{Al}$. From the polarization curves the new distribution of ε and c.d. is not solely connected with an increase in the elect. conductivity of the soln. but also with an increase in the cathodic polarization resistance. The c.d. on the bare Fe are greater in I (25–30 μ amp./cm.^{2}) than in II (20–23 μ amp./cm.^{2}) or III (5–7 μ amp./cm.^{2}), but despite this Fe in I is not cathodically protected by the Zn alone. Inhibitors readily protect it at the smaller c.d. R. gives curves showing the variation with distance along the bare Fe of the relative influences of anodic, cathodic, and ohmic control. In the presence of inhibitors the part played by the cathodic control is markedly increased (from 40–60% in I to 75–80% in II and 65–80% in III), and that of the ohmic control decreased. In each electrolyte, with increasing distance from the Zn, the part played by the cathodic control decreased, and that of the ohmic control increased, but they became const. at distances $>\sim$5 cm.; the share of the anodic control was almost const. The ohmic control on three-dimensional articles is always greater than on flat shapes.—G. V. E. T.

***On the Anti-Corrosive Action of Emulsive Oils: Electrochemical Analysis of Their Protective Action in Water in Conjunction with Other Inhibitors.** Antonio Ferri (*Met. Ital.*, 1950, **42**, (7), 261–267).—F. carried out electrochem. analysis of the mechanism of the inhibiting action of emulsive oils alone and with the addn. of other corrosion inhibitors ($K_2Cr_2O_7$; $K_2Cr_2O_7 + KOH$; K_2CrO_4; mixture of Na salts: Na_2SiO_3, Na_2CO_3, and Na_2HPO_4; $NaNO_2$). It was found that emulsive oils alone were anodic and liable to cause localized corrosion; the best additive was found to be $K_2Cr_2O_7$. 18 ref.—I. S. M.

Metal Spraying in the Motor Industry. H. Reininger (*Automobiltechn. Z.*, 1951, **53**, (4a), 125).—A short review of recent advances in the construction of metal-spraying pistols and their use in the motor-car industry, particularly for treating chassis and other parts as protection against corrosion. The design and operation of a recent type of wire pistol are dealt with and illustrated. 9 ref.—W. F. H.

8 — ELECTRODEPOSITION

The Plating of Aluminium Articles as a Production Process. [The Vogt Process.] A. W. Wallbank (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 209–217; discussion, 218–227; also *Metal Ind.*, 1952, **80**, (22), 442–444).—See *M.A.*, **20**, 423.

Current Methods for the Copper Plating of Iron and Steel and the Nickel Plating of Copper Alloys (Copper, Brass, Bronze).—I.–II. Roger Zirilli (*Pro-Metal*, 1951, **4**, (19), 778–792; (20), 811–820).—[In French and German]. [I.—] Post-war electroplating methods, using baths capable of operating at high c.d., are described in considerable detail. Perfect cleanliness of the articles in the plating bath is essential, and great care is taken to ensure this: the machined, ground, or polished article is degreased, pickled if oxides are present on the surface, degreased cathodically, and then pickled anodically to eliminate H pick-up. Cu plating is carried out in a variety of baths, mostly based on cyanide with Rochelle salt addn. A Cu undercoating is recommended for steel articles to be Ni plated because Cu deposits are more uniform and adherent and offer a very fine-grained base for the Ni plate. Cu-plated articles must be washed and immediately dried to avoid staining; they are then electroplated with other metals or protected by a varnish. [II.—] The methods used for Ni plating Cu alloys also apply to Cu-coated steel. The work is degreased, pickled, de-

greased electrolytically, and pickled in dil. acid; this is followed by a Cu flash, which reveals any areas that have been insufficiently cleaned. For bright Ni plating, baths contg. Co are recommended; organic baths are unstable, and the Ni deposits are highly stressed and therefore not very adherent. In Switzerland, experience has shown that the most economic method of obtaining a bright Ni-plated surface is to use a bright Cu bath followed by a bright Ni–Co bath; it is not necessary to polish the article before plating. Annular baths for continuous mass-prodn. plating, and barrel-plating installations are also described.—K. S.

The Electrodeposition of Molybdenum and Its Alloys. F. W. Salt (*Murex Rev.*, 1951, **1**, (9), 201–210).—A review of work on the deposition of Mo and its alloys with Fe, Co, and Ni. Details are given of bath compn., *p*H, c.d., efficiencies, and compn. and character of the deposits. 19 ref.

—D. M. P.

Some Experiences and Experiments on Bright-Nickel Plating of Copper and Brass. A. Hofmann (*Metalloberfläche*, 1950, [B], **2**, (3), 38).—The occurrence of areas of incomplete Ni deposition is not due to incomplete degreasing but to the presence of a thin oxide layer. Degreasing causes a lowering of adhesion between the metal and aq. soln., so that the surface, particularly on the upper part and edges of the article, becomes exposed to atmospheric O if transfer from washing to plating bath is delayed for >1–2 sec.

—E. J. E.

Hard-Nickel Plating. A. Pollack (*Metalloberfläche*, 1950, [B], **2**, (4), 54–55).—A brief account of the hard-Ni plating process and its advantages, with particular ref. to British practice.—E. J. E.

Modern High-Quality Nickel Anodes: Their Purity and Solubility. A. Meyer (*Pro-Metal*, 1951, **4**, (20), 822–823).—[In French and German]. The use of very pure anodes eliminates contamination of the bath, which might cause difficulties in plating or even render the entire plating bath useless. Modern methods of manufacturing anodes—not specified in detail—also ensure that they dissolve uniformly in the electrolyte, avoiding uneven attack, which would cause loss of metallic Ni and a dirty bath, on the one hand, and passivity, which would lead to Ni impoverishment of the electrolyte, on the other. Irregular soln. may occur even with modern anodes if the bath is insufficiently acid; it is clearly apparent in the rough surface of the anode.—K. S.

Beating the Nickel Shortage. —— (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 253–272; also *Metal Ind.*, 1952, **80**, (20), 402–405; (21), 423–425).—A general discussion on means of overcoming shortage of Ni in respect of the traditional Ni/Cr deposits. Substitute undercoats, substitute plates, and periodic reverse and Cu/Cr deposits were considered.

—N. B. V.

Material Economy: Cardinal Points in Nickel Conservation. [—II]. Frank Taylor (*Electroplating*, 1951, **4**, (9), 285, 291).—Cf. *ibid.*, (8), 249; *M.A.*, **19**, 665. Attention is drawn to the importance of the following for obtaining the max. material economy in electroplating shops: adequate polishing of base metal, replacing part Ni by Cu; direct Cr plating of Zn-base die-castings; the use of auxiliary or bipolar anodes.—H. A. H.

The Development, Production, and Manufacture of Electro-Tinplate. W. E. Hoare (*Sheet Metal Ind.*, 1951, **28**, (288), 309–321).—Abridged version of a paper presented to the West Wales Section of the Institution of Production Engineers.—N. B. V.

***The Electrodeposition of Tin–Antimony Alloys from Chloride–Fluoride Electrolytes.** J. W. Cuthbertson and N. Parkinson (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 195–201; discussion, 202–207).—See *M.A.*, **20**, 424.

***Electrodeposited Tin–Nickel Alloy Coatings [and Their Corrosion-Resistance].** N. Parkinson, S. C. Britton, and R. M. Angles (*Sheet Metal Ind.*, 1951, **28**, (292), 757–767, 770).—Summarizes papers by P. (*J. Electrodepositors' Tech. Soc.*, 1951, **27**, 129; see *M.A.*, **19**, 138) and by B. and A. (*ibid.*, p. 293; *M.A.*, **20**, 419).—N. B. V.

Automatic Barrel Plating [of Zinc]. —— (*Iron and Steel*, 1951, **24**, (6), 217–220).—An illustrated description of a plant for the Zn plating of screws, bolts, and nuts.—N. B. V.

***A Method for the Determination of Stresses Produced on Electrodeposition Using Electrical Strain Gauges.** E. G. Ramachandran and K. V. Chinnappa (*Trans. Indian Inst. Metals*, 1950, **4**, 173–181).—Experimental and theoretical details are given of a method of measurement of surface stresses, produced by electrodeposition, using elect. strain gauges. Results of the initial tests on the deposition of Ni on steel are discussed. 11 ref.—P. F. N.

Chromate Recovery. C. F. Paulson (*Metal Ind.*, 1952, **80**, (26), 523–524).—Abridged from *Metal Finishing*, 1952, **50**, (5), 48; *M.A.*, **20**, 36.

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9 — ELECTROMETALLURGY AND ELECTROCHEMISTRY

(Other than Electrodeposition.)

***The Galvanic Behaviour of Aluminium.** Leo Cavallaro and Giampaolo Bolognesi (*Met. Ital.*, 1951, **43**, (1), 13–17).—Measurements have been carried out on galvanic cells consisting of 99·9935% pure Al and varying types of cathode in a 3% NaCl soln. with or without the addn. of HgCl to bring the attacking medium to *N*/5000 with respect to the Hg^{++} ion. Together with other measurements, the results showed that high-purity Al had a very low potential in spontaneous corrosion with Cu, Pt, Co, Ni, and Ag. Theoretical and experimental results obtained by other workers are also discussed. 14 ref.—I. S. M.

***Influence of Temperature on the Irreversible Electrode Potential of Aluminium.** V. V. Romanov and G. V. Akimov (*Doklady Akad. Nauk S.S.S.R.*, 1951, **79**, (6), 989–991).—[In Russian]. Specimens of commercial Al rod (0·43% Fe, 0·13% Si) were fixed in a polystyrene clamp to give a working surface of ~0·3 cm.². Before the experiment they were ground with a barette file, then polished with Al_2O_3, washed, dried with alcohol, and kept for 18–20 hr. in a desiccator. The volume of electrolyte used was 250 c.c., and the apparatus was placed in a thermostat having an accuracy of ±0·1°. The electrolytes used were 1*N* in Cl ions, containing NaCl alone or with HCl or NaOH to give various *p*H (1, 3, 6, 11, 13). The potential referred to the saturated calomel electrode was determined at various intervals, and the results were converted into potentials relative to the normal electrode. Measurements were made at 0°, 20°, 50°, and 80° C.; potential/time and potential/temp. curves are given for various *p*H values. In neutral and acid soln. the potential becomes more negative with increase in temp.; at *p*H 1 the potential varies linearly with temp. For all temp. at *p*H 1 and for 0° and 20° C. at *p*H 3 or 6, the potential is almost independent of time, but in neutral soln. at 50° and 80° C. it becomes more negative. At these temp. in the soln. of *p*H 3, there is a sharp change in potential in the negative direction in the first 10–15 min., after which there is a smooth but small change in the positive direction. In the alkaline soln. the dependence of potential on temp. is determined by the shape of the potential/time curves. Initially, the potential at 20° C. is more negative than those at 0°, 50°, and 80° C. At 80° C. the potential changes sharply in the positive direction during the first 10 min., then slowly becomes more negative. After 2 hr. the most negative potential is that at 80° C. At *p*H 13 the metal surface turns black immediately it is immersed, except at 0° C., where there is an induction period of 3–4 sec. R. and A. suggest that the natural oxide film is replaced by a more complex film which is stable at 0°, 20°, and 50° C., but not at 80° C.—G. V. E. T.

***Anode and Cathode Polarization Curves for Iron and Copper in Sulphate Solutions Containing Oxidizing Additions.** N. D. Tomashov, G. P. Sinel'shchikova, and M. A. Vedeneeva (*Doklady Akad. Nauk S.S.S.R.*, 1948, **61**, (4), 669–672).—[In Russian]. In potential measurements on Cu in NaCl and Na_2SO_4 (0·5 and 0·01*N*) soln., the cathode depolarizing efficiency of H_2O_2 was found to be similar to that of O from the atmosphere, whereas the effect of addn. of $K_2Cr_2O_7$ to the soln. was negligible.—N. B. V.

***Cathodic Polarization in the Electrodeposition of Nickel.** A. T. Vagramyan and Z. A. Solov'eva (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (4), 629–631).—[In Russian]. V. and S. obtained the dependence of polarization (η) on c.d. by uniformly increasing the current (i) through the cell from zero to some max. value and then returning it to zero; this was done within a short time (15, 1·5 sec., and less), η being recorded photographically. In some experiments i was varied linearly, in others logarithmically. The cell used contained (g./l.): $NiSO_4.6H_2O$ 140, H_3BO_3 30, KCl 19, temp. 20° C. After switching off the current, the electrode potential had a high negative value which gradually changed in the positive direction. This change also occurred in the polarization of an electrode by a small current. From curves showing changes in η for a Ni electrode when the c.d. varied linearly from 0 to 30 to 0 m.amp./cm.^{2} the value of η at zero c.d. was −306 mV. for a 15-sec. cycle, and −212 mV. for a 1·5-sec. cycle. Taking 306 mV. as the equilibrium potential φ_0, the overvoltage is 486 mV.; if the "steady" value (at c.d. of 30 m.amp./cm.^{2}) be taken as φ_0, the overvoltage is 790 mV. The curves of η/log c.d. are linear over a greater range of c.d. for a 1·5-sec. cycle than a 15-sec. cycle, but the max. value of η is independent of speed. Glasstone's explanation of chem. polarization in terms of an active or metastable deposit (*J. Chem. Soc.*, 1926, **129**, 2887; *J. Inst. Metals* (Abstracts), 1927, **37**, 627) is not supported by the fact that scraping activates the surface of the electrode; more probably a completely pure Ni surface cannot exist for a prolonged time because foreign particles are absorbed on it and cause passivation. The passive film is absent from a scraped surface or from freshly deposited Ni, and hence the potential is more negative. The change in potential of freshly deposited Ni with time to a more positive value is explained either by passivation or by the as-deposited surface not having a normal equilibrium lattice, but contg. an excess of active places, and then undergoing ordering as time elapses. In any case, polarization is not wholly reduced to the slowness of the discharge on the pure surface, but indicates some change in its physico-chem. condition.—G. V. E. T.

***Nickel–Hydrogen Electrode.** S. I. Berezina, G. S. Vozdvizhensky, and G. P. Dezider'ev (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (1), 53–55).—[In Russian]. The behaviour of the Ni–H electrode (Ni plate 10 × 10 mm.) was studied in 0·1, 0·01, and 0·001*N*-HCl and NaOH, and in buffer soln. (Na acetate and HCl or NaH_2PO_4; H_3BO_3 and borax). A smooth electrode of sheet Ni, even after long treatment with gaseous H, did not give a stable and reproducible potential. In later experiments, the Ni electrode was coated with "black Ni" by electrodeposition from soln. contg. (g./l.) Ni ammonium sulphate 33, Na–K tartrate 14, at c.d. 0·1 amp./cm.^{2}, 20° C., pH 6·6, with electrolytic Ni anodes. By varying the conditions, deposits of different shades could be obtained, but the most stable potentials were given by greyish-black deposits. The black-velvety deposits (resembling Pt black) obtained at higher c.d. were less useful for determining pH, as their H potentials changed with time. For the standard deposits, the Ni–H electrode gave pH values of 1·6, 2·35, and 3·3 when the Pt–H electrode indicated pH of 1·1, 2·0, and 3·1, resp. For higher values (up to pH 12·8) the Ni–H and Pt–H electrodes gave identical values. Other electrodes were prepared by electrodeposition from baths contg. (g./l.): $NiSO_4$ 250, H_3BO_3 30, KCl 5, at c.d. 1 amp./cm.^{2}, 25° C., pH 4·8. These Ni–H electrodes indicated pH values of 2·38, 1·95, 3·50, 5·84, 7·10, 10·6, and 11·5, when the values according to the Pt–H electrode were: 1·10, 2·05, 3·90, 6·18, 8·10, 11·5, and 12·7, resp. The use of the Ni–H electrode in determining the pH of the cathode region in electrolysis, and especially in Ni electrodeposition, is discussed.—G. V. E. T.

Some Comments on Papers of A. L. Rotinyan [on Current Efficiency in the Electrolysis of Fused Salts]. G. A. Abramov (*Zhur. Priklad. Khim.*, 1950, **23**, (9), 942–948).—[In Russian]. Cf. the papers on electrolysis of fused salts by Rotinyan (*ibid.*, 1948, **21**, 755; *M.A.*, **18**, 282; *Tsvetnye Metally*, **1948**, (5), 45). R.'s equation $d\gamma = K[(\gamma_0 - \gamma)/D']dD'$ (in which $d\gamma$ is the increment in the amount of metal liberated, $\gamma_0 - \gamma$ is the loss of metal, and D' the ratio $D/D_{crit.}$, where D is the c.d. and $D_{crit.}$ the min. c.d. at which metal is deposited) is not a true statement of the relation between γ and D; also, in integrating this equation it was wrongly assumed that γ_0 is an independent quantity. The equations $\eta = 1 - (D_{crit.}/D)^K$, $\eta = 1 - (Dl_{crit.}/Dl)^K$, and $\eta = 1 - (A \cdot e^{-B/T}/Dl)^K$ do not agree with the experimental data (η is the current efficiency, l the distance between the electrodes, and T the temp.); in the absence of any numerical values for $D_{crit.}$ the first two of these three equations cannot be used. The coeff. K is not independent of temp. and values >1 are impossible. Both Alabyshev (*Zhur. Priklad. Khim.*, 1947, **20**, 558) and R. have mistakenly identified the solubility of the metal in the molten salt with the loss of metal on electrolysis.—G. V. E. T.

[Discussion on a Paper by S. Barnartt:] Primary-Current Distribution Around Capillary Tips Used in the Measurement of Electrolytic Polarization. —— (*J. Electrochem. Soc.*, 1953, **100**, (6), 295–296).—See *M.A.*, **20**, 504.

Electrochemistry and the Science of Metals. Roberto Piontelli (*Met. Ital.*, 1951, **43**, (9), 361–368, 373).—1951 Autumn Lecture to the Institute of Metals; see *M.A.*, **19**, 303.—I. S. M.

10 — REFINING

***Preparation of Rare-Earth Metals.** F. H. Spedding and Wm. J. McGinnis (*U.S. Atomic Energy Commission Publ.*, 1951, **(ISC-149)**, 29 pp.).—Brief consideration is given to the electronic structure of the rare-earth metals and to their usefulness in understanding alloying behaviour. This is followed by a detailed review of extraction techniques used for these metals, the present report being on the prepn. of high-purity Gd and Y. The oxides, Gd_2O_3 (98% pure) and Y_2O_3 (90% pure) were converted to the anhydrous chlorides, which were ultimately reduced by high-purity Ca. The reductions were carried in welded Ta crucibles under a He atmosphere to minimize contamination of the reduced metals; the charge, contg. 10% excess Ca, was compressed before reduction. In the case of Gd, the mixture, after firing, was raised to 1300° C. to allow sepn. of slag and metal; the slag was leached out with water. It was observed that the 2% $SmCl_3$ contained in the charge was not reduced, only 0·06% Sm_2O_3 being in the final metal. Reduction yields were in the range 97–100%. The 5% Ca contained in the melt was removed by vacuum distillation at 1200° C. The vacuum casting and the prodn. of powdered Gd are described. The process for Y was identical, except that after firing the temp. was raised to 1750° C. to allow the sepn. of the slag; owing to the fact that this temp. is above the b.p. of both the slag and the Ca the % yield in this case was only 69·5%. The casting technique for Y is identical to that for Gd. 55 ref.—J. W. T.

11 — ANALYSIS

***New Highly Specific Spot Reaction for the Detection of Aluminium.** L. M. Kul'berg and I. S. Mustafin (*Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, (2), 285–288).—[In Russian]. K. and M. studied a series of α-hydroxyanthraquinones as reagents for detecting Al. 5 : 8-dichlorquinizarin seemed especially interesting; if a few drops of a saturated alcoholic soln. of this reagent are added to 1–2 ml. of an almost neutral test soln. contg. Al^{3+}, the colour of the soln. changes on boiling from yellow-green to bright rose (an orange-rose fluorescence in ultra-violet light). The colour and fluorescence do not change on adding conc. HCl unless the acidified soln. is then boiled. However, the coloration is not obtained on adding the reagent to acid soln. of Al. The sensitivity is given as 0·5 γ Al^{3+} at a limiting dilution of 1 : 2,000,000 (0·1 γ Al^{3+} at a limiting dilution of 1 : 10,000,000). The test may also be carried out as a fluorescent spot test on filter-paper, and the sensitivity is then 0·002 g. Al at a limiting dilution of 1 : 1,000,000. Cu, Be, Zr, Th, U, and Fe^{3+} also react with the reagent in neutral soln., but except in the case of Fe^{3+} the colorations are removed on adding HCl. For detecting Al^{3+} in the presence of Be^{2+}, Th^{4+}, or Cu^{2+}, the test soln. is heated with a few drops of reagent and a little chalk, cooled, and acidified; <0·1% Al^{3+} can be detected in the salts of Be or Th, <0·5% Al in Cu. In the presence of large amounts of Fe, the reaction mixture must be diluted 5–10 times and a control test made with a soln. of pure Fe salt; 1% Al in Fe can be detected. Metals which do not interfere are listed.—G. V. E. T.

***Rapid Photometric Determination of Aluminium in Zinc and Steel.** Luther C. Ikenberry and Arba Thomas (*Analyt. Chem.*, 1951, **23**, (12), 1806–1809).—A simple photometric method has been developed for the detn. of small amounts (0·002–0·10%) of acid-soluble Al in Zn and steel. It is based on the reaction of Al with eriochromecyanin R to form a violet-red-coloured complex. Al may be determined in Zn in 20 min., and reproducibility is at least equal to that obtained by the grav. method. Details are given.
—N. B. V.

***Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. VIII.—3 : 3′-Dimethylnaphthidine as Indicator in the Titration of Cadmium, Calcium, and Indium with Ferrocyanide.** R. Belcher, A. J. Nutten, and W. I. Stephen (*J. Chem. Soc.*, 1951, (Dec.), 3444–3447).—Cf. *ibid.*, (Feb.), 550; *M.A.*, **20**, 1030. [Parts VI and VII are of no met. interest]. Naphthidine and 3 : 3′-dimethylnaphthidine can be used as internal indicators in the titration of Zn with ferrocyanide. It is now shown that Cd, Ca, and In can be titrated with ferrocyanide and the latter indicator. Naphthidine, *o*-dianisidine, and *NN′*-diphenylbenzidine are less satisfactory.—H. A. H.

***Application of the Trioxalatocobaltate (III) Colour System to the Spectrophotometric Determination of Macro Quantities of Cobalt.** J. P. Mehlig and G. J. Zeagas (*Chemist Analyst*, 1951, **40**, (4), 76–80).—The green trioxalatocobaltate (III) complex was measured at 605 mμ, in samples contg. ~1–70% Co, with an average accuracy of ⅓% compared with the iodide method. Factors affecting the colour system, including the effect of interfering ions, were investigated.—L. D. H.

***The Determination of Copper in Uranium-Copper Alloys.** M. Gibson (*Atomic Energy Research Establishment Rep.*, 1950, (C/R 526), 5 pp.).—A procedure is described for the estn. of Cu in U–Cu alloys without preliminary sepn. Cu is deposited from an acid soln. (H_2SO_4–HNO_3) by electrolysis on to a Pt cathode. Complete sepn. is obtained by dissolving the deposit and repeating the electrolysis. The current required for the standard type of rotating cathode is 2 amp. Alloys contg. 0·1–100% Cu can be readily analysed. The accuracy ranges from ±0·2% of Cu present at high levels to ±4% at low levels.—C. E. A.

***X-Ray Analysis of Two Gold Plates Obtained in Archæological Excavations.** (Mme) A. R. Weill (*Met. Ital.*, 1951, **43**, (12), 507–511).—[In French]. Two non-destructive methods (*d* measurement and X-ray-diffraction study of the crystal structure) were used to examine the compn. of two Roman Au objects at the Louvre. In one of the plates 1% Cu was found, while the other contained 16% Ag and 3% Cu. Annealing and strain-hardening in the process of working could be established, and some information was gained on the way in which the decoration was carried out. It is hoped that this and a series of similar investigations will eventually assist archæologists. Cf. *M.A.*, **20**, 20. 9 ref. —I. S. M.

***Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. V.—New Indicators for the Micro-Volumetric Determination of Gold.** R. Belcher and A. J. Nutten (*J. Chem. Soc.*, 1951, (Feb.), 550–551).—Cf. *ibid.*, p. 548; abstract below. 3-Methyl- and 3 : 3′-diethylbenzidine are good indicators for the micro-titration of Au with quinol in neutral or slightly acid soln.—H. A. H.

***A Supersensitive Colour Reaction for Ruthenium and Osmium.** V. I. Kuznetsov (*Doklady Akad. Nauk S.S.S.R.*, 1950, **70**, (4), 629–632).—[In Russian]. The reaction depends on the reduction of HNO_3 to HNO_2 in the presence of Ru or Os. The HNO_2 so formed is then made to take part in an azo-dye reaction. K. used a soln. of 2·5 c.c. HNO_3, 250 c.c. H_2O, 1 g. α-naphthylamine, and 1·5 g. sulphanilic acid. This soln. was filtered and added to a test soln. in equal vol. and heated in boiling water. A dil. soln. of Ru or Os gives a pink coloration after ~10–30 minutes' heating. The colour is compared with that of a control soln. Most elements do not interfere with the test.—Z. S. B.

***Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. III.—3-Methylbenzidine and 3 : 3′-Diethylbenzidine as Indicators in Argentometry.** R. Belcher and A. J. Nutten (*J. Chem. Soc.*, 1951, (Feb.), 547–548).—Cf. *ibid.*, p. 546; *M.A.*, **20**, 1031. 3-Methylbenzidine and 3 : 3′-diethylbenzidine are claimed to be superior indicators to conventional adsorption indicators for the titration of Ag soln. with Br or I.—H. A. H.

***Determination of Sodium Monoxide in Sodium.** Leonard P. Pepkowitz and William C. Judd (*Analyt. Chem.*, 1950, **22**, (10), 1283–1286).—The method described depends on the physical sepn. of Na from Na_2O by repeated extraction with Hg. The Na_2O is insoluble in the resulting Na amalgam and floats on the surface of the latter. After extraction, the Na_2O is dissolved in water and titrated to a phenolphthalein end-point or, alternatively, the Na equivalent to the O is determined with a flame photometer. The size of the sample is determined by titration of the separated Na amalgam. From these two detn. the % O can be calculated. A novel sampling technique is described.—N. B. V.

***Determination of Milligramme Quantities of Vanadium in the Presence of Uranium.** R. H. Gale and Eve Mosher (*Analyt. Chem.*, 1950, **22**, (7), 942–944).—The method depends on the selective reduction of V^{5+} with standard $Fe(NH_4)_2(SO_4)_2$ soln., the sensitivity and precision being increased by a wt. microburette and modified dead-stop procedure. Results of detn. in the range 0·10–4·0 mg. V are reported.—N. B. V.

***Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. IV.—Naphthidine as Indicator in the Determination of Zinc with Ferrocyanide.** R. Belcher and A. J. Nutten (*J. Chem. Soc.*, 1951, (Feb.), 548–549).—Cf. *ibid.*, p. 547; abstract above. Naphthidine is a very satisfactory internal indicator for the titration of Zn with ferrocyanide.—H. A. H.

Notes on the Analytical Use of Cupferron. L. A. Prince (*Chemist Analyst*, 1951, **40**, (3), 59, 62–63).—The method of prepn. and most suitable working conditions for the analytical use of cupferron are outlined, and its appn. to the detn. of Cu and Fe in the same soln., and to the detn. of U, are described.—L. D. H.

Complexones in Gravimetric Analysis. Rudolf Přibil (*Chimia*, 1950, **4**, (7), 160–163).—P. refers to the fundamental work of Schwarzenbach on the appn. of complex organic compounds of carboxylic acids (complexones) to metal analysis. The anions of ethylenediamine tetra-acetic acid (H_4Y) form

with most metal ions complex combinations of the MY^{2-4} type. S. studied these complexes and determined their phys.-chem. const. He also suggested methods for the volumetric detn. of a number of metals based upon the above reactions. P. gives a review of methods of grav. detn. of Be, W, Mo, Bi, and Sn in the presence of Al, Pb, Cu, Ni, Co, Mn, and Zn. 9 ref.—W. F. H.

***Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. II.—Reaction with Oxidizing Agents.** R. Belcher and A. J. Nutten (*J. Chem. Soc.*, **1951**, (Feb.), 546–547).—[Part I. is of no met. interest]. Benzidine is readily oxidized to a blue colour; a reaction frequently employed in analytical chemistry. A study was made of the behaviour of a number of substituted benzidines and related compounds with special ref. to colour reactions of a potential analytical use. Several amines were found to be more sensitive than benzidine.—H. A. H.

Spectrographic Analysis of Pure Metals. D. M. Smith (*Met. Ital.*, 1951, **43**, (3/4), 121–128).—Following a summary of spectrographic methods and apparatus, a brief review is given of published work on the detn. of impurities in Al, Cu, Pb, Mg, Ag, Au, Pt, and Zn. An account is given of methods developed by S. for qual. trace analysis. Stigmatic spectra were used for the study of the spectral characteristics of the const. D.C. arc; by correlating arc voltages with successive stigmatic spectra, a tentative theory was advanced for the mechanism of the Ag globule arc. 20 ref.—I. S. M.

***Rational Spectrographic Determination of Trace Elements.** A. Gatterer (*Met. Ital.*, 1950, **42**, (7), 244–248).—G. particularly deals with the twin problems of obtaining the max. blackening of trace-element lines and min. blackening of the background, and with the correct reading of spectra obtained. 14 ref.—I. S. M.

Some Photometric and Sensitometric Determinations in Spectrography. Oscar Masi and Cesaro Rossi (*Met. Ital.*, 1950, **42**, (11), 403–409).—Photometric and sensitometric measurements were carried out to arrive at a correct evaluation of "absolute" spectro-quant. results. Amongst the factors particularly considered was the size of the slit of the photometer. On blackened plates in white light, two types of lack of blackening uniformity were defined as "macro-defect" and "micro-defect". The latter may lead to analytical errors amounting to several %. Sensitometric curves for various λ were determined in the latter part of the study. 9 ref.—I. S. M.

The Importance of Plate Calibration in Spectrochemical Analysis and Methods for Putting It into Practice. F. Baldi (*Met. Ital.*, 1951, **43**, (3/4), 135–142).—In the course of an investigation of the internal-standard method of quant. spectrochem. analysis, the different methods used in plate calibration are critically discussed. A method in which a two-step filter is used, the second step having a transparency $<40\%$ of the first step, is described. 11 ref.—I. S. M.

The Calibration of Step Filters in Ultra-Violet Light. F. Baldi (*Met. Ital.*, 1951, **43**, (3/4), 129–134).—Tests were carried out to determine the transparency in ultra-violet light of the three steps of a filter. In a Qu 24 Zeiss spectrograph with a Hg vapour lamp as light-source a number of spectra obtained with various apertures of the intermediate diaphragm were compared. For the filters studied and the type of plates used transparencies and the contrast factor as a function of λ are reported, using the simpler graphic method of interpreting the photometric readings.—I. S. M.

***The Application of the Hollow-Cathode Source to Spectrographic Analysis. I.—Apparatus.** F. T. Birks (*Atomic Energy Research Establishment Rep.*, 1950, (**C/R 601**), 16 pp.).—Constructional and experimental details are given for a hollow-cathode source, gas-circulation system, and excitation unit. Halogens and alkali elements have been estimated in 10-mg. samples with sensitivities ranging from 0·1 to 10 p.p.m., using a gas mixture of A and He. The medium quartz spectrograph was found to have adequate dispersion for these elements. Interchangeable cathodes enable ready appn. to routine use. 22 ref.—C. E. A.

Polarographic Analysis in Metallurgy. Giovanni Semerano (*Met. Ital.*, 1950, **42**, (4), 121–128).—After dealing with general principles, S. describes some appn. of quant. polarographic analysis in metallurgy. The main use is in the analysis of metals (Al, Cd, Fe and steels, Mg, Ni, Pb, Cu, Zn, and U) and various alloys. The examination of protective metallic coatings and the study of corrosion are also briefly referred to. 101 ref.—I. S. M.

Instrumental Method of Analysis. A. B. Hollebon and J. F. Finlayson (*Proc. Australasian Inst. Min. Met.*, 1951, [N.S.], (**162/163**), 121–136).—H. and F. describe the use of the spectrograph and polarograph in met. analysis, and give methods for (*a*) detn. of Cu in Pb during drossing operations; (*b*) analysis of refined Pb; and (*c*) detn. of Cu in antimonial Pb.—N. B. V.

***The Application of Electronic Probes to the Chemical and Crystallographic Analysis of Very Small Areas.** R. Castaing (*Recherche aéronaut*, 1951, (**23**), 41–50).—Cf. *M.A.*, **18**, 296. C. outlines the underlying principle of the method and describes the necessary modifications to be made to a commercial electrostatic electron microscope. The ability of the method to analyse accurately very small areas ($\sim$1 μ sq.) enables it to be used in a number of met. studies, e.g. detn. of intermetallic diffusion curves and the study of local variations of compn. within an alloy, in particular the analysis of segregates, precipitates, or inclusions. Some examples are quoted. In favourable cases the crystal structure, parameters, and orientation may also be determined.—N. B. V.

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12 — LABORATORY APPARATUS, INSTRUMENTS, &c.

(See also "Testing" and "Temperature Measurement and Control".)

Design of a High-Temperature Resistance Furnace. F. H. McRitchie and N. N. Ault (*J. Amer. Ceram. Soc.*, 1950, **33**, (1), 25–26).—An elect.-resistance furnace is described that is capable of operating at temp. up to 3770° F. (2075° C.) *in vacuo* or in H or inert-gas atmospheres. It consists essentially of a Mo or Ta element surrounded by a water-cooled brass case which is Ag-plated on the inside to reduce radiation losses. Problems of outgassing and atmosphere contamination by furnace materials are largely circumvented by eliminating insulation.—N. B. V.

A High-Temperature Vacuum Induction Furnace. Harold T. Smyth, Robert H. Meinken, and Leonard G. Wisnyi (*J. Amer. Ceram. Soc.*, 1951, **34**, (5), 161–163).—A furnace has been designed which is capable of maintaining temp. $>$2000° C. indefinitely while phys. properties of materials are measured. Heat is developed by induction in a Mo or Ta tube located inside a helix of water-cooled Cu tubing. Power is supplied from a vacuum-tube H.F. generator. The entire furnace is enclosed in a brass shell and operated in vacuum.—N. B. V.

***Precision Equipment for Metallurgical Analyses.** L. L. Wyman (*U.S. Atomic Energy Commission Publ.*, 1950, (**KAPL-663**), 153 pp.).—W. discusses special apparatus developed at the Knolls Laboratory for the investigation of alloy systems. This includes full constructional details of a precision dilatometer operating on the rotating-mirror principle with automatic photographic recording for use in the temp. range 0°–1650° C. A more simple type of dial-gauge dilatometer is described for low-temp. work. In a thermo-resistivity unit, a plot of the change in resistance with temp. is obtained photographically by means of a series of mirrors operated by a galvanometer in the resistance circuit of a double-bridge type and a thermocouple. For the thermal-analysis equipment, a const. temp. difference

between the specimen and an outer Nichrome container is maintained by means of a Speedomax differential controller. 8 ref.—B. W. M.

***Apparatus for the Automatic Recording of Heat-Content Curves and for Thermal Analysis at Low Rates of Heating.** Werner Jellinghaus (*Arch. Eisenhüttenwesen*, 1951, **22**, (1/2), 65–71).—Sykes' method of determining sp. heats was adapted for thermal analysis on small specimens at low rates of heating. The specimen is a hollow cylinder with a heating coil in the bore; it fits into a Cu container which is ~5·7 times as heavy. A differential thermocouple has hot junctions embedded in the specimen and the Cu box, and is connected to a sensitive mirror galvanometer which throws a beam of light on to a photo-cell connected, through amplifiers and relays, to the switch controlling the heating coil; if the specimen is cooler than the Cu box, which is placed in a vacuum tube heated by a tube furnace with a commercial programme controller, the heating coil is switched on; when the specimen gets hotter than the Cu box, the heating current is switched off; the difference in temp. never exceeds 1° C. The current in the heating coil is measured on an integrating wattmeter, assuming const. voltage and neglecting the effect of the change in the resistance of the heating coil with temp. This instrument is calibrated in amp. sec. and carries a reduction gear with a ratio of 1 : 8100, the last cog of which carries a pin which deflects a lever actuating a mirror on a horizontal axis. Thus the vertical deflection of a beam of light thrown on this mirror is proportional to the heat content of the specimen, and can be calibrated in cal./g. The light beam is deflected horizontally by a mirror galvanometer actuated by a base-metal thermocouple in the Cu container, so that the point of light can be used to plot the curve of heat content against temp. on a suitably large photographic plate. The method is very sensitive, being capable of detecting the decompn. of as little as 5% retained austenite in steel.—K. S.

The Granulometric Separator. B. Bianchi (*Met. Ital.*, 1950, **42**, (4), 128–130).—A new apparatus is described which is a development of the sedimentation type of separator. It gives a granulometric distribution curve of any powder, &c., passing through it by a method of selecting particles according to their dia. The basis of calculation is the Stokes formula: $V = \frac{2}{9} \cdot \frac{g}{\eta} \cdot (\delta - \rho) r^2$, where V = velocity of fall in cm./sec.; g = gravity acceleration in cm./sec.^{2}; η = coeff. of viscosity of the liquid; δ and $\rho = d$ of the granule and liquid, resp., in g./c.c.; and r = radius of the granule in cm. A number of curves show examples of the appn. of the formula and apparatus. 6 ref.—I. S. M.

A Magnetostatic Electron Shadow Microscope as Electron-Diffraction Instrument. Bodo v. Borries (*Kolloid Z.*, 1950, **118**, (2), 110–111).—Where a permanent magnet is used for the pole pieces of an electron lens, a secondary lens can be energized from the same source. The specimen chamber, the objective, and projector lenses, together with the two magnets between them, can then be built as a complete mech.-opt. unit. If the electron beam is made to traverse this unit in the direction Object → Objective → Projector, then we have the standard electron microscope. If, however, the electron beam is allowed to traverse the unit in the opposite direction, then the projector lens becomes a condenser lens, reducing the image of the electron source. The objective lens, by a still further reduction in the immediate vicinity of the object, causes a strong concentration of the electron beam, as in an electron shadow microscope. By this means one can change over at will to an electron-diffraction camera by slowly cutting down the refractive power of the objective, so that the image of the electron source produced in the condenser lens is reproduced in the plane of the final image. 5 ref.—W. F. H.

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13 — PHYSICAL AND MECHANICAL TESTING, INSPECTION, AND RADIOLOGY

Report of [A.S.T.M.] Committee E-1 on Methods of Testing. —— (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 515–532).—See *M.A.*, **20**, 791.

***Examination of Fatigue-Testing Machines with the Aid of Strain Gauges.** Kurt Fink and Max Hempel (*Arch. Eisenhüttenwesen*, 1951, **22**, (7/8), 265–273).—The nominal stresses imposed by a number of fatigue machines were checked by actual stress detn. on a variety of rod and sheet specimens which carried strain gauges. The investigation covered a bending and torsion machine made by Schenck and two Losenhausen universal fatigue machines. Philips 600-ohm strain gauges were used. The fluctuating strain in the specimens was projected on to the screen of a cathode-ray oscillograph as a stationary image. Each specimen was calibrated in its testing machine with static stresses, and the calibration was checked after the fatigue test. It was found that the nominal stress was incorrect in a number of cases and that the error frequently exceeded the permitted value of ±3%. It is suggested that in some tests it may be desirable to determine the actual stress directly by means of strain gauges attached either to the specimen itself or to a weigh-bar which is subjected to the same stresses.—K. S.

***The Problem of the Fatigue Strength of Test-Pieces of Different Size.** Max Hempel (*Arch. Eisenhüttenwesen*, 1951, **22**, (11/12), 425–436).—The effect of the size of the test-piece on the fatigue properties of a material has never been clearly established, largely because other effects tend to mask it. The bend fatigue strength of test-bars of increasing size approaches a lower limit which is believed to correspond to the fatigue strength in alternating tension and compression. Attempts to explain this observation on the basis of elasticity theory led v. Philipp (*Forsch. Ingenieurwesen*, 1942, **13**, 99) to predict that the ratio of the bending fatigue strength to the tension–compression fatigue strength of small test-bars (7–10 mm. in dia.) should be ~1·70. A detailed study of the literature gives ratios in the range 0·93–1·13 and H.'s own experiments on polished bars (<10 mm.) give substantially the same fatigue limits in both types of test. Tension–compression tests on bars with and without changes in cross-section involving inhomogeneous stress distribution (e.g. flat specimens with holes) showed that a variation in the cross-sectional area by as much as five times does not significantly affect the results. The factors responsible for the size effect in bending fatigue tests were investigated, and the influence of test-bar prepn., internal stresses, and test conditions on the fatigue strength of small specimens is dealt with. Mech. polishing leads to compressive stresses of 40–60 kg./mm.^{2} to a depth of 0·02–0·05 mm. below the surface in normal rotating (Wöhler) fatigue bars, 7·52 mm. in dia. These internal stresses can be reduced or eliminated by a stress-relief anneal or by electrolytic polishing. The surface stresses of shot-blasted test-bars were determined in various conditions of heat-treatment and surface finish and at various stages of the fatigue test, and were shown to decrease with increasing number of reversals until they settled down to a const. value; the higher the fatigue stress, the lower the number of cycles required to achieve this equilibrium. Tests on electrolytically polished specimens showed that the fatigue limit was lowered by the removal of the cold-worked surface layer. Test conditions, particularly cooling of the specimen and any superimposed stresses, also affect the results obtained on different-sized test-bars. Although some detailed questions remain to be solved, it can be concluded that the effect of the size of test-bar on the result of a fatigue test is primarily a matter concerning the mechanism of the test itself and not any properties of the material. 105 ref.—K. S.

***Alternate Torsion Tests on Metal Wires.** R. Zoja (*Met. Ital.*, 1951, **43**, (10), 421–424).—Tests were carried out on steel, Cu, brass, Ni, Ni alloy, Al, and Al alloy wires. It is

shown that the alternate torsion test is superior to the continuous torsion and alternate bending tests as a useful supplement to the tensile test.—I. S. M.

Pneumatic Gauging Applied to the Measurement of Surface Finish. M. Granéek and H. L. Wunsch (*Engineering*, 1953, 175, (4551), 505–507; also *Machinery* (*Lond.*), 1952, 81, (2080), 701–706).—See *M.A.*, 20, 791.—D. K. W.

Relief Methods for [Studying] Metallurgical Problems of Surface Finish. L. Locati and B. Bianchi (*Met. Ital.*, 1951, 43, (5), 176–179).—A number of problems of a met. nature related to a study of surface roughness were examined by the Brush Surface Analyser. They included the finishing properties of metals (a light alloy being cited by way of example), the tendency of light alloys to "tear" while being machined, lubrication, the wear of sliding surfaces, and a study of sheet finishes. 7 ref.—I. S. M.

Non-Destructive Testing of Materials.—I.–III. Hch. Zoller (*Pro-Metal*, 1951, 4, (21), 839–844; (22), 871–877; 1952, 5, (25), 957–963).—[In French and German]. [I.—] Z. deals with the various uses to which X-rays can be put in non-destructive testing. Normal methods of X-ray crystallography are only used for detn. of internal stresses. [II.—] The use of radioactive isotopes as a source of γ-rays for the radiography of high-d materials is briefly described. Ultrasonic methods are discussed, the use of magnetostriction and the piezo-elect. effect for the transmission of ultrasonic waves is explained, and four methods of utilizing them for non-destructive testing are dealt with: transmission, echo-sounding, resonance, and the generation of an opt. image with a suspension of Al flakes. [III.—] Z. deals with methods which do not give an image of the test-piece and defect but measure the effect of the defect on some phys. property of the material. Measurements of resistivity or eddy-current losses are discussed, and various instruments are described. Among methods specially applicable to ferromagnetic materials., ref. is made to magnetic crack detection and to hysteresis measurements; the latter are said to be too sensitive to variations in hardness, which tend to mask more serious defects such as cracks. The increased sensitivity of differential methods is emphasized.—K. S.

The Non-Destructive Investigation of Surface Defects. W. Stauffer and A. Keller (*Escher-Wyss News*, 1950–51, 23/24, 98–101).—N. B. V.

New Instruments for Non-Destructive Magnetic Testing. Werner Jellinghaus (*Arch. Eisenhüttenwesen*, 1951, 22, (3/4), 111–115).—A number of instruments designed by Förster are described. All are based on the detn. of the inductive field. The A.C. induced in the test circuit is balanced by a circuit using a specimen of standard dimensions and magnetization characteristics; the difference is projected on to the screen of a cathode-ray oscillograph. It is claimed that the indication for different characteristics is most sensitive at certain phase angles, so that by selection of the phase angle the instrument can detect cracks, or internal stresses, or segregation. A probe of small dimensions has been developed which can move over a component previously magnetized by D.C. and can reveal local differences in the magnetic field. This procedure is more sensitive than magnetic powder methods and does not depend on the surface condition of the work. The lack of detailed correlation between size of defect and the quant. indication of the instrument is pointed out.—K. S.

Development of Methods for Testing Ferromagnetic Materials. Werner Jellinghaus (*Arch. Eisenhüttenwesen*, 1951, 22, (11/12), 401–409; discussion, 409–410).—The development of magnetic testing in the last twelve years is reviewed, and a number of testing installations and circuits are illustrated. The measurement of the induction and permeability of magnetically soft materials is carried out to an increasing extent in A.C. fields, using phase-sensitive measuring rectifiers and D.C. voltmeters. In the detn. of the remagnetization losses, efforts are made to reduce the size of the specimen; this may lead to low voltages and the need for amplification in the measuring circuit. High-permeability materials for use in transformers are very sensitive to mech. stresses, and instruments for testing finished cores have been developed. The new permanent-magnet alloys of the Fe–Ni–Al type have led to the use of much smaller magnets; measuring technology has not yet fully caught up with these developments. The measurement of magnetic fields and of the saturation has been facilitated by the development of new designs of probes. Tests for magnetostriction and H.F. magnetization characteristics have also been improved, but further developments are required.—K. S.

Recent Developments in Non-Destructive Testing [of Ferromagnetics]. Fritz Förster (*Berg- u. hüttenmänn. Monatsh. Montan. Hochschule Leoben*, 1950, 95, (12), 284–291).—A description of developments in magnetic flaw-detection and testing of materials.—E. J. E.

***A Non-Destructive X-Ray Method for the Determination of the Thickness of Surface Layers.** P. Gay and P. B. Hirsch (*Brit. J. Appl. Physics*, 1951, 2, (8), 218–222).—The method requires that the X-ray absorption coeff., μ, of the surface layer be known. A pencil of monochromatic X-rays is diffracted from a suitable family of planes of the substrate, whether this is mono- or polycryst. The intensity of the diffracted beam is measured, photographically or by Geiger counter, as a function of the angles of incidence and emergence of the X-rays. The variation of intensity is due to the varying *effective* thickness of the surface layer, the true thickness of which can hence be found. One appn. was the measurement of the thickness t of a layer of Al on polycryst. Cu, ~20 μ thick, to an accuracy of ~1 μ. The approx. limits of t over which the method is applicable are 0·1–50 μ.

—R. W. C.

Pin-Pointing of Defects by X-Rays. Francesco Baldi (*Met. Ital.*, 1950, 42, (4), 133–136).—A method is described for the three-dimensional pin-pointing of defects below the surface of specimens. Two radiographs are made, using two different films. 13 ref.—I. S. M.

The Radiographic Examination of Welds: An Attempt at the Quantitative Evaluation of Defects. Oscar Masi (*Met. Ital.*, 1951, 43, (7), 261–269).—Photometric measurements and microphotometric tests were carried out on test-bars representing three typical defects (insufficient penetration of the weld, porosity, and non-metallic inclusions). The film used was calibrated according to the relation $D = f(s)$, D being photographic d, and s the thickness of the piece tested. 5 ref.—I. S. M.

15—FOUNDRY PRACTICE AND APPLIANCES

Casting Characteristics of Some Aluminium Alloys. —— (*Mech. World*, 1951, 130, (3365), 35–37).—N. B. V.

Direct-Chill Casting of Aluminium Ingots. W. E. King (*Mech. Eng.*, 1951, 73, (11), 887–891).—A description of the direct-chill method of semi-continuous casting, as developed and used in the plants of the Aluminum Company of America.

—N. B. V.

[Discussion on a Paper by W. Babington and D. H. Kleppinger:] Aluminium [Pressure] Die-Castings: The Effect of Process Variables on Their Properties. —— (*Proc. Amer. Soc. Test. Mat.*, 1952, 52, 197–200).—See *M.A.*, 19, 805.

Aluminium Remelting. K. K. Bhasin (*Trans. Indian Inst. Metals*, 1950, 4, 203–207).—An outline of furnace requirements for the remelting of Al and operational notes on charging, stirring, fluxing, skimming, pouring, and temp. control.—P. F. N.

Review of the More Common Casting Defects and Their Respective Causes in Aluminium-Alloy Castings. Mario Barbero (*Met. Ital.*, 1951, 43, (11), 482–486).—In an attempt to present a concise classification of casting defects and their causes as far as Al alloys are concerned, B. lists nine main classes, giving a number of possible causes for each. Illustrations are given by way of example.—I. S. M.

The Development of Casting Methods for Liquid-Cooled Cylinder Blocks in Aluminium-Silicon-Magnesium Alloy. Philipp Schneider and Wilhelm Petzka (*Neue Giesserei*, 1950, **37**, (21), 461–466; (22), 488–491; (23), 515–520).—A detailed account of the development of moulding and casting techniques for the mass-produ. of a difficult Al-alloy cylinder block. The following methods of mould fabrication were investigated: (1) sand mould and cores; (2) construction entirely from sand cores; (3) permanent half mould combined with a "mixed" half mould of sand and metal parts; (4) a permanent steel mould. Of these, (3) is the most promising for further development; it has the advantages of simplicity in assembly, of higher adaptability than (4), good accuracy and sand economy, with a casting time of 10–14 min. (1) and (2) permit of greater speed (6–7 min. cycle) and are more adaptable. (2) obviates the use of moulding boxes and requires less sand, but more bonding agent, than (1) and is rather less accurate than (1). (4) offers the highest degree of accuracy and sand economy, and a total saving of foundry space of 30% compared with (1). Its casting time is somewhat longer (15 min.), the cost of fabrication is high, and the mould cannot be adapted to any changes in the design of the casting.—E. J. E.

Manufacture of an Aluminium Double Match-Plate of the Monobloc Type for Moulding in Sand. —— (*Fonderie*, 1951, (64), 2439–2446).—Detailed instructions for making the match-plates are given, with numerous illustrations.—N. B. V.

***The Effect of Preliminary Oxidation on the Corrosion of Cast Irons in Molten Aluminium and Aluminium-Silicon Alloys.** Paul Bastien and Pierre Azou (*Fonderie*, 1950, (55), 2111–2121).—Cf. B. and Daeschner, *ibid.*, 1948, (31), 1217; *M.A.*, **16**, 591. Tests carried out on specimens of grey Fe, malleable Fe, 32% Cr cast Fe, and mild steel by immersing them for 8 hr. in molten Al and Al–Si alloys contg. 11·57 and 15·92% Si at 850° C. after exposure for varying periods up to 96 hr. in air at 850° C., showed that a short preliminary oxidation treatment notably reduced the rate of attack by molten Al. The results confirm the conclusion reached in previous work that the greatest resistance to attack by molten Al and Al–Si alloys is offered by a pearlitic grey cast Fe contg. fine and uniformly distributed graphite particles.—N. B. V.

Mechanized Job-Shop Foundry for Aluminium. C. H. DeLamater (*Mech. Eng.*, 1950, **72**, (3), 211–215).—An account of the mechanized materials-handling and conveyor system in the Bridgeport, Conn., foundry of the Aluminum Company of America.—E. J. E.

***Moulding and Testing Non-Ferrous [Copper Alloy] Hydraulic Castings.** W. Thomson (*Proc. Inst. Brit. Found.*, 1951, **44**, B102–B109).—Details are given of the moulding equipment and foundry plant. Moulding sands and core mixes are given in full, the casting procedure and core-drying technique are described and illustrated. The alloy used contains Cu 83, Sn 7, Zn 5, Pb 5%, +1½% cupro nickel. The various types of test-bar, both keel and shaped, and also cast-on and separate test-bars are discussed and the results of tensile and pressure tests given. It was found that whilst the casting itself and the separate test-bar were up to specification, the cast-on test-bar was always under specification. The effect of a cupro-nickel addn. to 83 : 7 : 5 : 5 alloy on the bursting pressure was investigated.—G. J. S.

The Melting and Casting of Aluminium Bronzes. Edmund R. Thews (*Neue Giesserei*, 1948, **33/35**, (4), 110–116).—A survey of the melting and casting properties of Al bronzes. The effects of addn. of Fe, Ni, Mn, Pb, and Si are discussed, and melting, alloying, and casting techniques are described in some detail.—E. J. E.

The Production of Ships' Propellers and Windows. —— (*Engineer*, 1951, **192**, (5004), 808–810).—An account of the prodn. methods employed at Bull's Metal and Melloid Co., Ltd., Glasgow, in the manufacture of ships' propellers and windows.—D. K. W.

Zinc Pressure Die-Casting [Outside Germany]. Kurt Bayer (*Neue Giesserei*, 1949, **36**, (8), 232–236).—A survey of the development and appn. of Zn alloy die-casting in Britain and the U.S.A. Descriptions of some American pressure die-casting machines are given.—E. J. E.

Continuous-Casting Practice in the Non-Ferrous Industries. R. Chadwick and J. F. Hobbs (*J. B'ham Met. Soc.*, 1951, **31**, (1), 13–24).—A short review, dealing particularly with the casting of high-strength Al alloys.—N. B. V.

Aspects of Continuous Casting. D. R. Wood (*J. B'ham Met. Soc.*, 1951, **31**, (1), 25–30).—W. considers briefly the thermal equilibrium in the open-mould continuous casting process and examines the conditions under which various metals and alloys may be cast by such a method.—N. B. V.

Continuous Billet Casting: Application to High-Melting-Point Alloys. J. C. Wright (*Iron Coal Trades Rev.*, 1951, **162**, (4339), 1319–1323).—Based on a prize-winning essay. Problems associated with the continuous casting of high-m.p. metals are reviewed. The Williams, Goss, and Junghans machines are said to be suitable for high-m.p. metals.
—N. B. V.

The Manufacture of Multiple-Groove Pulleys. François Simorre (*Fonderie*, 1951, (66), 2513–2520).—S. comments on an article by Birch (*Amer. Foundryman*, 1950, **17**, (1), 25; *M.A.*, **17**, 853) and makes suggestions of his own for the successful casting of a 3-groove pulley.—N. B. V.

Determination of the Content of a Casting Ladle During Pouring. P. Sahmel and H. Pieper (*Neue Giesserei*, 1950, **37**, (11), 211–213).—A formula is derived and tables and graphs are given for the detn. of the weight of metal in a tilted ladle of known dimensions.—E. J. E.

Precision Casting by the Lost-Wax Method. —— (*Alluminio*, 1947, **16**, (11/12), NdO 119–136).—Report from the Istituto Sperimentale dei Metalli Leggeri. An account of the historical development of the lost-wax process and of the modern technique; compn. of ferrous and non-ferrous alloys in common use are stated.—E. J. E.

Pressure Die-Casting. P. Uebbing (*Neue Giesserei*, 1950, **37**, (25), 571).—A brief note.—E. J. E.

Graphite and Its Applications in the Foundry. Charles Dennery and François Pensa (*Fonderie*, 1951, (67), 2547–2564).—After an account of the properties of graphite, various appn. in the foundry are described, viz.: for crucibles and moulds, as addn. to mould and core sand, in the construction of melting and reheating furnaces, &c.—N. B. V.

Recent Progress in the Cement-Sand Moulding Process. Martin Beilhack (*Neue Giesserei*, 1950, **37**, (15), 296–300).—Criticisms of the cement-sand process are discussed; the advantages are held greatly to outweigh the disadvantages. The moulding technique is much simplified, the quality of castings improved, costs are reduced, and lower demands are made on the skill of the foundry worker.—E. J. E.

Synthetic Moulding Sand. H. Herschenz (*Neue Giesserei*, 1950, **37**, (26), 595–596).—A brief account of the use of synthetic sand for mould and core fabrication.—E. J. E.

The Influence of Coal-Dust Additions to Moulding Sand (for Non-Ferrous Castings). Edmund T. Richards (*Neue Giesserei*, 1948, **33/35**, (5), 147–148).—The effect of addn. of 5–7% coal dust on the properties of moulding sand and on the casting is described. Comparisons are made with sawdust, which is, on the whole, preferred.—E. J. E.

Study of Some Factors Influencing the Heat Characteristics of Foundry Sands. Mario Ongaro (*Met. Ital.*, 1950, **42**, (10), 352–356).—O. studied the influence on hot permeability and cohesion of humidity and sand compn. and the influence on thermal stability of grain-size and cold cohesion properties.
—I. S. M.

The Siliceous Sands of Torre del Lago and Their Application in the Foundry. Guglielmo Somigli and Antonio Catelani (*Met. Ital.*, 1951, **43**, (7), 281–295).—Properties, commercial types, and appn. of Torre del Lago foundry sands are given. Results of tests are reported which concern the appn. of the sands in ferrous and non-ferrous foundry work.—I. S. M.

Rational Analysis of Clay-Containing Foundry Sands. Ermenegildo Zan (*Met. Ital.*, 1951, **43**, (8), 337–338).—An analytical method is described by which it is possible to determine the proportions of sand constituents and their influence on foundry properties.—I. S. M.

***A New Measuring Quantity for Testing Moulding Sands.** W. Reitmeister (*Neue Giesserei*, 1950, **37**, (12), 225–231).—The " sp. vol." of sand (the vol. of 1 kg. subjected to standard compression defined by R.) passes through a max. with increasing water content. This peak in the " swelling curve " is characteristic of the sand; it can be used as a basis for comparison and can be related to grain-size and gas permeability. —E. J. E.

The Nature of Moulding Sand and Its Examination by New Methods of Testing. W. Reitmeister (*Neue Giesserei*, 1950, **37**, (26), 585–588).—The relation of the " swelling curve " (*ibid.*, (12), 225; preceding abstract) to changes of gas permeability and strength with increasing water content is further examined. R. characterizes two main types of sand: (i) the curves relating g.-vol. and gas permeability with moisture content are roughly parallel, and the strength rises sharply in the swelling range; (ii) the strength is low and rises slowly, and g.-vol. and gas permeability curves are not closely related. (See also *M.A.*, **20**, 909.)—E. J. E.

***Evaluation of Sieve Analyses of Mould and Core Sands.** Wilhelm Bültmann (*Neue Giesserei*, 1949, **36**, (9), 264–265; discussion, 265–266).—Report to the Verein Deutscher Giessereifachleute. The grain-size analysis of a sand is plotted graphically in the form of an additive (integral) curve. From this, two values can be read off, which are proposed as measures of grain-size distribution; the " mean " grain-size is that corresponding to 50% of the grains, and the percentage of grains in the range from $\frac{2}{3}$ to $\frac{1}{3}$ of the " mean " grain-size is taken as an index of the " evenness of distribution ".—E. J. E.

Core Blowers. Jakob Hagen (*Neue Giesserei*, 1950, **37**, (1), 2–8).—A general description of core blowers and of the factors affecting the successful and economical manufacture of cores. Recently, core blowers have been adapted to make simple moulds.—E. J. E.

Compressed-Air Moulding Machines: Simple and Jolt-Ramming Lifting and Turnover Types. B. Gebhardt (*Neue Giesserei*, 1950, **37**, (19), 397–405).—An illustrated review of compressed-air moulding machines for small and medium-size moulds.—E. J. E.

The Problem of Dust Extraction and Ventilation in the Foundry Industry. Wolf Mulhard (*Fonderie*, 1951, (70), 2671–2684).—N. B. V.

Foundry Practice and Research. G. Masing (*Neue Giesserei*, 1949, **36**, (9), 273–275).—A lecture. The interdependence of practice and research is illustrated by ref. to the formation of surface cavities in castings and the development of porosity in bronze castings.—E. J. E.

The Moulder's Profession. L. Frede (*Neue Giesserei*, 1949, **36**, (5), 155–158).—A brief account of the professional requirements and prospects of apprentices in the moulding profession. —E. J. E.

Theoretical and Practical Training of Apprentices, Skilled Men, and Engineers in the Foundry Trade. Erich Hugo (*Neue Giesserei*, 1950, **37**, (19), 405–412).—A review of the work of a Committee of the Verein Deutscher Giessereifachleute on educational and training requirements.—E. J. E.

Training of [Foundry] Apprentices. Wilhelm Esch (*Neue Giesserei*, 1950, **37**, (12), 231–232).—E. comments on the report of a Committee of the Verein Deutscher Giessereifachleute, which defines the technical standards for the moulding trade, and its significance in training methods.—E. J. E.

Do You Consider the Protection of Your Foundry Workers? Heinz Bönig (*Neue Giesserei*, 1950, **37**, (2), 25–29).—A survey of accident and health hazards in foundries and measures for their prevention.—E. J. E.

16 — SECONDARY METALS: SCRAP, RESIDUES, &c.

The Treatment of Aluminium Scrap in the U.S.A. G. Gürtler (*Aluminium*, 1951, **27**, (4), 98–101).—A report of observations made during a visit sponsored by the O.E.E.C. (cf. *M.A.*, **20**, 672).—E. J. E.

17 — FURNACES, FUELS, AND REFRACTORIES

The Present State of Development of Melting Furnaces for Light Metals. Philipp Schneider (*Neue Giesserei*, 1950, **37**, (14), 269–274).—A critical survey of gas- and coke-fired furnaces for melting Al and Mg and their alloys.—E. J. E.

Electric Melting Furnaces for Light Metals. Philipp Schneider (*Neue Giesserei*, 1950, **37**, (17), 339–346).—(Cf. *ibid.*, (14), 269; preceding abstract). Elect. resistance hearth and L.F. induction furnaces are reviewed, with particular ref. to the melting of Al and Mg alloys.—E. J. E.

The " Bora " Low-Frequency Induction Furnace for Melting Non-Ferrous Metals. —— (*J. Four élect.*, 1951, **60**, (3), 76–78).—Describes an Italian furnace suitable for melting Al- and Cu-base alloys. Melting costs are compared with those for other types of melting furnace.—N. B. V.

[Discussion on a Paper by S. F. Radtke, R. M. Scriver, and J. A. Snyder:] Arc Melting of Titanium Metal [and the Mechanical Properties of the Resulting Ingots]. —— (*J. Metals*, 1951, **3**, (11), 1046).—See *M.A.*, **19**, 319.

[Discussion on a Paper by W. J. Kroll, W. W. Stephens, and J. P. Walsted:] Graphite-Rod Hairpin-Resistor Furnace for High Temperatures. —— (*J. Metals*, 1951, **3**, (11), 1074).—See *M.A.*, **19**, 551.

The Theory of the Generation of Heat in High-Frequency and Arc Furnaces. Fritz Walter (*Arch. Eisenhüttenwesen*, 1951, **22**, (11/12), 355–365).—The nature of H.F. induction and of the elect. arc are briefly discussed, and the main characteristics of melting furnaces depending on these sources of heat are outlined. The influence of the frequency, the permeability, and elect. conductivity of the charge on the absorption of energy are discussed. The elect. resistance of round and flat bodies is calculated, and the energy absorbed from the electromagnetic field of force of an induction coil is determined. The influence of the nature of the supply and of the gas atmosphere on the heating effect of an arc is considered, and the irregularities in the arc energies in three-phase furnaces are attributed to the lack of symmetry in the linking of the three low-tension circuits.—K. S.

A Review of Progress in Electric Furnaces. D. M. Dovey and I. Jenkins (*G.E.C. Journal*, 1951, **18**, (4), 194–211). —N. B. V.

General Features of Radio-Frequency Heating and Its Industrial Applications. M. G. Favre (*Brown–Boveri Rev.*, 1951, **38**, (11), 317–319).—N. B. V.

Power Required for the Radio-Frequency Heating of Metals. A. Leemann (*Brown–Boveri Rev.*, 1951, **38**, (11), 331–332). —N. B. V.

Soldering, Annealing, Melting, and Sintering with Radio-Frequency Heating Equipment. G. Küchli (*Brown–Boveri Rev.*, 1951, **38**, (11), 339–343).—N. B. V.

Guide to the Choice, Construction, and Operation of Core Ovens. —— (*Fonderie*, 1951, (66), 2521–2535).—A comprehensive review.—N. B. V.

The Use of Infra-Red Radiation for Drying Moulds and Baking Cores. —— (*Fonderie*, 1951, (69), 2659–2664). —N. B. V.

18 — HEAT-TREATMENT

Improved Annealing Methods: A Step Towards Raising Quality. —— (*Pro-Metal*, 1951, **4**, (21), 850–853).—[In French and German]. The early development of bright-annealing furnaces for Cu alloys is briefly reviewed and the merits of continuous furnaces are discussed. A continuous bright-annealing furnace recently installed in Switzerland is described. Burnt and purified town's gas supplies the atmosphere, and 500 kg./hr. of Cu or nickel silver sheet, plates, discs, tubes, wires, or sections, travel through the furnace. Gas consumption is unavoidably higher than in older batch-annealing muffles, and the process is more expensive; the improved quality of the product justifies the additional cost, however.—K. S.

The I.S.M.L. Method for the Codification of Symbols for the States of Heat-Treatment of Light Alloys. —— (*Alluminio*, 1949, **18**, (3), 297–304).—Report from the Istituto Sperimentale dei Metalli Leggeri. The principal methods of heat-treatment (annealing, soln.-treatment, and ageing) are classified and discussed. A notation is proposed for indicating the condition of heat-treatment of Al alloys.—E. J. E.

19 — WORKING

Aluminium Seamless Tubing. M. F. Cook (*Mech. Eng.*, 1950, **72**, (9), 723–726, 732).—A description of the processes involved in the manufacture of Al and Al alloy tubes by direct extrusion and by cold drawing of extruded blooms. Ref. is also made to the heat-treatment and straightening of the tubes.—E. J. E.

Semi-Manufactures [in Copper]. [—I.–X.] M. Bourdier and C. Lachaud (*Cuivre, Laitons, Alliages*, 1951, (1), 9–13; (2), 8–14; (3), 9–14; (4), 11–19; 1952, (5), 7–15; (6), 9–16; (7), 9–14; (8), 9–15; (9), 6–13; (10), 9–15).—A series of articles dealing with methods of fabrication (casting, rolling, drawing, &c.) of Cu (and to a minor extent of its alloys), mainly for the benefit of the users of such products. It is phrased in fairly simple terms, and is well illustrated with drawings and photographs of typical plant. [I.—] Covers foundry work in producing the shapes such as rolling slabs, wire-bars, extrusion billets, &c., used in fabricating plant. Descriptions are given of reverberatory, tilting, and rotating furnaces, with the particular field of appn. of each, details of working and the most suitable fuels. Brief mention is also made of elect. arc furnaces. [II.—] Deals with the types of furnaces employed in the melting and casting of Cu alloys, brass, cupro-nickel, bronze, &c. These include fixed crucible, tilting crucible, L.F. and H.F. induction. Methods of operation, capacities, and fuel or power consumption are dealt with in some detail, particularly for the elect. furnaces. [III.—] Mainly devoted to ancillary equipment in the foundry, and control of the melting and casting operations, such as prepn. of the charge, and compn. control of the molten metal before casting, followed by descriptions of the methods of casting, with some notes on the mechanism of solidification. A fairly comprehensive section is devoted to continuous casting and a description given of the Junghans-Rossi process, followed by some notes on centrifugal casting. [IV.—] Methods of scalping are touched on lightly, chiefly for extrusion billets, and the rest of the instalment deals with extrusion presses, working on both the direct and inverted principle. Particulars are given of the range of alloys that can be successfully extruded, including pure Cu, with details of the temp. and pressures employed for each. Results of researches into the flow of metal in both types of press are given, the largest press illustrated being of 5000 tons. [V.—] Covers the prodn. of tubes by oblique rolling by the Mannesmann process. The operation and limitations of this process are discussed in some detail, and descriptions given of a Mannesmann mill, of a Steifel mill, and of a Pilger mill. The remainder of the instalment deals with the prodn. of Cu tubes and plates by electrolytic deposition, with particulars of the Cegedur plant at Dives. [VI.—] Deals with the drawing of wire, sections, and tubes on both chain and hydraulically operated drawbenches with both single and multiple dies. The drawing of tubes is dealt with at some length, both with and without internal mandrel. Methods of pointing are described, including " push-pointing " equipment. [VII.—] Deals with various types of straightening machines for rod and tubes, most of them working on the multi-roll principle. An illustrated description is also given of a combined drawing, straightening, and polishing machine. The operation of wire-drawing machines of the bull-block type, with coiling mechanism is described. [VIII.—] Describes the hot and cold rolling of wire stock from wire-bars. Descriptions are given of preheating furnaces, breaking-down and finishing trains, with both vertical and horizontal layout and with automatic loop guides. Methods of coiling finished rods, pickling and rinsing tanks and other equipment are illustrated. [IX.—] Deals with equipment for the high-speed continuous drawing of fine and very fine wires on variable-speed tandem machines, with methods of guiding the wire between successive machines to avoid breakages. Methods of producing wire in metals too brittle to draw down from rod are also described. [X.—] Devoted mainly to the prodn. of stranded and co-axial cables and of special types of bare and insulated cables, including hollow conductors. Illustrations are given of single and tandem stranding machines, of stranders with tandem spools and of squirrel-cage cabling machines. The drawing of special shapes of wire, such as trolley wire, taper-section wire for hollow conductors, and semi-hexagonal wires for close-packed strands, is also dealt with.—W. F. H.

Making [Textile] Printing Rolls in France. Michel Denoix (*Cuivre, Laitons, Alliages*, 1951, (1), 21–24).—A short illustrated description of the prodn. of hollow Cu rolls, supported by solid steel mandrels with conical fit, and methods of engraving, for use in the silk- and calico-printing trades. Metal compn., phys. properties, methods of fabrication, and heat-treatment are given, with notes on methods of engraving, which vary with the class of material to be printed. Mention is also made of alternative metals—steel, Zn, Al, and brass.
—W. F. H.

The Manufacture of Clock Cases: Some Thoughts on Present-Day Manufacture of Clock Cases in Switzerland. Charles Hirschy (*Pro-Metal*, 1951, **4**, (24), 934–936).—[In French and German]. The requirement for artistic design adapted to mass prodn., or at least serial prodn., leads to the use of materials which lend themselves easily to a variety of processes, pressing, hammering, machining, enamelling, electroplating, engraving, &c. The producers of non-ferrous metals in Switzerland go out of their way to make a wide variety of alloys and forms available, so that the designer has a wide choice of semi-manufactured material on which to base his conception.—K. S.

***Cold-Rolling Technique: The Application of Theory and Experiment to the Practice of Rolling. VI.—Methods of Calculating Roll Force and Torque Based on Theories of Rolling (4).** Hugh Ford (*Sheet Metal Ind.*, 1951, **28**, (292), 693–704).—Cf. *ibid.*, (289), 427; *M.A.*, **18**, 778. Concluding article of the series.—N. B. V.

A Note on the Cold Rolling of Very Thin Strip. R. Hill and I. M. Longman (*Sheet Metal Ind.*, 1951, **28**, (292), 705–706).—It is shown that, owing to elastic resilience of the rolls, there is a min. thickness of strip that can be rolled to a given percentage reduction. Calculations of min. thickness are given.—N. B. V.

A Large Swiss Hot-Rolling Mill. —— (*Pro-Metal*, 1951, **4**, (20), 804–810).—[In French and German]. The Schwei-

zerische Metallwerke Selve und Co., Thun, have installed a new hot-rolling mill for cogging and blooming ingots of a variety of non-ferrous metals. The two-high reversing mill, driven by D.C. motors, deals with ingots up to 1000 kg. in weight and 200 mm. thick and rolls them into slabs up to 1400 mm. wide. There is an auxiliary fine adjustment of the rolls by means of an oil pressure cylinder. The rolls can be dismantled easily for dressing. The roller tables are covered and the rollers are independently driven in sets of four. The elect. installation ensures a continuously variable speed and very rapid reversal.—K. S.

The Technological Mechanics of Deep Drawing. Hans Kostron (*Arch. Eisenhüttenwesen*, 1951, **22**, (7/8), 205–213).—The geometry of deep drawing is considered, and the local deformation is calculated in relation to the drawing ratio, the instantaneous position of the edge of the blank, and the depth of the draw, assuming (i) that the thickness of the sheet remains const., and (ii) pure compression without radial extension. Assuming that the work-hardening follows a parabolic curve, the radial "drawing in" stresses are calculated for materials of different work-hardening capacities. Using the principal-shear-stress theory, the tri-axial state of stress can be established for all points in the blank and for any instant in the drawing process. This leads to positive conclusions regarding the actual conditions of flow during deep drawing; in the inner part of the blank the thickness decreases in the early stages of the draw, but increases after a definite time, which is shorter the greater the work-hardening capacity of the material.—K. S.

***Investigation of a New Hot Deep-Drawing Process.** Dieter Lenz (*Arch. Eisenhüttenwesen*, 1951, **22**, (7/8), 215–224).—A 30-ton press was adapted for experiments on the hot deep-drawing process developed at the Vereinigte Leichtmetall-Werke at Hanover, which involves the use of a high temp. in the zone where deformation is actually taking place and a normal temp. in the part which has already been drawn down and carries the stress. The upper surface of the die and the holding grip are heated elect., the vertical inner die face is water-cooled; the sheet is pre-heated in a bath of mineral oil. Thus the resistance to deformation in the drawing zone is low, while the strength of the drawn shell is high; as a result higher drawing ratios are permissible in the first draw. Thus, with an Al alloy at 400° C., a ratio of 3·92 gave perfectly satisfactory results, while at room temp. the ratio must be kept $<2{\cdot}0$. Investigations of the course of the stress variation during drawing and of the max. drawing stress in relation to the drawing ratio and the temp. of deformation laid the basis for a theoretical consideration of individual experiments; it is shown that the drawing stress for various depths of draw can be calculated for this hot deep-drawing process, using the method of Kostron and the results of detailed studies of the mech. properties of the alloys employed. In practice, the new process saves a number of draws. The necessary equipment can easily be built into existing presses; it must be interchangeable so that different components can be drawn and different sheet thicknesses employed. The temp. in the deformation zone depends on the alloy, but it must be above the recrystn. temp., and it is necessary to avoid temp. ranges in which severe grain growth may occur.—K. S.

Some Technical Considerations on the Coining of Metals. Paul Huguenin (*Sheet Metal Ind.*, 1951, **28**, (288), 345–352, 356).—Translated from *Pro-Metal*, 1950, **3**, 587; *M.A.*, **20**, 918.—N. B. V.

***Some Friction Effects in Wire Drawing.** G. D. S. McLellan (*J. Inst. Metals*, 1952–53, **81**, (1), 1–13).

Practical Considerations of [the Role of] Cemented Carbides in the Mechanical Working of Materials. Carlo Alfredo Bertella (*Met. Ital.*, 1950, **42**, (8/9), 299–304).—A general survey outlining the important part played by cemented carbide tools in the working of materials, particularly metals. B. notes that their use in Italy is less widespread than elsewhere, and points the way to their progressively increasing adoption. 7 ref.—I. S. M.

Contribution to the Study of the Cutting Capacity of Tools. M. Cociglio (*Met. Ital.*, 1951, **43**, (5), 170–175).—After reviewing various methods for determining an index value to indicate the cutting capacity of a tool, a testing procedure is described based on the wear of the tool at const. speed and uniform path. 6 ref.—I. S. M.

The "Building Up" of Chips in Machining. Giuseppe Carro-Cao (*Met. Ital.*, 1951, **43**, (7), 270–280).—A study has been made of the building-up phenomenon encountered in machining metals. An attempt is made to relate the embrittling factors in plastic deformation to this problem.—I. S. M.

Precision Turning on Automatic Lathes : A Swiss Speciality. —— (*Pro-Metal*, 1951, **4**, (22), 859–866).—[In French and German]. The precision turning of small components for a variety of industries is undertaken by a number of Swiss firms specializing in the development and use of automatic lathes. Much of their work is done in brass, because of its easy machinability and because the rods, tubes, sections, &c., are manufactured locally and the large quantities of scrap can be re-sold easily.—K. S.

Colloidal Graphite Serves as Lubricant in Hot and Cold Forming of Metal. Alden Crankshaw (*Materials and Methods*, 1951, **34**, (4), 180, 182–183).—The use of colloidal graphite as lubricant in deep drawing and stretch-forming, wire drawing, extrusion, spinning, casting, &c., is described.—N. B. V.

Waxes Now Used to Process as Well as Protect Materials. Kenneth Rose (*Materials and Methods*, 1951, **34**, (4), 104–107).—Waxes are now being used not only for protective films on metals but also as lubricants in such processes as cutting, deep drawing, cold heading, wire drawing, &c. Animal, vegetable, mineral, and synthetic waxes are available in many forms for these purposes.—N. B. V.

Some Industrial Experiences with Synthetic Lubricants. C. H. Sweatt and T. W. Langer (*Mech. Eng.*, 1951, **73**, (6), 469–476).—The appn. of polyalkylene glycols and their derivatives are discussed, some ref. being made to use in metalworking operations such as deep drawing, and to their behaviour in contact with bronze gear-wheels.—N. B. V.

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20 — CLEANING AND FINISHING

(See also "Protection" and "Electrodeposition".)

Experiences with Chemically Brightened Table Ware in Reflectal [and Super-Pure Aluminium]. W. Helling and H. Neunzig (*Aluminium*, 1951, **27**, (4), 95–97).—An illustrated account of household and catering ware of brightened "Raffinal" (99·99% Al) and "Reflectal" (0·5–2·3% Mg), with a brief discussion of problems encountered in anodic and chem. brightening.—E. J. E.

High-Purity Aluminium–Magnesium Alloys for Anodic Brightening. J. Hérenguel (*Met. Ital.*, 1951, **43**, (2), 72–73).—[In French]. Conditions for obtaining bright surfaces by electrolytic polishing of Al–Mg alloys are briefly set out. They include the absence of separate phases and of macroscopic segregations in the Mg content of solid soln., fine grain-size, absence of preferential orientation, and anodizing conditions not conducive to anisotropy in the growth rate of the Al_2O_3 film. 5 ref.—I. S. M.

The Chemical Descaling of Copper-Base Alloys. [—I.–III.] Jean Bigeon (*Cuivre, Laitons, Alliages*, 1951, (1), 15–18; (2), 23–26; (3), 21–25).—[I.—] A general review of the more common methods of pickling Cu and Cu alloy wrought products after hot working or heat-treatment. The principal oxides involved are CuO, Cu_2O, and ZnO, all of which are attacked by mineral acids, while any insoluble oxides such as SiO_2 and PbO are precipitated in the bath as slime. The acids used are H_2SO_4, HCl, and HNO_3. [II.—] Details are given of the methods employed, strength of acid, temp., &c., for

Cu, brass, bronze, nickel silver, cupro-nickel, and Be-bronze. Recent developments include electrolytic descaling, use of accelerators, and treatment with chromic acid. [III.—] A new process of pickling is described, using $Fe_2(SO_4)_3$ in place of H_2SO_4, which results in a big saving in acid. The process as applied to Cu, bronze, and cupro-nickel is described in detail, with illustrations of items of plant.—W. F. H.

Lacquering to Obtain Brilliance and Metallic Lustre. H. H. Vevers and G. E. Gardam (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 179–186; discussion, 187–193; also *Metal Ind.*, 1952, **80**, (23), 463; discussion, 463–464).—See *M.A.*, **20**, 439.

Practical Considerations in the Application of Vacuum Coatings for Metal Finishing. L. Holland (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 167–178; discussion, 187–193).—See *M.A.*, **20**, 440.

Pickling Vats for Copper-Base Alloys. —— (*Cuivre, Laitons, Alliages*, 1951, (4), 31–35).—Covers the choice of materials of construction for pickling vessels to contain the acids commonly used—H_2SO_4, HCl, HNO_3, CrO_3, $ZnCl_2$–NH_4Cl, and $FeSO_4$. The materials dealt with are Pb, Monel, stainless steel, pitch pine, stoneware, Neoprene, rubber, acid-resisting cement, and volcanic rock.—W. F. H.

More Careful Washing [Degreasing]. F. Kauffungen (*Pro-Metal*, 1951, **4**, (19), 795–797).—[In French and German]. Assembled components and Ni-plated surfaces frequently hold soln. used for chem. treatment by capillary attraction. Unless great care is taken in washing, remnants of these chemicals are retained during storage or use, and corrosion may occur. Tap-water may leave Ca salts on the surface, and distilled water should be used for washing out alkaline soln. or for boiling; oil or grease should be removed by washing in an organic solvent, but a very fine film will still remain. The effectiveness of washing should be checked regularly by testing for residues of the reagents used in the earlier treatment.
—K. S.

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21 — JOINING

A New Method for Joining Aluminium and Steel and Its Use in the Motor Industry. [Al-Fin Process]. G. Gürtler (*Automobiltechn. Z.*, 1951, **53**, (4a), 102–105).—An illustrated description of the Al-Fin process developed in America for joining Al and Al alloy parts to cast Fe and steel, with particular ref. to the securing of Al fins to the cylinders of air-cooled engine cylinders. The process is based upon the prior formation of a thin Fe–Al layer, 0·02–0·03 mm. thick, on the surface of the cylinder, on to which the Al fins are subsequently cast or otherwise formed. Examples of other appn. of the process are also given.—W. F. H.

Hard Soldering (Brazing) of Aluminium and Aluminium Alloys. Ernst Blohm (*Automobiltechn. Z.*, 1951, **53**, (4), 84–85).—A short illustrated description of the process of hard soldering or brazing of Al and its alloys by means of a thin layer of low-m.p. alloy rolled on to or otherwise affixed to or interposed between the two parts to be joined and subsequently heated to a controlled temp., either in a furnace or in a salt bath.—W. F. H.

New Publications on Soldering. H. v. Hofe (*Schweissen u. Schneiden*, 1951, **3**, (2), 63–64).—A short review. 62 ref.
—N. B. V.

***Welding of Aluminium Alloys : Value of Laboratory Tests.** W. I. Pumphrey and D. C. Moore (*Trans. Inst. Weld.*, 1949, **12**, (5), 116–124; discussion, (6), 146–150).—Cf. *J. Inst. Metals*, 1947, **73**, 33, 197, 273; 1948, **74**, 227, 425, 439; 1948–49, **75**, 203, 235, 257, 727. To establish whether laboratory ring-casting and restrained-welding tests previously described accurately predict the tendency to cracking of an Al alloy when welded under industrial conditions, results of such tests have been compared with those of large-scale patch-welding tests on super-purity and commercial-purity Al, 3 Al–Si alloys of high purity, and 10 commercial Al alloys. In the case of all but two of the alloys (Al + 1½% Si and Al + 1¼% Mn), the relative susceptibilities to cracking during welding established in the laboratory tests were in very close agreement with the results obtained in the large-scale patch tests. The three tests are described in detail, and the results are discussed. The value of the two laboratory tests (in particular the restrained-welding test) for predicting the probable behaviour of an Al alloy when welded is emphasized.—N. B. V.

High-Efficiency Spot Welding in Light-Metal Road-Transport Construction. K. Rupin (*Glasers Ann.*, 1951, **75**, (4), 83–84).—A short illustrated description of a special design of spot-welding machine developed by Schlatter for fixing light-metal panels to light-metal framework. The differences in properties of steel and Al are pointed out, calling for differences in design and operation. The design incorporates automatic switching on of the current at a predetermined mech. pressure between the two parts and automatic switching off after a predetermined time, according to the thickness of the metal. Some notes are given of methods of setting up, prepn. of surfaces, &c.—W. F. H.

***A.C. Argon-Arc Process for Welding Aluminium : An Oscillographic Analysis of Effects of Welding-Transformer Open-Circuit Voltage on Arc Re-Ignition.** L. H. Orton and J. C. Needham (*Weld. Research*, 1951, **5**, (6), 252*r*–274*r*).—The elect. parameters of the welding arc were studied by oscillographic techniques using recording equipment with time resoln. extending from hundredths of a sec. down to microsec. The open-circuit voltage was varied between 45 and 175 V. r.m.s., the current was kept approx. const. at 80 amp. r.m.s., and 6-cm. melting runs were made on Al and an Al–5% Mg alloy. 45 sec. after the arc was initiated welding conditions were regarded as stable, and the oscillographic recording was made. There are five types of arc re-ignition behaviour : (1) failure to ignite, i.e. complete rectification; (2) more than one injected spark from an H.F. spark oscillator is required for re-ignition; (3) a single spark is sufficient to break down the gap and re-ignite the arc (this is the condition for stable welding with an H.F. oscillator in the circuit); (4) delayed self re-ignition (soft gap); and (5) immediate self re-ignition (i.e. the open-circuit voltage is high enough to break down the gap). These stages occur at increasing open-circuit voltages and the precise values depend on welding conditions, such as the alloy being welded and its surface condition, arc gap, &c. The use of an H.F. spark oscillator and a series capacitor can lower the open-circuit voltage required for satisfactory A-arc welding to ~45 V.—K. S.

***600-Amp. Argon-Arc Torch for Manual Welding Thick Aluminium Alloy Plate.** J. H. Cole (*Weld. Research*, 1951, **5**, (2), 157*r*–162*r*).—Single-run welds give the best results on thick Al alloy sheets, but with standard 300-amp. equipment, pre-heating is essential; this can be avoided by using higher welding currents, and a water-cooled manual welding torch has been designed for currents up to 600 amp. It weighs 2lb. without the lead, and experimental butt and fillet welds on 1-in-thick plate have been found satisfactory. With thick W electrodes there is a danger of molten W dropping into the weld pool; for very high currents, C electrodes can be used in larger sizes, but they are still rather fragile.
—K. S.

***An Investigation of the More Common Binary [Aluminium] Alloys During Argon-Arc Welding.** D. C. Moore (*Sheet Metal Ind.*, 1951, **28**, (292), 737–752).—An investigation was made of binary Al alloys with Cu, Fe, Mg, Mn, Si, and Zn, using methods similar to those employed in earlier work by the Aluminium Development Association Welding Research Team (*J. Inst. Metals*, 1947, **73**, 33, 197, 273; 1948, **74**, 227, 249, 439, &c.). It was found that alloys in all 6 systems can be A-arc welded in the as-received condition, though weldability is improved if the alloys are cleaned before welding.

In similar assemblies supported in the same way, much less cracking occurred than during oxy-acetylene welding. Al alloys with Fe, Mg, and Mn were not subject to cracking during A-arc welding under severe conditions of restraint; under the same conditions alloys contg. Cu, Si, and Zn cracked to varying extents, depending on compn. The relationship between cracking and compn. shown by alloys in these 6 systems was found to be generally similar to that reported for oxy-acetylene welds, viz. an increase in cracking with initial addn. of alloying element, followed by a decrease with further addn.—N. B. V.

Machine Characteristics for Flash Welding Aluminium Alloys. H. E. Dixon and J. H. Gameson (*Weld. Research*, 1951, **5**, (2), 163*r*–172*r*).—The high conductivity, low m.p., high oxidation rate, and the softness of Al alloys demand great care in the control of the flashing and upsetting cycle, high currents, rapid welding, and fast appn. of the forging pressure. Surface oxide considerably affects the contact resistance, and must be pickled off; oxide formed during flashing must be squeezed out during the upsetting cycle. The forging action may lead to strain-hardening of the material near the joint, and in annealed alloys this may displace the flow lines away from the joint. In heat-treated alloys over-ageing may occur near the joint, but it is possible for this softened metal to be eliminated by adequate upsetting. Thus the essentials for strong welds are rapid flashing, sudden cut-off, and heavy and rapid upsetting. 26 ref.—K. S.

Copper Hand-Basins for Railway Carriages Made by Welding and Brazing. —— (*Pratique du Soudage*, 1951, **5**, (6), 102–104).—Deep concave blanks of Cu sheet are used uncut for basins to be mounted on a flat wall; for corner mounting half the vertically divided blank has the cut edges acetylene-welded together. The oxy-acetylene flame is also used in brazing on the outlet and overflow pipes, soldering for the brass surround for the outlet, and braze-welding for fixing the back plates in position. The whole assembly is plated.
—P. R.

***Welding of Molybdenum.** W. H. Kearns, H. B. Goodwin, D. C. Martin, and C. B. Voldrich (*U.S. Atomic Energy Commission Publ.*, 1951, (**BMI-703**), 36 pp.).—Factors causing brittleness in Mo welds have been studied. Tests were made on high-purity Mo and on commercial-purity material in the form of swaged powder-metal bar and vacuum-arc-melted rod; the main differences in purity were in the O, N, H, C, and S contents. Upset welds were made in a flash-welding machine or in a modified vacuum-arc furnace, and could be carried out *in vacuo* or in an inert atmosphere. A const.-moment bend test was used to measure ductility and a dye-penetrant method to detect cracks and porosity in the welds. High-purity forged Mo welded in H, and cast high-purity Mo welded in H, He, and *in vacuo* gave brittle welds with impurities present on the grain surfaces. Metallographic polishing of the surfaces before welding removed surface impurities, and welding *in vacuo* gave a ductile weld, (6% and 14% elongation); meticulous mech. prepn. also resulted in a ductile weld. Welding of powder-metal bar invariably resulted in a porous weld. However, it was found that ductility, to the extent of 1–2·5% elongation, could be induced by post-weld heat-treatment. Several attempts were made to purify the Mo by heat-treatment *in vacuo*, H, and O before welding; these apparently did improve ductility of the weld, but the high porosity of all the welds obscured the effect. Work is continuing to elucidate the cause of pronounced porosity in all welds made in powder-metal bar. Welds in arc-cast Mo were free from porosity and had a ductility which could be increased by post-weld heat-treatment; carbide was detectable at the grain boundaries of the fracture.—J. W. T.

Welding the High-Heat-Resistant Materials. J. L. Solomon (*Weld. Eng.*, 1952, **37**, (2), 38–42).—See *M.A.*, **20**, 732.—P. R.

The Spot Welding of Thick Sheet with Multiple-Current-Impulse Control. F. Rosenberg (*Schweissen u. Schneiden*, 1951, **3**, (4), 115–116).—Spot welding of thick sheet is difficult on orthodox machines because the time required for the welding temp. to be reached increases more steeply than the thickness of the sheet; as a result heat is conducted away through the sheet and the hot zone increases in size. This not only means that a larger area of the sheet suffers modification of its mech. properties, but it may also lead to indentation of the surface by the welding electrodes and to hot metal being squeezed out of the weld along the gap between the sheets. Similar difficulties may be encountered in thin sheets when the joint before welding has been pressed together by an earlier operation, so that the contact resistance plays a relatively minor part in the welding mechanism, and heating is due mainly to the actual resistance of the metal. Successful welds can be made in thick sheets and tight joints by interrupting the welding current so that it is broken up into a series of short impulses. The water-cooled electrodes conduct heat away from the surface, which is kept relatively cool, while heat is retained in the centre of the joint; the resistance of the metal increases at higher temp., so that in later impulses more heat is generated in the zones which have retained their high temp. from the earlier impulses, and heat is concentrated at the joint itself; thus welding occurs without excessive heating of material away from the weld.
—K. S.

Stud Welding. C. C. Macfarlane (*Trans. Inst. Weld.*, 1949, **12**, (5), 110–115).—A description is given of 4 types of modern stud-welding equipment, followed by an account of results achieved in a wide range of appn. and a note on some developments in hand.—N. B. V.

New Publications on Resistance Welding. W. Bottländer (*Schweissen u. Schneiden*, 1951, **3**, (4), 122–124).—A short review. 24 ref.—N. B. V.

Resistance Welding: Research Progress by the British Welding Research Association. H. E. Dixon and H. G. Taylor (*Sheet Metal Ind.*, 1951, **28**, (296), 1121–1130, 1136).—A paper presented to the Sheet and Strip Metal Users' Technical Association.—N. B. V.

A Review of the Theory and Practice of Inert-Gas Shielded-Arc Welding. W. J. Jackson (*Sheet Metal Ind.*, 1951, **28**, (296), 1131–1136).—Student's prize essay.—N. B. V.

Welding with Argon as a Protective Atmosphere. H. Bühler and W. Günther (*Schweissen u. Schneiden*, 1951, **3**, (4), 110–112).—The A-arc and Aircomatic processes are described, and their characteristic features are briefly reviewed. The need for H.F. stabilization of the arc is mentioned, and details of welding speeds, currents, &c., for different thicknesses of sheet are given for Al, Mg, and stainless steel. In the Aircomatic process the filler wire forms one electrode and is fed to the weld at a controlled rate, which maintains a const. arc length; very high currents and rapid welding are possible in this process.—K. S.

Systematic Classification of Welding Processes Reveals New Possibilities. H. v. Neuenkirchen (*Schweissen u. Schneiden*, 1951, **3**, (10), 311–314).—All existing welding processes are classified according to three points of view: (1) Type of weld (recrystn., pressure weld at temp. between solidus and liquidus, and welds in which complete melting occurs); (2) source of heat (14 groups are enumerated); (3) protection from atmosphere. It is possible to draw up tables in which vertical columns are groupings of one type (e.g. nature of weld) and horizontal rows groupings of another type (e.g. source of heat); the information in 23 possible tables can conveniently be presented in three. Existing processes are incorporated in these tables, and gaps represent possible combinations which may be worth considering. The system presented offers 252 possible combinations, but it is recognized that many of them are not practicable.
—K. S.

A Survey of Modern Theory on Welding and Weldability. [I.–X]. D. Séférian (*Sheet Metal Ind.*, 1950, **27**, (283), 935–949, 952; 1951, **28**, (285), 59–72, 76; (290), 553–565; (291), 643–652, 657; 1952, **29**, (297), 53–61; (299), 239–248, 254; (301), 441–446; (302), 529–532, 540; (303), 627–634, 642; (305), 827–832, 840).—Cf. *ibid.*, (280), 727; *M.A.*, **18**, 444. [I.–II.—] The weldability of C and alloy steels is considered in detail. [III.—] S., in discussing the welding and weldability of Al alloys, says weldability depends on (1) overcoming the

Al_2O_3 film by the use of suitable flux which gives a light, easily eliminated slag and (2) avoiding in some alloys the thermal cycle that causes pptn. in the basis metal and molten zone which may lead to loss of strength and resistance to chem. attack. The incidence and effect of these phenomena are discussed for the various alloys. The first section deals with oxy-acetylene welding, the second with elect. arc welding, and the third with arc welding in a monatomic gas. The last section deals with the various kinds of brazing. [IV.—] Welding methods, prepn. of materials, &c., for Cu, Ni, Zn, Mg, and Pb and their alloys are described. [V.—] Oxy-acetylene and arc welding of cast iron is discussed. [VI.—] Arc-welding electrodes are considered in detail. The functions of an electrode coating, including the phys. and elect. action, and met. functions, are discussed. Acid and basic slags from the welding operation are briefly described. [VII.—] S. considers electrode coatings, in particular : (*a*) the refining effect of the coating—this depends on the type of coating. Metal may be refined in the presence of a reducing gas, by Mn in acid coatings, or by the action of Mn or carbonate in basic coatings. Examples are quoted. (*b*) Refining by reducing agents—Mn, C, or Si. (*c*) The slag–metal equilibrium depending on the nature of the coating (acid or basic). (*d*) The Mn reaction. [VIII.—] The consideration of arc-welding electrodes is concluded by S. discussing acid slags, the equilibrium of basic slags, and distribution of O between metal and slag. [IX.—] A consideration of the mech. properties of welds begins with a discussion of the influence of the electrode coating. The effect of H is discussed, and S. concludes that H may be the cause of flakes, blowholes, and cracks. Factors affecting flake formation are discussed. The Fe–H equilibrium and the effect of C are also discussed. [X.—] Electrodes are manufactured by dipping or extrusion, and details of both methods of manufacture are given. S. discusses the operational characteristics of electrodes: elect. conditions, current intensity, and voltage necessary for melting the electrodes depend on several factors, and these are examined. S. concludes by considering various faults which may occur in coated electrodes.—R. J.

Welding Technique in the U.S.A. H. v. Hofe, E. Kauhausen, E. Koch, K. L. Zeyen, and E. Zorn (*Schweissen u. Schneiden*, 1951, **3**, (12), 359–370).—A report on visits made to a number of American works under the auspices of O.E.E.C. —N. B. V.

Maintenance by Welding: A Survey. M. Riddihough (*Trans. Indian Inst. Metals*, 1949, **3**, 347–357).—A review of hard-surfacing practice and of its appn. in various branches of engineering. 19 ref.—N. B. V.

The Metallurgy and Applications of Hard-Surfacing. A. Schmidt (*Berg- u. hüttenmänn. Monatsh. Montan. Hochschule Leoben*, 1950, **95**, (12), 342–348).—An account of the met. principles and practical aspects of hard-surfacing. Non-ferrous metals are only briefly mentioned.—E. J. E.

Hard-Facing of Mine Drills. E. Cosyns (*Pratique du Soudage*, 1951, **5**, (10), 189–190).—Mine drills for use on hard granitic strata were successfully refaced with a mixture of WC and other refractory carbides (nature not stated), over a preliminary coating of high-speed steel, which should be almost fused when the carbide is applied. Bonding is ensured by torch-heating with reducing flame. The tool can be ground 3 times without further refacing, which can eventually be done with the carbides only.—P. R.

Safety in the Practice of Welding. E. Fuchs (*Trans. Inst. Weld.*, 1950, **13**, (3), 87–94).—A review of hazards due to radiation, explosions, and fumes. Necessary precautions are indicated.—N. B. V.

Welding Mask or Hand Shield? G. Zweiling (*Schweissen u. Schneiden*, 1951, **3**, (10), 314–317).—The use of masks or helmets instead of hand shields is making slow progress in Germany. The advantages of helmets are enumerated: the left hand is free and can be used to support the work, the welding torch, sometimes even the welder, and the work is found less tiring. The requirements of satisfactory masks and shields are discussed, and the main features of some designs available in Germany are described.—K. S.

The Radiographic Examination of Welds: An Attempt at the Quantitative Evaluation of Defects. (Masi). See col. 1036.

22 — INDUSTRIAL USES AND APPLICATIONS

Applications of Cast Aluminium [and Aluminium Alloys]. K. Schneider (*Aluminium*, 1951, **27**, (4), 88–94).—S. illustrates the use of cast Al and Al alloys in the motor and marine engineering, textile, dairying, mining, building, and other industries, where lightness, good corrosion-resistance, non-toxicity, high elect. and thermal conductivity, and good workability are of importance. Some of the engineering problems arising from the substitution of Al for steel are very briefly mentioned.—E. J. E.

The Pakistan Government Survey Vessel "Ain-el-Bahr" with Prestressed Hull. André Chevrier (*Rev. Aluminium*, 1951, (177), 196–200).—See *M.A.*, **19**, 81 ; **20**, 529. —N. B. V.

Birth of a [Light Alloy] Life-Boat. —— (*Alluminio*, 1950, **19**, (6), 548–553).—An illustrated account of the construction of a life-boat from Al-3·5% Mg alloy.—E. E.

Prefabricated Houses of Light Metal Standard Units. D. F. Reidemeister (*Aluminium*, 1951, **27**, (4), 102–103).—A description of French Al alloy houses designed by Jean Prouvé. Wall and roof panels are supplied as finished interchangeable units of standard dimensions, and may be used in conjunction with other building materials.—E. J. E.

135 Tons of Anticorodal in the New Station in Rome. —— (*Alluminio*, 1951, **20**, (1), 45–53).—Al alloy has been extensively used in the construction of the frontage, concourse, and platforms of a new railway terminus in Rome. —E. J. E.

The Economics of Light-Metal Construction in Transport. M. Preuss (*Glasers Ann.*, 1951, **75**, (4), 76–78).—Deals with the economics of weight-saving in rail and road transport under 4 headings: (i) lower frictional losses on the level, (ii) lower power consumption in accelerating, (iii) lower power consumption on up-gradients, and (iv) lower frictional losses in braking. These savings are shown in the form of curves, with some notes on the weight-saving possible with modern forms of construction in rail, tramway, omnibus, and motor-coach designs, based upon published data. 7 ref. —W. F. H.

The Use of Light Metals [Aluminium] in Stress-Bearing Coachwork of Buses, Trolley Buses, and Railway Vehicles. Arne Brinck (*Aluminium*, 1951, **27**, (2), 36–39 ; (3), 67–70 ; (4), 106–110).—Over 300 vehicles have been constructed with stressed light-alloy coachwork over the past 20 years in Norway. B. discusses the savings in weight resulting directly from the substitution of Al for steel, and indirectly from the use of lighter motors, the relatively higher capacity of the lighter bodies, &c. The problems encountered in the construction and servicing of Al coaches for the Norwegian railways and of trams and trolley buses for service in Oslo are described in some detail. The higher initial cost of Al vehicles is offset by resultant savings, maintenance costs are no higher than for steel bodies, and corrosion can be combated. Repairs after accidents are, however, more costly than in the case of steel vehicles. No definitive data are yet available on the life of such Al vehicles.—E. J. E.

The Talgo Train. J. M. Gruitch and O. H. Philips (*Mech. Eng.*, 1950, **72**, (10), 787–791 ; also (abridged) *Eng. J.* (*Canada*), 1950, **33**, (7), 602–603).—An account of the design and construction of this train, built largely of Al alloys ; see *M.A.*, **18**, 227.—E. J. E.

General-Purpose Steel-Cored Aluminium Conductors. Karl Kohler (*Z. Metallkunde*, 1951, **42**, (7), 213–216).—Equations

are developed, from which nomograms have been constructed, for determining the weight and the mech. properties (modulus of elasticity) of steel-cored Al conductors, taking into account the temp. variations to which they may be subjected, this being of importance when calculating the tension in, and sag of, such cables. General principles governing the design of these conductors are discussed. Sheathing materials should have the highest possible U.T.S., small elastic modulus, and low sp. gr., if optimum use is to be made of the core. Very high-tensile steel clad with Electron would appear to be suitable for extremely high-voltage cables where a somewhat lower conductivity can be tolerated.—E. N.

The Use of Light Metals in the Construction of Radar Equipment by the C[ompagnie] F[rançaise] T[homson]-H[ouston]. G. Frigot and G. Turré (*Rev. Aluminium*, 1951, (180), 329–334).—N. B. V.

Aluminium Photographic Process Has Industrial Applications. Eugene Wainer (*Materials and Methods*, 1952, **35**, (4), 176, 178, 180, 182, 184, 186).—A description of the Swiss "Aluphot" process; see *M.A.*, **20**, 307.—N. B. V.

Standard Sizes of Aluminium and Aluminium Alloy Sheets [in France]. Maurice Besnard (*Rev. Aluminium*, 1951, (180), 345–346).—N. B. V.

Copper and Copper Alloys in Industry. [—I.–IV]. J. Bourguignon (*Cuivre, Laitons, Alliages*, 1951, (2), 17–20; (3), 17–19; (4), 21–27; (5), 17–21).—A comprehensive series of articles dealing with the chem., elect., and phys. properties of Cu and its alloys in the various forms employed in industry (based largely on publications of the Copper Development Association). [I.—] Gives the properties and chief uses of cathode Cu, electrolytically refined, fire-refined (blister), oxygen-free, high-conductivity, and standard 99·5% purity. Curves are given of effect of cold working on properties of H.C. strip and wire. [II.—] Deals fairly shortly with special alloys of Cu with Ag, Cd, Sn, Cr, Be, and Te and various complex alloys. [III.—] Devoted to Be-bronze, with 2% Be, and deals with chem., phys., and mech. properties, corrosion-resistance, hot and cold working, heat-treatment, descaling, soldering, brazing, arc welding, resistance welding, and plating. [IV.—] Covers industrial uses of Be-bronze in measuring instruments, non-sparking tools, elect. and radio equipment, moulds for plastics, high-speed bearings, watch parts, and parts of elect. resistance welding machines (Cu–Co–Be alloy).—W. F. H.

Notes on Copper Roofing and Coping. E. Laenneg (*Cuivre, Laitons, Alliages*, 1951, (1), 27–30).—A short note in the nature of a supplement to a pre-war publication on Cu roofing by the Centre d'Information du Cuivre. The present article is concerned mainly with illustrations of some recent installations of Cu roofing in France. Details are also given of a new material called Cupraspha, consisting of long wide strips of soft Cu covered on both sides with bitumen, used for coping (*chape*). Notes are added on the design and installation of Cu roofs, and precautions to be taken against corrosion.—W. F. H.

[The Significance of] Copper in the Brewing Industry. Peter Schoellhorn (*Pro-Metal*, 1951, **4**, (19), 776–777).—[In French and German]. Many of the large vessels, vats, and conduits employed in brewing are made of Cu because it resists corrosion by the organic acids and other constituents of beer, because it is easy to keep clean and sterilized, and because it can be formed into the elaborate shapes required and is not seriously affected by internal stresses due to uneven heating, which may frequently occur in brewing. Brass is widely used for stirrers, piping, valves, and similar fitments.—K. S.

Copper Water Pipes. —— (*Cuivre, Laitons, Alliages*, 1951, (2), 29–33).—A short illustrated account on methods of installing Cu piping in domestic water-supply systems. Portable bending and jointing equipment is illustrated, with details of standard types of junctions and branches to suit all sizes of piping.—W. F. H.

Copper and Copper Alloys in Heat-Exchangers. E. Laenneg (*Cuivre, Laitons, Alliages*, 1951, (4), 37–44).—A well-illustrated account of methods of construction and operating characteristics of various types of fluid and vapour heat-exchangers made of Cu and Cu alloys, mainly of the tubular type, either plain or with fins. Temp. differences, speed of circulation, degree of turbulence, and materials used all affect the efficiency and the cost. Design calculations, governing choice of type and materials of construction, are given.—W. F. H.

Duplex Copper/Lead Tubes for Sulphuric Acid. —— (*Cuivre, Laitons, Alliages*, 1951, (2), 35).—A short note on the use of Pb-clad Cu tubing for the heating coils of Pb-lined vessels contg. H_2SO_4, and of Pb-lined Cu tubing for conveying H_2SO_4, made in the U.S.A. Cu gives strength and resistance to action of steam, and Pb resists action of the acid.—W. F. H.

Brass Curtain Rails. —— (*Pro-Metal*, 1951, **4**, (21), 834–838).—[In French and German]. The advantages of thin extruded brass sections for curtain rails are discussed, and a number of suitable sections and methods of mounting them are illustrated.—K. S.

Manufacture of [Brass] Containers for Cosmetics. Leon Reboul (*Cuivre, Laitons, Alliages*, 1951, (4), 45–47).—W. F. H.

Copper Alloys in the Watchmaking Industry. —— (*Pro-Metal*, 1951, **4**, (24), 928–932).—[In French and German]. The various components of the case and works of a watch are briefly described, and the alloys used for their manufacture are discussed. Brass or nickel silver is used for most purposes; components made principally by cold working, i.e. cases, bridges, bearing plates, &c., are made in α alloys of high purity, rolled to close tolerances of dimensions and hardness; for parts which are made mainly by machining, Pb-bearing free-machining alloys are preferred. A number of special-quality products have been developed by Swiss firms, such as brass strip for the watch face, which has an exceptionally good surface and fine grain-size. Enamelled faces are made of pure Cu, a special grade of which has been found particularly suitable for enamelling. Cf. *M.A.*, **20**, 947.—K. S.

Copper Alloys in the Manufacture of Watch Movement Blanks. Philippe de Coulon (*Pro-Metal*, 1951, **4**, (24), 917–918).—[In French and German]. The small components which hold the movement of a watch in place comprise its housing; they are made from a free-machining brass, contg. 38% Zn and 1·5–2% Pb. They must be rigid and stable, and must be machined with great accuracy. Shapes are stamped from strip, and the location of holes for bearings is marked in another stamping operation. Excess metal is then machined away. A de-burring operation is usually necessary, and research is in progress with the aim of developing alloys and machines suitable for stamping and machining without subsequent de-burring. Cf. *M.A.*, **20**, 947.—K. S.

Nickel Silver Watch Cases. —— (*Pro-Metal*, 1951, **4**, (24), 321–322).—[In French and German]. Most watch cases are made of nickel silver with a separate base of stainless steel. Brass is used for very cheap watches, but its resistance to corrosion is inferior. Nickel-silver is easily cold worked, machined, and electroplated. Galvanic coatings of Ni, Cr, and Au may be used; there is a recent trend for Au coatings to be applied in a cladding process, so that they are thicker and more resistant to wear and corrosion than plated Au deposits. Cf. *M.A.*, **20**, 947.—K. S.

Brass in the Manufacture of Anchor Escapements [for Watches]. A. Simon-Vermot (*Pro-Metal*, 1951, **4**, (24), 923–925).—[In French and German].—The teeth of the escapement wheels are subjected to considerable wear against a jewelled seating, with min. lubrication and under very unfavourable conditions. In addn., considerable fatigue and repeated impacts must be taken into account. The brass must be very hard, without, of course, cracking during the cold-stamping operation. It is necessary for the grain structure to be fine in relation to the extremely small size of the components, which implies an exceptionally small actual grain-size. The brass strip must therefore be of consistent quality and meet very rigid specifications, and each consignment is subjected to chem. analysis, mech. tests, and metallographic examination. Cf. *M.A.*, **20**, 947.—K. S.

Problems of Watchmaking. André Chappuis (*Pro-Metal*, 1951, **4**, (24), 919–921).—[In French and German]. The

severe demands on springs, bearings, and temp.-compensating devices are pointed out, and the need for non-magnetic, corrosion-resistant spring alloys of high strength and elastic limit is emphasized. Temp. compensation by means of balance springs whose modulus of elasticity is not sensitive to temp., or by the use of bi-metallic strip, makes it possible for modern watches to keep good time under extreme and very variable conditions.—K. S.

Report of [A.S.T.M.] Committee B-5 on Copper and Copper Alloys, Cast and Wrought. —— (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 165–177).—See *M.A.*, **20**, 947.

Notes on the Metallurgical Design of Tungsten-Carbide Rock Bits. L. C. Bogan (*Proc. Australasian Inst. Min. Met.*, 1950, [N.S.], (158/159), 193–215).—B. discusses in detail the properties of the Co-cemented WC bit and the brazing of it to the steel body.—N. B. V.

Notes on the Engineering Design of Tungsten-Carbide Rock Bits. James E. Lewis (*Proc. Australasian Inst. Min. Met.*, 1950, [N.S.], (158/159), 217–262).—L. attempts to determine and evaluate the characteristics of a rock bit that make for efficient drilling performance.—N. B. V.

Whither Agriculture? [Materials Used in Agricultural Machinery]. Maurice Victor (*Rev. Aluminium*, 1951, (177), 201–214).—A review of the equipment exhibited at the 22nd Agricultural Machinery Show held in Paris.—N. B. V.

Wear and Wear-Resistant Materials. Albert Knickenberg (*Neue Giesserei*, 1948, **33/35**, (4), 104–110).—Wear may arise from mech., thermal, or chem. causes, or from the interaction of any of these. K. gives a table classifying types of wear and their occurrence. After a brief consideration of the constructional problems involved in reducing wear, a survey is made of the wear-resistant properties of a number of ferrous materials. Non-ferrous alloys are mentioned only very briefly.—E. J. E.

Materials of Construction for Use at Low Temperatures. E. W. Colbeck (*Trans. Inst. Chem. Eng.*, 1949, **27**, 55–67; discussion, 67–69).—A review, concerned mainly with ferrous materials.—N. B. V.

New Materials in Engineering. T. E. Allibone (*Proc. Roy. Inst.*, 1951, **35**, [I], (158), 200–210).—A comprehensive review of recent developments in elect. engineering, including ref. to insulators (polythene and silicones), ferro-electrics (Ba and Sr titanates), adhesive plastics, semi-conductors (Si and Ge), photoconductors (Cd and Pb sulphides), and metals and alloys. Important developments in metallurgy have been the introduction of low-hysteresis-loss steel, high-permeability Ni–Fe alloys, heat-resistant Ni–Cr alloys, and metal–ceramic mixtures and the prodn. on a commercial scale of purer Zr, Ti, and other refractory metals.—S. V. R.

Report of [A.S.T.M.] Committee B-2 on Non-Ferrous Metals and Alloys. —— (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 148–149).—See *M.A.*, **20**, 954.

Report of [A.S.T.M.] Committee B-7 on Light Metals and Alloys, Cast and Wrought. —— (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 201–203).—See *M.A.*, **20**, 945.

Report of [A.S.T.M.] Committee B-4 on Electrical Heating, Resistance, and Related Alloys. —— (*Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 152–164).—See *M.A.*, **20**, 954.

23 — MISCELLANEOUS

The Circulation and Recovery of Aluminium. Herbert Wegner (*Metall*, 1951, **5**, (23/24), 564–566).—A theoretical flow-sheet illustrates the consumption and recovery of Al in the various stages of prodn. Actual figures vary widely; on the average, scrap accounts for ~ ½ of total consumption.
—E. J. E.

Survey of the Development of the Aluminium Industry in Canada. Ernst Rauch (*Metall*, 1951, **5**, (15/16), 353–355).—An account of the development in Canada of the Aluminum Company of America, of its reorganization, in 1928, as an independent subsidiary, Aluminium, Ltd., Montreal, and the present extent of the company's activities.—E. J. E.

Bibliography on Beryllium Health Problems. N. W. Bass (*Bull. Amer. Ceram. Soc.*, 1951, **30**, (3), 79–80).—50 ref.
—N. B. V.

***Notes on the Toxicology of Cobalt Metal.** H. E. Harding (*Brit. J. Indust. Medicine*, 1950, **7**, (2), 76–78).—A suspicion that metallic Co dust was responsible for chronic damage to workers' lungs in a particular factory was unconfirmed. It was shown, however, that Co metal powder suspended in saline or air produced severe acute damage to capillaries and in the lungs of experimental animals (principally rats) leading to severe, usually fatal, œdema and hæmorrhage. The action of Co is related to its solubility in protein-containing fluids.
—H. A. H.

Copper: Its Production, Consumption, and Supply Prospects. —— (*Pro-Metal*, 1951, **4**, (23), 890–900).—[In French and German]. The present and future supply position for Cu is discussed, both generally and from the point of view of Swiss user industries, in relation to the occurrence, mining, smelting, and refining of the metal, which are all briefly described. The importance of scrap circulation is emphasized, and it is concluded that the overall supply should be adequate for our generation and the next, but that any sudden increase in consumption due to political causes will lead to temporary shortages.—K. S.

Copper Through the Ages. R. Lantior (*Cuivre, Laitons, Alliages*, 1951, (1), 39–41; (2), 46–49; (3), 48–51; (4), 60–63; 1952, (5), 52–55; (6), 24–26; (7), 40–43; (8), 44–47; (9), 50–53; (10), 34–37).—An historical review of the mining, smelting, working, and uses (chiefly the latter) of Cu and bronze from the earliest days. The present series covers the period from ~6000 B.C. to ~A.D. 200 and consists mainly of illustrations of Cu and bronze articles unearthed in various parts of the world. It is thought that the very earliest articles were fashioned by hand from pieces of native Cu and, after the discovery of fire, native Cu may have been melted and cast into rough shapes. It was probably first smelted from the ore malachite (Cu carbonate) ~3500 B.C. Castings made in proper sand moulds appeared ~3000 B.C. and the "lost wax" process was probably known to the Egyptians. The greatest development of bronze, which was also probably produced accidentally by using mixed ores, was due to the Greeks and later to the Romans. The development of the industry in Gaul up to the time of the Roman occupation, is dealt with at length, with many illustrations of statuary, tools, implements of war, domestic utensils, and ornaments.—W. F. H.

Birmingham Brass. C. H. M. Holden (*J. B'ham Met. Soc.*, 1951, **31**, (1), 5–12).—Presidential Address. A brief history of the brass industry in England.—N. B. V.

The Application of Indium Abroad [i.e. Outside Germany]. Norbert Lowitzki (*Z. Erzberg. u. Metallhüttenwesen*, 1950, **3**, (3), 94–95).—A review, with 25 ref.—N. B. V.

Two Hundred Years of Nickel. Robert A. Mackay (*Bull. Inst. Metallurgists*, 1951, **3**, (3), 15–27).—N. B. V.

Daniel Gabriel Fahrenheit's Share in the Discovery of Platinum. Friedrich Albert Meyer (*Z. Erzberg. u. Metallhüttenwesen*, 1951, **4**, (6), 221–222).—A brief account of work done by Fahrenheit on the *d* of Pt.—E. J. E.

New Publications on Thallium in the Years 1938–48. N. Lowitzki (*Z. Erzberg. u. Metallhüttenwesen*, 1950, **3**, (6), 201–202).—N. B. V.

Health Hazards in Working with Zinc. Karl H. Sroka (*Metall*, 1951, **5**, (13/14), 309).—A brief account of the toxic action of Zn.—E. J. E.

[E.C.A.] Mission to American Non-Ferrous Metals Fabricating Plants. M. Holleaux (*Cuivre, Laitons, Alliages*, 1951, (4), 3–8).—Summarized report by the Head of the Mission arranged by the Chambre Syndicale des Métaux under the auspices of E.C.A. which visited the United States in July and August 1951, and made a tour of some of the leading brass and Al fabricating plants. The general conclusions are that there are no outstanding differences in methods com-

pared with European practice, except in some of the more recent large-scale mass-prodn. units. On the non-tech. side members were much impressed by the good relations between management and workmen and on the general atmosphere ruling in the works, and on the tech. side by the extent to which mechanization and labour-saving had been introduced and the far greater use of elect. equipment in place of manual operation, dictated largely by the relatively high cost of labour and cheapness of power. The various lessons to be learned are summarized.—W. F. H.

Metalwork from Franconia. Max Körner (*Metalloberfläche*, 1949, [B], **1**, (9), 83–85).—A brief illustrated account of modern artistic metalwork by members of the school of the Nürnberg Akademie der Bildenden Künste.—E. J. E.

The Metallizing (Making Conductive) of Glass and Plastics. —— (*Metalloberfläche*, 1950, [B], **2**, (1), 9–11).—An account, based mainly on that of Upton (*J. Electrodepositors' Tech. Soc.*, 1947, **22**, 45–72; see *M.A.*, **15**, 415), of the deposition of Ag and other metals by the reduction of aq. soln., and of metal films as a basis for electrodeposition.—E. J. E.

Polychrome Effects in [Metal] Engraving. W. Braun-Feldweg (*Metalloberfläche*, 1949, [B], **1**, (12), 133).—A note on the technique of metal-inlay work.—E. J. E.

Amalgam Chemistry: The Future of the Amalgam Process. Jacques Fleck (*Chimia*, 1951, **5**, (7), 145–147).—In the production of Cl from salt, soda is produced at the same time, usually as NaOH. The rapid increase in consumption of Cl in recent years in the pulp and paper industry, in plastics, and in the synthesis of organic compounds, coupled with a decreased use of soda in the soap industry owing to competition of synthetic detergents, has led to a search for processes of producing Cl without producing soda. F. compares the economics of the usual electrolytic diaphragm process with the new electrolytic amalgam process, in which Cl is liberated at the graphite anode and alkali-metal amalgam at the Hg cathode. This amalgam can either be used as such in certain reactions or electrolysed to recover the Na as metal or as soda. Few tech. details are given. 3 ref.—W. F. H.

Water Pollution by Industry: A Survey of State Legislation and Regulations. D. F. Othmer, M. D. Weiss, and R. S. Aries (*Mech. Eng.*, 1951, **73**, (9), 706–708).—N. B. V.

Research Methods in Metallurgy. S. Ramamurthy (*Trans. Indian Inst. Metals*, 1950, **4**, 151–154; discussion, 154).—R. presents a classification of met. research methods in chart-form.—P. F. N.

The Physico-Chemical Viewpoint in Metallurgy. S. Ramamurthy (*Trans. Indian Inst. Metals*, 1950, **4**, 155–160; discussion, 161).—The development of met. thermodynamics and the physico-chem. viewpoint of chem. potential and activity are briefly discussed. 2 ref.—P. F. N.

Some Metallurgical Aspects of Engineering. J. M. Robertson (*Bull. Inst. Metallurgists*, 1951, **3**, (2), 4–18; discussion, 18–24).—N. B. V.

Le Laboratoire Fédéral d'Essai des Matériaux et Institut de Recherches: Its Functions and Programme. W. Bühr (*Pro-Metal*, 1951, **4**, (23), 902–910).—[In French and German]. The history of the various establishments which combined to form the Institut Fédéral (L.F.E.M.) is briefly reviewed, and its present organization is described. There are three main departments, dealing with mech. properties, with chem. analysis, and phys. properties, and with the testing of textiles, leather, and paper. The 19 testing departments are organized into three "job groups", for metals, for non-metallic inorganic materials, and for organic chemicals, resp. Apart from routine testing of samples submitted by industry, a considerable amount of research is carried out. The wide variety of testing machines and laboratory apparatus is illustrated. —K. S.

The Organization of Metallurgical Research in Great Britain. C. J. Smithells (*Met. Ital.*, 1951, **43**, (9), 369–373).—[In French]. Exchange Paper read at the 5th National Convention of the Associazione Italiana di Metallurgia, 1951. A survey of the organization of met. research in Great Britain with special ref. to the Al industry, showing the complementary character of universities, Government, and private research organizations, and individual companies' research establishments.—I. S. M.

Utilization of Power in Non-Ferrous Metallurgy [in India]. M. S. Thacker (*Trans. Indian Inst. Metals*, 1950, **4**, 6–23).—Presidential address. T. reviews the elect. power consumption of the Indian met. industry and compares the cost with that of other types of fuel for non-ferrous operations. The water-power potential is estimated at ~40–50 million kW., and the place of power and its possibilities in metal prodn. are discussed. The paper is directed towards the conclusion that full utilization of the available resources of raw materials and elect. power would enable India to become self-sufficient in the met. industry.—P. F. N.

Standardization: An Aid in the Economic Production and Distribution of Commodities. W. Kuert (*Pro-Metal*, 1951, **4**, (22), 879–883).—[In French and German]. After a brief account of the history of the Swiss Standardization Bureau, the economic advantages of the standardization of alloy compn. and properties, of the dimensions of various products, and of testing methods, are discussed.—K. S.

Critical Comparison of Italian, French, and U.S. Systems of Metallurgical Classification. Massimo Scortecci (*Met. Ital.*, 1951, **43**, (3/4), 110–120).—After dismissing the Universal Decimal Classification as being unsuited for the specific demands of metallurgy, S. compares the French system Alpha Numérique with the Italian system worked out by the Associazione Italiana di Metallurgia, and the U.S. system jointly evolved by the American Society for Metals and the Special Libraries Association. Theoretically the latter is thought the better; but its use of edge-punched cards in practice is seen as a limitation.—I. S. M.

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25 — BOOK REVIEWS

Metales y Aleaciones: Su Constitución, Estructura, Propiedades y Tratamientos. Tomo I.—Constitución y Estructura. Por Rafael Calvo Rodés. 24 × 17 cm. Pp. xxxi + 627, with 333 illustrations. 1948. Madrid: Instituto Nacional de Técnica Aeronáutica.

This book, the first of two volumes, deals with Constitution and Structure, while the second is to cover Properties, Treatments, and their Relation to Constitution and Structure. The present volume is a Metallography in the grand style; after reading it one is almost left with the impression that the author takes all knowledge for his province. In the opening chapter, "Generalidades", the scope of the subject is surveyed. Such a comment as: "The constitution of a body reveals to us, then, its essence or character and from it stem its intrinsic properties . . ." conveys an impression of a philosophical rather than a purely scientific approach, yet when the author comes to grips with detail, his treatment is usually concrete (though never taut) and it is often illuminating. A marked predilection for fundamental physics is apparent throughout. Thus, much space is lavished on the structure of the atom, wave mechanics, and zone theory (which are very clearly presented), valency and the nature of interatomic bonding, systematic crystallography, and the physics of the generation, diffraction, and absorption of X-rays. Often this is distinctly helpful in understanding the more experimental parts of the book, such as some observed features of binary equilibrium diagrams, but at other times one cannot avoid the impression that a disproportionate amount of space is devoted to the physical aspect. Thus it is unnerving to be confronted, at the start of a chapter on grain structure, with a recapitulation of the laws of the gaseous and liquid states. Again, the excellent section on radio-

graphy is prefaced by a preamble on the quantum mechanics of X-ray absorption, which might well disconcert the industrial reader in quest of practical information.

The experimental parts of the book are well organized and presented. The author has chosen to expound principles and typical apparatus rather than go into exhaustive detail, and this makes for easy reading. The book does not aim to be a work of reference on, say, etching reagents or thermostats. The theoretical background of technique is on the whole well presented, though some important topics are treated in a purely empirical way. Thus no attempt is made to explain the relation between the numerical aperture and the resolving power of an objective, or the purpose of dark-ground illumination. There are also a few omissions. Two pages are devoted to means of distinguishing diffraction lines due to K_β radiation from those due to K_α, but nothing is said about the methods and principles of filtering out the K_β radiation. There is no discussion of precision parameter determination or the important uses of this technique in determining solid-solubility limits.

The systematic treatment of equilibrium diagrams is in terms of the phase rule rather than of free-energy curves, but it is detailed and sound. The treatment of the grain structure of alloys, e.g. of eutectics and eutectoids, is illuminating, though inclined to be empirical. Much has been published on the theoretical interpretation of microstructure since the book was written.

A weakness on the theoretical side is the mode of discussion of such topics as nucleation and the effect of impurities on grain-size, which are treated in an old-fashioned mechanistic manner. Thus, the grain-refining influence of some impurities in melts is attributed to impurity atoms getting in the way of fast-moving liquid atoms which, if not so prevented, would provoke a sort of nuclear fission on colliding with potential nuclei of the solid. Statistical mechanics have not been introduced, which is a pity in view of the excellence of other theoretical sections. Old-fashioned, too, is the discussion of the nature of grain boundaries. The author claims that no evidence to refute the amorphous boundary-cement theory has yet been forthcoming, which is hardly fair to at least one eminent member of the Institute.

Few specific errors in tables or figures have been found. The axial ratio of hexagonal titanium is 1·587, not 1·501. The free-energy curve of Fig. 169 corresponds to an equilibrium between two phases of identical structure but different compositions (such as the $\alpha + \alpha'$ field in the Al–Zn system), not, as stated, to an ordinary two-phase field. There are few misprints, with the notable exception of the names of non-Spanish scientists, as Drs. Humme Rothery and Smithells would, among others, agree.

The book represents a monumental effort and is a pioneer of scientific metallurgy in the Spanish language. Notwithstanding the criticisms which have been made, it can be confidently recommended to Spanish-speaking undergraduates and also to graduates seeking to widen their fundamental knowledge. They can be certain that there are few serious mistakes and that they will acquire a reliable bird's-eye view of the state of the whole subject as it was at the end of the War.

R. W. Cahn.

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Printed in Great Britain by
Richard Clay and Company, Ltd.,
Bungay, Suffolk.

714
896
P. 99/LXXXI