Form A. (*Membership Application*) *No*..................

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

The INSTITUTE of METALS

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

Founded 1908. *Incorporated* 1910.

To the Secretary,
The Institute of Metals.

I, the undersigned...

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

Name of applicant in full...

Address...

Business or Profession..

Qualification...

Degrees and/or honorific distinctions...

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

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

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

To be filled up by the Council.

....

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

Chairman.

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

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

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

52.

EXTRACTS FROM THE RULES

(MEMORANDUM AND ARTICLES OF ASSOCIATION.)

MEMBERS AND MEMBERSHIP

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

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

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

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

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

(*a*) Students of Metallurgy; or

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

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

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

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

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

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

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

SUBSCRIPTIONS

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

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

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

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

DUTIES AND OBLIGATIONS OF MEMBERS

Rule 12.—Every member shall be bound:

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

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

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

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

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

No. 2 1933

THE JOURNAL
OF THE
INSTITUTE OF METALS

VOLUME LII

EDITED BY

G. SHAW SCOTT, M.Sc.

SECRETARY

LONDON
PUBLISHED BY THE INSTITUTE OF METALS
36 VICTORIA STREET, LONDON, S.W.1
1933

Past-Presidents.

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

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

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

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

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

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

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

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

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

WALTER ROSENHAIN, D.Sc., F.Inst.Met., F.R.S., 1928–1930.

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

LIST OF OFFICERS
OF
THE INSTITUTE OF METALS
1933-1934

President.

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

Past-Presidents.

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

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W. R. Barclay, O.B.E.	London.
C. H. Desch, D.Sc., Ph.D., F.R.S.	Teddington.
A. G. C. Gwyer, B.Sc., Ph.D.	Warrington.
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Professor R. S. Hutton, D.Sc., M.A.	Cambridge.
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Honorary Treasurer.

John Fry	London.

Members of Council.

S. L. Archbutt	(Representing the Local Sections.)
H. W. Brownsdon, M.Sc., Ph.D.	Birmingham.
Engineer Vice-Admiral Sir Robert Dixon, K.C.B.. D.Eng.	London.
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Wesley Lambert, C.B.E., A.K.C.	London.
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James Steven	Glasgow.
F. Tomlinson	Manchester.
H. B. Weeks	London.

Secretary and Editor.

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

Assistant Secretary.

S. C. Guillan.

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

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

December, 1933.

CORRESPONDING MEMBERS TO THE COUNCIL.

Australia.

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Department of Metallurgy, The University, Melbourne, Victoria.

Belgium.

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Canada.

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

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

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Germany.

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Dott. C. SONNINO, Corso Italia 23, Milano.

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P.O. Box 1176, Johannesburg, Transvaal.

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Switzerland.

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

United States of America.

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

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Chairman : S. L. Archbutt, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

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Chairman : J. E. Newson, M.Met.

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Chairman : Captain F. Orme, M.Met., 24 Storth Avenue, Fulwood, Sheffield.

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

Swansea.

Chairman : A. G. Ramsay, Ph.D., B.Sc., Messrs. I.C.I. Metals, Ltd., Landore, Swansea.

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

CONTENTS

MINUTES OF PROCEEDINGS.

Contents

LIST OF PLATES

CORRIGENDA

1929, Volume 41. Page 459, line 23.	*For* "MgHg in Hg" *read* "MgHg in Mg."
1929, Volume 42. Page 456, line 14.	*For* "MgZn$_3$" *read* "MgZn$_5$."
1931, Volume 47. Page 96, line 36.	*For* "Determination of Zinc in Zinc-Base Die-Casting Alloys," *read* "Determination of Aluminium and Magnesium in Zinc-Base Die-Casting Alloys."
,, 695, 2nd col., line 44.	*Insert* "estimation in zinc-base die-casting alloys, **47**, 96*A*."
,, 701, 1st col., line 39.	*Add* "; in zinc-base die-casting alloys, **47**, 96*A*."
,, 702, 1st col., line 20.	*Add* "; in zinc-base die-casting alloys, **47**, 96*A*."
,, 702, 2nd col., line 3 from bottom.	*Delete* "; in zinc-base die-casting alloys, **47**, 96*A*."
,, 748, 1st col., line 13 from bottom.	*Add* "in zinc-base die-casting alloys, **47**, 96*A*."
,, 781, 2nd col., line 55.	*Delete* "in zinc-base die-casting alloys, **47**, 96*A*."
,, 796	*For* "Craighead, Charles M. Detn. of Zn in Zn-base Die-casting alloys," *read* "Detn. of Al and Mg in Zn-base die-casting alloys."
1932, Volume 50. Page 474, line 1.	*For* "1000°–1500° C.," *read* "1000°–1050° C."
,, 686, line 16.	*For* "1932, 7, 267–271" *read* "1930, 7, 267–271."

THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS.

SILVER JUBILEE AUTUMN MEETING.

The Twenty-Fifth (Silver Jubilee) Autumn Meeting of the Institute of Metals was held in Birmingham from September 18 to 21, 1933.

Monday, September 18.

The meeting opened in the evening in the Medical Theatre of the University, Edmund Street, Birmingham, the President of the Institute, Sir Henry Fowler, K.B.E., LL.D., D.Sc., occupying the Chair, when Mr. W. R. Barclay, O.B.E., Vice-President, delivered the Institute of Metals Twelfth Autumn Lecture, on "Twenty-Five Years' Progress in Metallurgical Plant," a full report of which is given on pp. 19–38.

On the motion of the President a hearty vote of thanks was accorded to Mr. Barclay for his lecture.

Following the lecture, members adjourned to the Queen's Hotel for an informal conversazione.

Tuesday, September 19.

Official Welcome.

At the morning session held in the Examination Hall of the Central Technical College, Suffolk Street, Birmingham, the Deputy Lord Mayor of Birmingham (Alderman J. B. Burman, J.P.) welcomed the members of the Institute to the City of Birmingham.

The President thanked the Deputy Lord Mayor for the kind welcome extended to the Institute on the occasion of its return to Birmingham, in which city the original headquarters of the Institute were situated.

Welcome to Overseas Members.

The President welcomed the various overseas members attending the meeting. As his name was mentioned, each visitor rose from his seat and was greeted with applause.

Messages of Greeting.

The Secretary (Mr. G. Shaw Scott, M.Sc.) read the following messages of greeting received from the under-mentioned Societies and Institution :

" On behalf of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, we extend to the Institute of Metals the very best wishes, as well as my personal felicitations as Honorary

Corresponding Member of the Institute, on the occasion of your Silver Jubilee Meeting in Birmingham. It has been my pleasure and my privilege to be associated with your Institute since its foundation 25 years ago, and I voice the hope of your American friends that the next 25 years will be as successful as the first, and that your fiftieth anniversary will mark still greater progress towards the consummation of the objects for which the Institute was organized."—W. M. CORSE.

"To the Institute of Metals, on the occasion of its Silver Jubilee, we send heartiest greetings and best wishes for the future."—G. MASING, President, Deutsche Gesellschaft für Metallkunde.

"In the name of the Stattlichen Materialprüfungsamt I send to you on the occasion of the Silver Jubilee Meeting now being held in Birmingham, our best wishes for a further period of successful activity."—R. OTZEN, President.

MINUTES OF LAST MEETING.

The PRESIDENT moved, and it was agreed, that the minutes of the last meeting, held in London on May 10, 1933, be taken as read.

NOMINATION OF OFFICERS FOR 1934–1935.

The SECRETARY read the following list of members nominated by the Council to fill vacancies as officers for the year 1934–1935:

President.

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

Vice-Presidents.

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

Honorary Treasurer.

JOHN FRY.

Members of Council.

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

The PRESIDENT: I have to remind members that this list is that submitted by the Council and that, according to the rules, any ten members may put forward other names, provided that these are communicated to the Secretary before the conclusion of this meeting at 12.30 p.m. to-morrow.

ELECTION OF MEMBERS AND STUDENT MEMBER.

The SECRETARY announced that the following members and student member had been elected on July 13 and September 15, 1933:

MEMBERS ELECTED ON JULY 13, 1933.

JONES, Brinley, M.Met.	Perivale.
LANCASTER, Roderick Locke Hutcheson	Weybridge.
POUNTNEY, Cyril Graham	Calcutta, India.
SCARPA, Professor Dr. Oscar	Milan, Italy.
TALLMANN, Addison Herbert, Jr.	Hamilton, Ont., Canada.
WOYSKI, Bruno	Buffalo, N.Y., U.S.A.

MEMBERS ELECTED ON SEPTEMBER 15, 1933.

BOHACEK, Karl Albin	Halle-Trotha, Germany.
CLASEN, Andrew Joseph, Dr.-Ing., A.R.S.M., B.Sc.	London.
COLLINS, Albion George	Durban, South Africa.
COX, Charles Raymond	Beaver Falls, Pa., U.S.A.
DHAVERNAS, Joseph	Paris, France.
EDDY, Professor Corbin Theodore, E.Met., M.S.	Houghton, Mich., U.S.A.
FIRTH, Ambrose	Sheffield.
FORCELLA, Dr. Pietro	Rome, Italy.
FRENKEL, Gennady, Ph.D., M.A.	Kingston-on-Thames.
FUJII, Engineer-Commander Yoshiro, I.J.N.	London.
GALL, Carl	Northfleet.
HUMMEL, Professor Joseph	Pribram, Czechoslovakia.
JANNIN, Lucien Gustave	Billancourt, France.
MCPHERSON, Thomas	Tynemouth.
MITTON, Eric John	Birmingham.
PARRETT, Henry Hilton, B.Eng.	Manchester.
SAUNDERS, Horace	Weston Turville.
SCHOFIELD, Allan	London.
SHAW, Leonard Isaac	Birmingham.
STEDMAN, Group-Captain Ernest Walter, A.R.C.Sc.	Ottawa, Canada.
SUTTON, Miss Lilian Mary, M.Sc.	Leeds.
WEBSTER, Frederick Philip	Wolverhampton.
WOLFF, James Daniel	London.
WYATT, Reginald James	Wembley.

STUDENT MEMBER ELECTED ON SEPTEMBER 15, 1933.

ERICHSEN, Per. Fabritius	Hampton-in-Arden.

FUND IN CONNECTION WITH SILVER JUBILEE.

The PRESIDENT: In the absence of our Honorary Treasurer, it is a great pleasure to me to be able to announce to you that in connection with the Silver Jubilee of the Institute the Original Members have united to present to the Institute the sum of £525, to be used as a special fund for Institute purposes. This very generous gift was received with much gratitude by the Council.

It has come to the knowledge of the Council that certain other members and firms in the industry, both in this country and abroad, would also like to contribute to this fund. The Council would welcome such contributions, and proposes to use this fund to promote the further progress of the Institute, particularly in regard to its publications. Such donations should be sent to the Secretary of the Institute and an early response will be appreciated.

NEW METHOD OF PUBLISHING ADVANCE COPIES OF PAPERS.

Dr. RICHARD SELIGMAN, F.Inst.Met., Past-President: The President has asked me to announce to you a change which is to be made forthwith with regard to the publication of the *Journal*. It will be remembered that at the beginning of the present year there was some liveliness in the correspondence columns, and suggestions were put forward for the improvement of the *Journal* and for the conduct of the meetings. A strong committee was appointed by the Council to consider these questions, and I was asked to take charge of its deliberations. The whole field has been mapped out very carefully for detailed discussion, and for the past five months we have conducted an intense investigation of the one question of the method of issuing the papers. As a result of these deliberations, it has been unanimously decided to abandon the issue of the advance copies of papers, and to publish them in future month by month in the (monthly) *Journal* of the Institute.

There are two main reasons for this change of procedure. One is to give to authors earlier publication of their papers; the other is to give members a longer time in which to consider the papers before they are discussed. A further advantage of issuing the papers as part of the monthly *Journal* is that every member will automatically secure all the papers. Hitherto only those members who have made application for papers have received the advance copies. The new scheme will not affect the bound volumes of Proceedings, which will be issued as heretofore, and will contain the papers, the discussions, and correspondence on them as at present.

For the new method of publishing papers to operate smoothly, it will be necessary for a steady flow of papers to be received by the Institute. Prospective authors are, therefore, requested to notify the Editor without delay of any papers that they may intend to present to the Institute. Papers for the March Meeting should be received as soon as possible, in order that they may be refereed and, if accepted, published in the monthly *Journal* well in advance of the Meeting. If there is delay in submitting papers there will be no opportunity for members to read them before the meeting.

COMMUNICATIONS.

The PRESIDENT called on Dr. Walter Rosenhain, F.R.S., Fellow and Past-President, to deliver an address, prepared by invitation of the Council, on "Some Steps in Metallurgical Progress, 1908–1933."

Communications by the following authors were then presented and discussed: H. W. Brownsdon, M.Sc., Ph.D., M. Cook, M.Sc., Ph.D., and H. J. Miller, M.Sc.; D. G. Jones, M.Sc., L. B. Pfeil, D.Sc., A.R.S.M., and W. T. Griffiths, M.Sc.; O. F. Hudson, D.Sc., A.R.C.S. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

The proceedings adjourned at 12.30 p.m. until 10 a.m. on the following day, Wednesday, September 20.

Afternoon.

Members and their ladies were the guests at luncheon at the Grand Hotel of the following bodies: Aluminium Hollow-Ware Association, Brass & Copper Tube Association, Brazed Brass Tube Association, Brass Wire Association, Brassfounders' Employers' Association, Cold Rolled Brass & Copper Association, Manufactured Copper Association, and the Nickel Silver Association. Mr. A. H. Wolseley occupied the chair.

In the afternoon members visited by invitation the works of the following firms: Earle, Bourne & Co., Ltd.; the Austin Motor Co., Ltd.; the General Electric Co., Ltd.; I.C.I. Metals, Ltd.; the London Aluminium Co., Ltd. The ladies, after tea at the Winter Garden Café, paid a visit to the B.B.C. Studios.

Evening.

In the evening members and their ladies were the guests of the Chancellor, Council, and Senate at a Reception in the Great Hall of the University of Birmingham, Edgbaston, where they were received by the Pro-Chancellor (Mr. Walter Barrow, LL.M.) and Mrs. Barrow.

Prior to the Reception there was a reunion of the Original Members of the Institute in a reconstruction of the first office of the Institute in the Metallurgical Museum. Professor T. Turner, M.Sc., A.R.S.M., on behalf of the Original Members, handed to the President a cheque for £525 which had been subscribed as a special fund in connection with the Silver Jubilee of the Institute.

Wednesday September 20.

The meeting was resumed under the Chairmanship of the President, Sir Henry Fowler, K.B.E., LL.D., D.Sc.

COMMUNICATIONS.

Communications by: N. P. Allen, M.Met.; W. H. J. Vernon, D.Sc., Ph.D.; G. D. Bengough, D.Sc., M.A., and L. Whitby, M.Sc.; W. E. Alkins, M.Sc., and W. Cartwright, O.B.E., M.Sc., were presented and discussed. Papers by the following were taken as read and were not discussed: N. Ageew, Met.Eng., and D. N. Shoyket, Chem.Eng.; H. J. Gough, M.B.E., D.Sc., Ph.D., F.R.S., and D. G. Sopwith, B.Sc.Tech.; W. Hume-Rothery, M.A., Ph.D.; B. Jones, M.Met.; H. O'Neill, M.Met., D.Sc., G. S. Farnham, B.A., M.Sc., and J. F. B. Jackson, B.Sc.; D. Stockdale, M.A., Ph.D. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

CONCLUDING BUSINESS.

The PRESIDENT moved: That the best thanks of the members of the Institute of Metals in general meeting assembled be accorded to:—

(1) The Deputy Lord Mayor of Birmingham (Alderman J. B. Burman, J.P.) for his welcome to the City;

(2) The Lord Mayor of Birmingham (Councillor H. E. Goodby) for his hospitality;

(3) The Chancellor, Council, and Senate of the University for permitting the use of halls and rooms of the University and for their hospitality;

(4) The Birmingham Education Committee and the Principal of the Municipal Technical College, for permitting the use of their Examination Hall and Committee Rooms, and for many facilities;

(5) The firms in Birmingham and district who have granted permission for members to visit their works, and for their hospitality;

(6) The Non-Ferrous Metal Trades Associations, for their hospitality;

(7) The firms and individuals who have entertained the ladies, and for their hospitality;

(8) The Chairman (Mr. H. O. Smith) and members of the Local Reception Committee; the Chairman (Mr. G. W. Mullins) and members of the Executive Committee; and the Local Secretary (Mr. Graham Squiers), to whom the Institute is indebted for the well-considered and very successful plans for this most memorable twenty-fifth anniversary gathering.

The resolution was seconded by Dr. H. Moore, C.B.E. (President Designate), and was carried with acclamation. The business meeting then terminated.

Afternoon.

In the afternoon members visited by invitation the works of the following firms: W. & T. Avery, Ltd.; Joseph Lucas, Ltd.; Henry Wiggin & Co., Ltd.; the Birmingham Aluminium Co., Ltd. The ladies proceeded by motor coach to Wootton Wawen, where they were received at tea at Austey Manor by Mr. W. H. Williams, M.B.E., and Mrs. Williams.

In the evening members and their ladies were the guests of the Lord Mayor and Lady Mayoress (Councillor and Mrs. H. E. Goodby) at a Civic Reception held at the Council House.

Thursday, September 21.

Members and their ladies took part in a whole-day motor-coach excursion to the Cotswolds, visiting Stratford-on-Avon, where they inspected the new Memorial Theatre, Broadway, Bourton-on-the-Water, and various other Cotswold villages, returning via Winchcombe and Evesham.

AUTUMN LECTURE, 1933

TWENTY-FIVE YEARS' PROGRESS IN METALLURGICAL PLANT*

TWELFTH AUTUMN LECTURE TO THE INSTITUTE OF METALS, DELIVERED SEPTEMBER 18, 1933

By W. R. BARCLAY,† O.B.E., Vice-President.

Synopsis.

Developments in metallurgical plant and equipment over the last quarter of a century are reviewed under four headings:

(*a*) Developments in melting and casting equipment;
(*b*) Rolling-mill machinery;
(*c*) Rod- and wire-drawing plant;
(*d*) Auxiliary equipment—annealing furnaces and general.

The outstanding features of these developments are the introduction and widespread adoption of electric melting; the use of water-cooled moulds, and the Durville system in casting; improvements in rolling methods and machinery—particularly individually-driven "precision" mills of "two-high," "three-high," "four-high," and more complex types; the wider application of hot-rolling and of "mirror" finish rolls in final cold-rolling operations. Illustrations of the various stages of progress in mill construction are included, and attention is directed to the main features of modern rolling-mill design and also to developments now under consideration.

Improvements in annealing equipment are described and modern furnaces are compared with the older types in common use in the earlier years of the period. Reference is made to extrusion processes and their increased application to products other than rods and profiles.

All sections of the industry share in greater or lesser degree the general improvements in methods and machinery.

Introductory.

I think that it will be agreed by all who have known the non-ferrous metal industries for the past thirty or forty years, as some of you have, that probably no previous period in their history has been more prolific of the development of machinery and equipment than the last twenty-five years. My own recollection goes back to about 1893, when I first entered a works making and using German silver (nickel–copper–zinc

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* The title is perhaps too wide. The scope of the lecture being limited to those industries in which the Institute is chiefly interested, the subject of mining, smelting, and refining plant is necessarily excluded, as also is plant peculiar to the ferrous industries.—W. R. B.

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

alloys). At that time, and for some considerable time afterwards, any new plant erected, whether for casting, rolling, drawing, annealing, or other section of manufacturing production, was designed on strictly conventional lines. Only types of plant already well tried and tested were considered suitable for installation in new works or in extensions, and it is really surprising, when one looks back, how universally the older designs were followed in spite of advances then being made in machine construction in other industries. This conservatism was particularly noticeable in rolling and drawing practice. There were here and there a few notable exceptions—for example, I remember that one firm had the audacity (as it was then considered), about the year 1908, to go over to Germany for new and improved types of cold-rolling mills, but such firms were few indeed, and their example was rarely followed. It is an exceedingly interesting, and possibly a significant, fact that a change of outlook, at first slow and almost imperceptible but none the less real, coincided almost exactly with the founding and growth of the Institute of Metals. I do not desire to make exaggerated claims for the worth of the Institute—its prestige and status call for no such justification—and I will not say that the Institute has been directly responsible for this indubitable change of outlook, but I do say that it has not been without influence in this evolution, both directly and indirectly. While it is true that the pages of its *Journal* have only rarely contained descriptions of new plant or new developments in metallurgical equipment,* it has yet accomplished much to arouse interest and to inspire inquiry by its many-sided activities; for it should be borne in mind that the Institute does much more than publish technical and scientific papers: it brings together men of kindred interests in informal and close contact. Its scientific members rub shoulders with its technological members; these in turn meet others whose interests are more purely commercial and financial—and a closer relationship among all has been established. These contacts in the course of the past twenty-five years have engendered a wider, more scientific, and at the same time more practical outlook on the part of those connected with all sections of the non-ferrous metals industry.

In addition to these opportunities for internal contact, the inception and growth of the Institute have resulted in provision of fuller opportunities for establishing contacts with other countries and gaining

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* See, however, W. H. A. Robertson, *J. Inst. Metals*, 1909, **1**, 268–285. Various Authors, *ibid.*, 1917, **17**, 149–301. R. Genders, *ibid.*, 1924, **32**, 313–323. D. F. Campbell (and discussion), *ibid.*, 1927, **37**, 287–327. D. F. Campbell (and discussion), *ibid.*, 1929, **41**, 37–64. M. Tama (and discussion), *ibid.*, 1929, **42**, 103–118. G. L. Bailey (and discussion), *ibid.*, 1932, **49**, 203–235. Barclay, Russell, and Williamson, *ibid.*, 1932, **49**, 391–409.

knowledge of practice and development abroad. Particularly is this true of those centres in America and Central Europe where the non-ferrous metal industries are specially active and progressive.

It was, I believe, some such thoughts and ideas as these that prompted the Council of the Institute to invite me to address you to-night on the subject of modern plant development in the industries we represent.

It is obviously a wide field that we have to cover, and one that it is impossible to discuss with any degree of adequacy. It is also a field which suggests the advisability of a symposium from many contributors rather than a lecture by any one individual, whose experience must of necessity be limited. I hope, however, to set out in reasonable perspective the main features of metallurgical plant development during the period under review, and I shall endeavour to keep particularly in mind those sections of the industry in which the majority of my hearers are interested.

For convenience I propose to divide this survey into the following sections:

1. Developments in melting and casting equipment;
2. Rolling-mill machinery;
3. Rod- and wire-drawing plant;
4. Auxiliary equipment; annealing furnaces and general.

I.—DEVELOPMENTS IN MELTING AND CASTING EQUIPMENT.

In this category I include the production of ingots, which is the basis of metallurgical manufactures. As a convenient starting point for a review of this section, we may recall for a moment the type of casting equipment in common use in the early years of the present century. The great majority of the non-ferrous manufacturing works in this Country were equipped only with crucible furnaces of the pit type—for the most part coke-fired. A limited use was made of oil or gas fuel for metals and alloys of high melting points, such as nickel and its richer alloys, but the furnaces used even for this type of product were essentially of the conventional crucible type. The main development prior to the period now being considered was the provision of forced draught and mechanical tilting. So far at least as non-ferrous metals are concerned, electric furnaces were non-existent. The idea, however, was "in the air," for, during the first decade of this century, the ferrous industries of Europe had begun experimental production of steel from such furnaces as the Héroult and the Kjellin, and the possible application of these methods in non-ferrous melting practice was the subject of much discussion.

At that period the only furnaces which, to the works' metallurgist, held out any substantial promise of successful operation were the Héroult and the Kjellin types. The former is an arc furnace, the latter an induction furnace, and the advent of both these types coincided with the beginning of the present century. I believe that the earliest industrial Kjellin furnaces for steel melting were installed in Germany in the year 1900, and most probably at about the same time in Sweden. It is not surprising, however, that at this period we were decidedly reluctant to experiment on a works' scale either with the arc or the induction furnace, and the proposals for electric melting of non-ferrous metals most favoured at that time were those embodying the "resistance" principle. To make use of the ordinary crucible and surround it by graphite or other refractory resistance elements electrically heated was a natural suggestion arising out of conventional practice. Investigation of the possibilities of this type of furnace, however, quickly revealed not only the practical difficulties, but also the serious problem of securing anything like economic operating costs. Apart, therefore, from spasmodic experiments in individual works and laboratories, little or nothing was done in this country until soon after the outbreak of the War, 1914–1918. By this time further experience had been gained in the working of both the "arc" and the "induction" electric furnace in steel melting, and in America matters had so far progressed that the utilization of such furnaces for the melting of brass and other copper alloys had definitely entered the field of practical possibilities.

A detailed description of the various types of furnaces introduced during this earlier period of our review is not possible within the limits of our time. For our purpose it is sufficient to point out that it was really the advent of the Ajax–Wyatt low-frequency induction furnace which made the electric melting of brass and copper alloys generally a commercial success and led to the adoption of electric melting on a wide scale.

In the meantime, however, I must mention one landmark of importance, namely, that in 1917 the late Mr. Kent Smith * and I conceived the idea of utilizing the electric arc furnace for the melting of copper–nickel alloys for war purposes. Our decision was influenced rather strongly by the possibility of effecting some degree of *refining* during melting operations, an achievement which had been successfully demonstrated in steel practice. Our earlier experiments were carried out in the "bottom electrode" type of arc furnace—a design of furnace introduced by Greaves and Etchell and then beginning to be adopted

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* Whose untimely death in Detroit was notified as these sentences were penned.

in English steel works—but for a number of reasons we considered that for our purpose the Héroult "top electrode" design would be more satisfactory, and with the approval of the Ministry of Munitions, a Héroult furnace with a capacity of 1200–1500 lb. was erected in a corrugated-iron shed at Sheffield (Fig. 1, Plate I). The incident is worth recalling, since this was the first electric furnace, so far as I am aware, ever used for the melting of non-ferrous nickel alloys.

As is not unusual in new ventures, we passed through periods of grave anxiety and had to face many difficulties. It is, however, satisfactory to note that to-day this type of electric furnace is standard practice throughout the world for the melting of nickel and its richer alloys, although recently the position of the arc furnace has been somewhat challenged by the "high-frequency" furnace.

During the last ten years progress has been exceedingly rapid. In the non-ferrous industries both the arc type and the induction type of electric furnace may be said to be definitely established. The resistance type of furnace has also been developed with considerable success in the melting of aluminium and aluminium-rich alloys. For copper and its chief alloys, induction furnaces of the Ajax–Wyatt and Russ designs are most generally favoured (Fig. 2, Plate II). For higher-temperature metals, such as nickel and its alloys, the arc furnace of the Héroult type is most popular. The latter type of furnace design has been appreciably varied by different makers both in Europe and America, but in essential principle all such furnaces depend on radiation heating by the electric arc.

From a technical point of view, the most interesting advance of the latter part of our period is the introduction and development of the "high-frequency" induction furnace, due in the main to Northrup in the United States. This furnace (Fig. 3, Plate III) is a modern development, made possible only by advances in the science of electrical engineering, and as a melting proposition, at least in theory, presents extremely attractive features to the metallurgist, since it provides the possibility of melting under conditions ideally suitable for the exclusion of extraneous impurities. It must be admitted, however, that the high-frequency furnace is more suitable for high- than for low-temperature alloys, and consequently its adoption in the non-ferrous metals industry has been somewhat slow. By far the great majority of these high-frequency furnaces have been erected in steel works for the melting of alloy steels, and in the steel trade during the last few years a number of large installations have commenced production in America, in England, and on the Continent of Europe. The high-frequency furnace as at present designed is unfortunately a somewhat costly proposition in capital expenditure, and it cannot be claimed that it is appreciably more economical in power consumption than the arc furnace. These facts have undoubtedly retarded its progress in the non-ferrous industries. Up to the present time its main use in this field lies in the production of high-purity nickel-containing alloys.

An important factor in the working of both high- and low-frequency induction furnaces is, of course, the furnace lining or container in which the metal is melted, and it is worth while mentioning here that electric furnace development has led to considerable improvements in the composition and use of refractory materials, and these improvements have in turn effected appreciable economies in furnace operating costs.

Before leaving the subject of metal-melting equipment, perhaps I may be allowed for a moment to deal with a question which I have been repeatedly asked during the last few years—namely, how does the cost of electric melting in this country compare with that of coke-, gas-, or oil-fired crucible practice so far as non-ferrous metals are concerned? The difficulty in replying to this question is one relating largely to the scale of production. It is unquestionable that with furnace linings of modern composition and construction, and electric energy at anything like a reasonable price, electric melting is decidedly more economical than coke-fired crucible melting, if the quantity dealt with is sufficient to keep an electric installation reasonably fully employed. For production on a small scale, and particularly where a large number of individual and special alloys is made, the coke-fired crucible furnace still holds its own in this country. In countries where coke is more expensive these remarks apply to gas- or oil-fired furnaces. In this comparison I have purposely omitted consideration of the question of quality, but it should be remarked that the manufacture of crucibles, as well as the design and construction of the furnaces themselves, have been so greatly improved during the last ten or fifteen years that many of the disadvantages of crucible furnaces from the point of view of the metallurgical quality of the product have disappeared.

Moulds.

The production of liquid metal, from whatever form of furnace, is, of course, only one stage in the production of ingots. A further radical factor in casting equipment is the *ingot mould*. In this type of equipment again considerable developments have been witnessed, the most important of which is undoubtedly the advent of the water-cooled mould. This development, like many others in modern metallurgical practice, was under discussion long before it became a practical proposition. The chief credit for its industrial evolution must be given to

Otto Junker * and Erichsen both operating in Germany.† The designs adopted by both makers are based essentially upon the use of a mould lining of copper or some other suitable alloy, surrounded by a steel jacket through which provision is made for a continuous flow of water, hot or cold. The lining of the Junker mould (Fig. 4, Plate III) has always been of copper. Erichsen, on the other hand, developed the idea of using a nickel–iron alloy of the Invar type, and claims thereby certain improvements in results in solidity of ingot casting.

The advantages and disadvantages of the two types of mould are somewhat controversial and need not be considered here. What must be said is that the advent of the water-cooled mould marks a decisive stage of progress towards the industrial production of sounder ingots. Amongst the advantages of the water-cooled mould is the possibility of obtaining uniform temperatures throughout practically the whole period of solidification. In the older type of mould, which was usually a cast box of hematite iron, rectangular, square, or round, it was almost impossible to obtain any degree of uniformity in the relation between the pouring temperature of the metal and the temperature of the mould into which it was being poured. It is obvious that the relationship between the two is important in securing uniformity of cast structure, and the water-cooled mould certainly relieves the operating metallurgist of considerable anxiety. It must, however, be pointed out emphatically that the use of such a mould does not remove the need for strict attention to the other factors essential to the production of sound ingots, particularly the "feeding of pipe."

Apart from the possibility of obtaining more accurate temperature control, the principal advantage secured by the water-cooled mould is economy in casting costs; this is without doubt very considerable. In the use of the older type of cast ingot mould, the wastage, particularly where fairly high temperature alloys were being produced, was extremely serious, and was no small factor in the cost of ingot production. Some very remarkable results illustrating this point were obtained in the earlier days of experimental work with such moulds when I was engaged in their development for the casting of nickel–brasses. With the older type of mould it was no uncommon thing for a set of moulds to deteriorate after three weeks' work so seriously as to necessitate either removal from service altogether or complete reconditioning. In contrast to this, one of the earliest water-cooled moulds that I installed was in

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* O. Junker, "Wassergekühlte Kokillen" (Water-Cooled Moulds), *Z. Metallkunde*, 1926, 18, 312–314. Anon., "Water-Cooled Moulds in Brass Foundries," *Met. Ind. (Lond.)*, 1927, 31, 465–466. O. Junker, "The Casting of German Silver in Water-Cooled Chill Moulds," *Met. Ind. (Lond.)*, 1930, 37, 103–104.

† "Chill Mould for Casting Non-Ferrous Metals." British Patent 299,850.

continuous service for more than eighteen months, and even at the end of this period the surface of the inner lining was in a much better condition than the best of our cast-iron moulds.

The modern casting shop, with its equipment of electric furnaces and water-cooled moulds (see Fig. 2, Plate II), is the most remarkable development of the period we are discussing; the adoption of such equipment has not merely raised the whole standard of casting practice, at the same time effecting considerable economies and making possible an increase in unit production, but has led to many minor advances in metallurgical practice. It is no small item in works' economics, for example, to be able to increase the unit melt of brass from quantities of the order of a maximum of 250 or 300 lb. to units of the order of 1000–2000 lb., and it is decidedly better metallurgical practice.

The introduction of the water-cooled mould is, however, by no means the only improvement in ingot casting practice which the last quarter of a century has witnessed, and, although only brief reference can be made, I must not omit mention of such improvements as the introduction of the Durville system of casting. This is the outcome of a study of the technological factors involved in the pouring of molten metal into ingot moulds. As you are aware, the Durville principle is that of rotating the mould and the molten metal container about a common horizontal axis during the operation of pouring metal into the mould, thus producing cast ingots with only the minimum of disturbance in the liquid metal immediately before and during solidification. There can be no doubt that this type of mould and the improvements in casting technique thus developed by the work of Genders and his colleagues at Woolwich, under the auspices of the British Non-Ferrous Metals Research Association, have made possible the casting, on an industrial scale, of several metals and alloys which would otherwise present almost insurmountable difficulties.

A broad review of the subject of casting practice, indeed, reveals the fact that the developments of the last twenty-five years as compared with any previous period have been literally revolutionary. Their importance lies not merely in engineering design and construction, but in their metallurgical advantages. A scientific metallurgist finds in the tools now at his disposal in this field far greater possibilities of reaching high standards of quality than were imagined twenty-five years ago.

II.—Rolling-Mill Machinery.

The development of rolling-mill machinery, whilst perhaps not so fundamental in nature as that which has occurred in casting equipment, has nevertheless been important and perhaps even more impressive, particularly in the production of sheet and strip metal. Twenty-five years ago the general equipment of practically all non-ferrous rolling-mills in this country consisted of what are termed "train rolls," *i.e.*, a series of two-high mills of various sizes driven by one prime mover (steam or electric) and linked up either in series or parallel by reduction gearing. In many cases an entire mill equipment of fifteen to twenty pairs of rolls was driven from one prime mover by the aid of a large and heavy flywheel (see Figs. 5, 6, and 7, Plates IV–VI). Several such mills driven by the old "Watt type" of beam engine still remain in this country.

It must be admitted that these mills were usually run at a low cost per unit of power in the prime mover, but their disadvantages increased seriously as demands became more diverse and erratic, as in the case of modern industry. It is, of course, practically impossible to run one mill without running all, and often one or two mills may be employed at full capacity, since the product required is the size and gauge for which they are designed, whilst others in the same train are either idle or only partly occupied. It is this primary disadvantage, in conjunction with other minor incidental drawbacks, which has led to the most spectacular (if not the most important) development of the period.

Since 1908, and particularly since the outbreak of the War, "train mills" have repeatedly given place to mills "individually driven" by electric power. The chief advantage of such individually driven mills is that if a considerable quantity of sheet or strip metal of similar widths and gauges is in demand, such mills can be run independently and continuously without regard to other mills or subsidiary plant, the product of which may temporarily not be required. The development of the individually driven mill has led, however, to other changes which, whilst not so obvious to the casual observer, are yet vitally important in regard to both cost and quality of production. It is, indeed, not too much to say that the advent of the individually driven mill has led to a revolution in rolling-mill *design*.

The non-ferrous rolling-mill of a generation ago consisted of rolls and housings and wobblers and pinions almost literally thrown together, with little regard either to precision in construction or economy in power consumption. A modern individually driven mill, whether of the two-high, or the more complex, type is, on the other hand, a *precision* machine, designed and built with all the skill and attention to detail required in a high-grade machine tool (note, *e.g.*, Figs. 18–21, Plates XVII–XX). As a consequence, the rolling process has become much more scientific, the percentage of reduction during passes is more uniform and regular (with obvious advantages to uniformity in cold-working), and gauging is more accurate, both in cross-section and longitudinally.

I must, however, here interpose a tribute to the really extraordinary skill of the workmen of a generation ago in the manipulation of the older type of mill. I have often expressed admiration for the way in which experienced rollers succeeded in producing, from mills that had not the slightest claim to "precision," sheet and strip of quite remarkable uniformity of gauge. Much more labour and certainly much greater skill were involved in such effort than in the modern mill, and with all this skill, it was very difficult for the scientific metallurgist to exercise any supervision over such factors as the uniformity of cold-working and the degree of cold-working effects. There can be no possible doubt that the advent of the "precision" cold-rolling mill has marked a definite advance both metallurgically and from the economic point of view in the production of non-ferrous sheet and strip metal.

A specially important feature of the modern precision cold-rolling mill is the adoption of hardened nickel–chromium steel rolls with water-cooling devices. Such rolls have a scleroscope hardness of from 95 to 100, and possess remarkably good surfaces. Their outstanding advantages to the metal roller are:

(*a*) The improved surface obtainable on cold-rolled sheet or strip metal;

(*b*) The retention of uniformity of camber and greatly reduced liability to distortion during heavy service.

Both of these factors are particularly important in finishing operations.

During the last few years considerable publicity has been given to the more complex individually driven mills of the four-high and six-high (cluster) type. Such mills should certainly find an important place in any review of rolling development in our industry. In some respects they represent a further improvement even on the precision two-high mill, particularly when, for any reason, metallurgical or economic, appreciable percentage reductions per pass are required. Fortunately, the four-high mill was not introduced into the non-ferrous industry until the two-high mill itself had been vastly improved both in design and construction. The refinements that had already found a place in individually driven two-high mills undoubtedly gave the four-high and cluster mills an opportunity to demonstrate their possibilities, which would have been impossible without the previous experience of precision construction.

This is neither the place nor the time at which to enter into a detailed discussion of the comparative values of the two-high, three-high, four-high, or six-high rolling-mill, but as I was personally responsible for the introduction of the four-high rolling mill into the non-ferrous industry in this country, I trust that I may be allowed to say that because the four-high or six-high mill possesses certain qualities, it does not necessarily follow that in the development of rolling-mill equipment and in the replacement of obsolete plant these latter mills should *always* be substituted for the older two-high type. The answer to the question as to whether the installation of four-high or six-high mills is advisable depends entirely on conditions, and on more than one occasion I have in certain circumstances advised the erection of a two-high rather than a four-high mill.

The more complex mill, with its backing-up rolls and roller-bearing equipment, is undoubtedly economical in power, and with properly cambered working rolls is exceedingly accurate in product, capable of giving big reductions with uniformity of gauge, but its advantages cannot be either demonstrated or experienced unless the type of output required is suitable. These complex mills are essentially "mass-production" machines, requiring quantity and standardization of product in order to realize their full possibilities. The industry as a whole is, unfortunately, not yet "standardized," and in meeting the varied demands which come to the manufacturer of rolled-metal products in non-ferrous metals to-day it is often more economic to continue to use the two-high mills rather than incur the increased capital cost of the four-high or cluster mill. At the same time, I hold strongly that the introduction of these latter mills is a further definite step forward in rolling-mill design, and it will, I believe, pave the way in the future to still greater improvements.

Amongst other incidental factors, these mills have brought before us the advantages of roller bearings, and have also made an important contribution to progress by revealing the possibilities of the smaller working roll. Their design has been appreciably improved during the last year or two by the addition of suitable appliances for feeding strip and sheet into the working rolls, the need for which is obvious when the small rolls of these four-high or six-high mills are recessed somewhat, as they must be from the face of the housings and backing-up rolls. At their first introduction it was a matter of some appreciable difficulty to feed such mills, particularly when in the earlier stages sheet or strip of a thickness of the order of 0·1 in. to 0·2 in. was being rolled in preparation for finishing. The provision of pneumatic feeding devices has materially improved the mills in this respect. (See Figs. 24 and 26, Plates XXIII and XXV.)

A further development of cold-rolling mills is the Steckel mill,* which, although not as yet at all widely adopted in the non-ferrous

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* British Patent No. 292,494, January, 1928.

industries, deserves at least a brief mention. This mill is a distinct departure from conventional rolling-mill design, both from engineering and metallurgical points of view. The metallurgist regards cold-*rolling* as a process of cold-*working*, and is therefore able to appreciate the essential difference between the *type* of cold-working effected by the ordinary rolling-mill operations and the *type* effected by "drawing" such as is carried out in the production of rods, wire, and tubes, in which the crystal grains of metal are drawn one over the other and elongated more or less uniformly, instead of being compressed in one direction only. The fundamental principle of the Steckel mill is the subjecting of strip or sheet metal to the latter type of cold-working rather than to the former. The strip to be cold-rolled is passed through small working rolls which have an action corresponding rather to that of dies through which metal is drawn than to that of rolls subjected to pressure. The metal is fed into these working rolls from drums which are electrically driven and capable of rapid reversal. The working rolls of the Steckel mill are exceptionally small (2 in. to 2·5 in. in diameter), and have consequently to be supported by backing-up rolls. The drive is almost entirely by tension on the strip itself, and the small rolls thus constitute in effect a frictionless rotary die. It is claimed for this mill that by its use considerably greater percentage reductions can be obtained without intermediate annealing than by any other method, and those of you who are aware of the greater percentage reductions usually obtainable in the operations of "drawing" as compared with those of "rolling," will appreciate the possibility of such a result.

Theoretically, I regard the Steckel mill as being essentially sound from a metallurgical point of view, but here again it is vital that the class of product manufactured should be suitable. The Steckel mill, like the four-high mill, is virtually a mass-production machine, and can be successfully operated only when strip is being produced in quantity in very long lengths. Its most general adoption so far appears to have been in steel mills, particularly in America, where large quantities of standard widths and gauges are required in normal conditions of trade.

In the preceding paragraphs I have dealt exclusively with cold-rolling. I must now turn briefly to the subject of hot-rolling, which up to a few years ago was not considered to be a very important factor in the production of non-ferrous metals.

During recent years the importance of hot-rolling has been more widely appreciated, and it is being more and more generally adopted as the result of our increased knowledge of the possibilities of hot-working in the production of a large proportion of industrial non-ferrous alloys. Not many years ago it was considered that very few such alloys could be hot-rolled, 60 : 40 brass being an outstanding exception. To-day in modern plants even alloys of the nickel–brass type may be, and are being, hot-rolled.

In the earlier part of the period under review, very little change occurred in the mills put down for hot-working non-ferrous metals. They were almost invariably two-high mills of the purely conventional type. Since the War, however, a change of a kind not dissimilar to that which has occurred in cold-rolling plant has occurred also in hot-rolling mills, and practically every hot-rolling mill put down since the period at the end of the War has been of the individually driven type, with a number of detailed improvements which have raised the standard of efficiency and accuracy.

The majority of the mills recently erected for the hot-rolling of non-ferrous metals are probably of the three-high type, but several important modern installations, particularly for the hot-rolling of copper and brass, consist of two-high mills, although these depart in many ways from the older designs.

A three-high mill equipment of the "Universal" and "Lauth" types recently erected in this country for the hot-rolling of nickel and its alloys has been described fully in the *Journal* of this Institute,* and on the Continent of Europe three-high mills have also been adopted in most cases for these high-temperature alloys.

Some interesting installations of three-high mills have recently been erected both in Europe and America for aluminium and its alloys.

The accompanying illustrations, Figs. 8 (Plate VII) to 28 (Plate XXVII), have been chosen in order to exemplify the various stages of progress in rolling-mill design † for both hot and cold operations. I wish particularly to direct attention to the factors making for greater precision, *e.g.*, the development of machine-cut helical gears; the greater width of pinions and their improved mechanical design, with provision for more efficient lubrication; the mechanizing of screw-down gear, with the adoption of fine adjustments; and the remarkable improvement in coupling spindles. Not the least of the recent advances in detail of construction of the modern rolling-mill is the provision of automatic lubrication, which effects considerable economies in power consumption while at the same time lengthening the life of wearing parts.

Before leaving the subject of rolling-mills, I must make brief reference to the latest of all developments in this field. I refer to what is

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* W. R. Barclay, G. A. V. Russell, and H. Williamson, *J. Inst. Metals*, 1932, 49, 391–409.

† For a technical dissertation on the evolution of the modern rolling-mill, see Johann Puppe, "Entwicklung der Walzenstrassen," *Stahl u. Eisen*, 1933, 53, 265–270, 300–305.

known as the Hazelett rolling process, on which considerable experimental work is now being carried out in the United States of America. While this cannot be regarded as a development brought to completion within the period under review, I feel justified in referring to it, since the experimental work which has led up to it certainly belongs to this period. It must, I am sure, have occurred often to observers of the processes of casting and hot-rolling that considerable loss of heat energy, as well as delay in processing, occurs in the cooling down of ingots and their re-heating for rolling purposes. The Hazelett process seeks to remedy this. Instead of using the normal ingot mould, molten metal is poured between water-cooled rollers in such a way that immediately the metal begins to solidify the rollers can be set into operation and the process of reduction to sheet be begun almost instantaneously. Full details of the Hazelett equipment are not available for publication, and the process is still in an experimental stage. The results of this experimental work so far reported are said, however, to be highly encouraging, and it is at least possible that this process will become an important factor in the future development of the hot-rolling of metals. Experiments are being carried out not only with metals of lower melting point such as copper alloys and the brasses, but also with those of higher melting points, including the rich nickel-containing alloys. The fundamental idea of the Hazelett process is extremely attractive, since the possibility of economy is obvious. Apart, however, from this factor, the claim is made, probably with considerable justification, that the process is capable of producing sounder material, since pressure is applied at the very earliest stages of solidification of the metal, with resultant elimination of blow-holes and defects due to pipe and inadequate feeding.

III.—Rod- and Wire-Drawing Plant.

In this field new developments of machinery have scarcely been so far-reaching as in the other fields already surveyed. Cold-drawing benches for rods and tubes remain to-day much as they were twenty-five years ago, except for modification in engineering details such as direct electrically-driven worm-gearing. The improvements in rod and tube production during the period have been by no means negligible, but such improvements have resulted from factors other than the process of cold-drawing. The improvements arise mainly from the increased use now being made of extrusion processes.

In wire-drawing machinery, however, developments have been very considerable, and are in some degree comparable with those in cold-rolling, particularly in regard to the greater precision and efficiency of modern machines. The production of rod and wire involves, of course,

PLATE I.

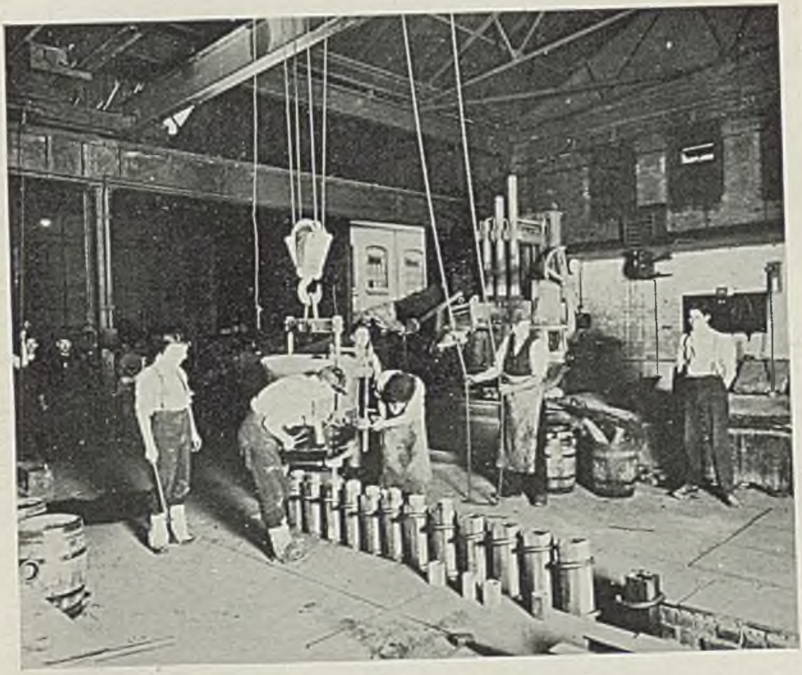

FIG. 1.—In the Background First Héroult Furnace Used for the Melting of Nickel and its Alloys. In the Foreground Bottom-Pouring from a Ladle into Rod Moulds. (*By courtesy of Henry Wiggin & Co., Ltd., Birmingham, England.*)

PLATE II.

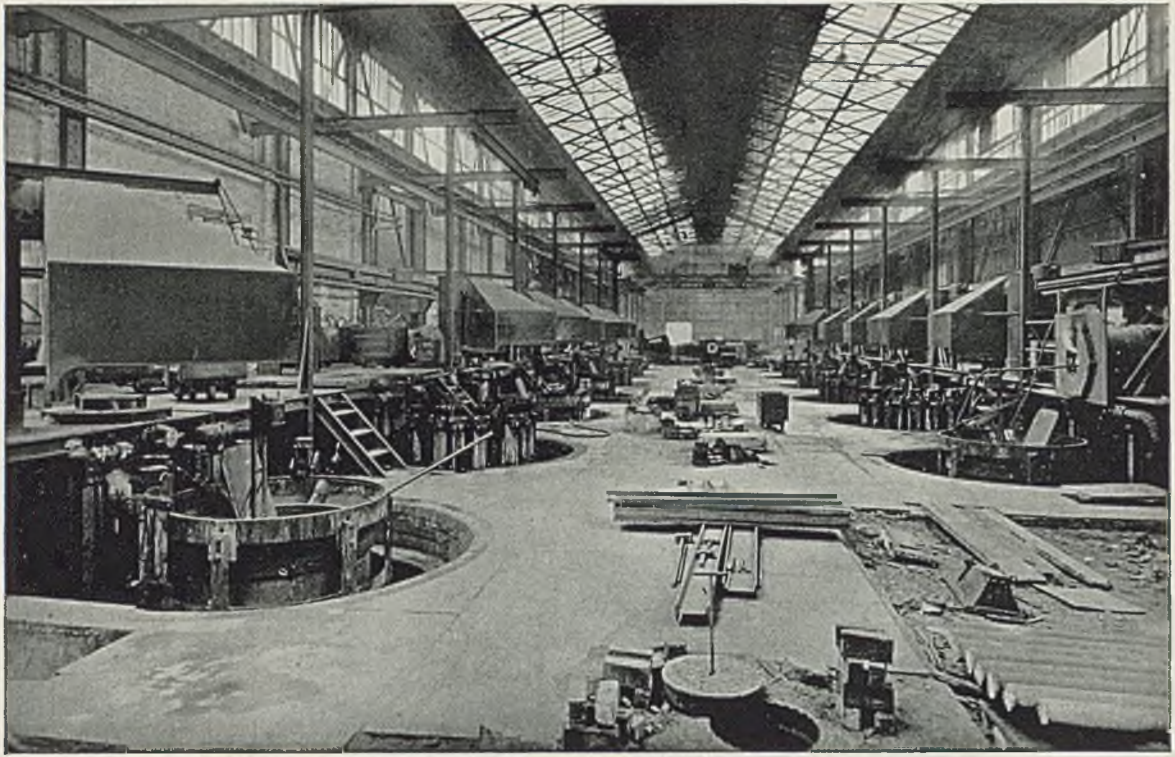

FIG. 2.—Modern Casting Shop Equipped with Ajax-Wyatt Electric Induction Furnaces. (*By courtesy of I.C.I. Metals, Ltd., Birmingham, England.*)

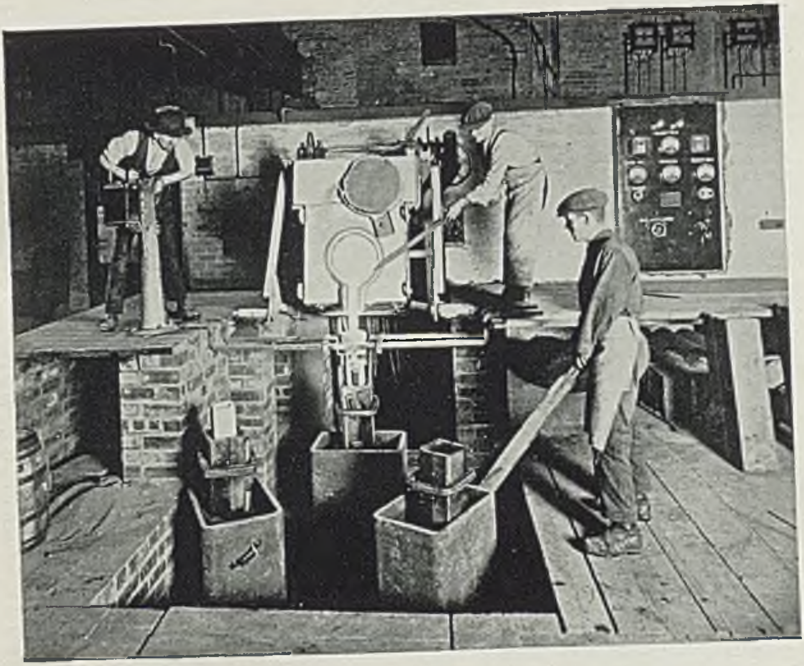

FIG. 3.—Northrup Electric High-Frequency Furnace (250 kg.) for the Melting of Nickel Alloys. *(By courtesy of Henry Wiggin & Co., Ltd., Birmingham, England.)*

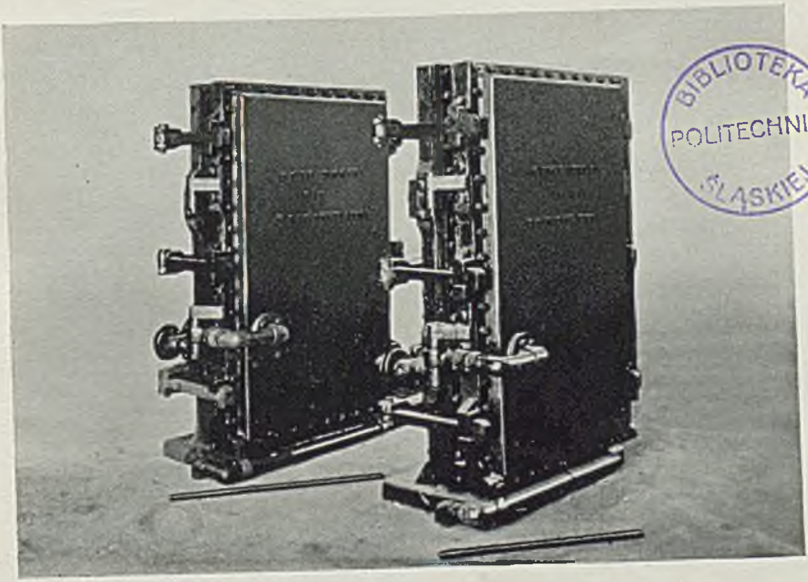

FIG. 4.—Junker Water-Cooled Ingot Mould. Note Water Connections on Steel Jacket. *(By courtesy of Otto Junker G.m.b.H., Lammersdorf, Germany.)*

PLATE IV.

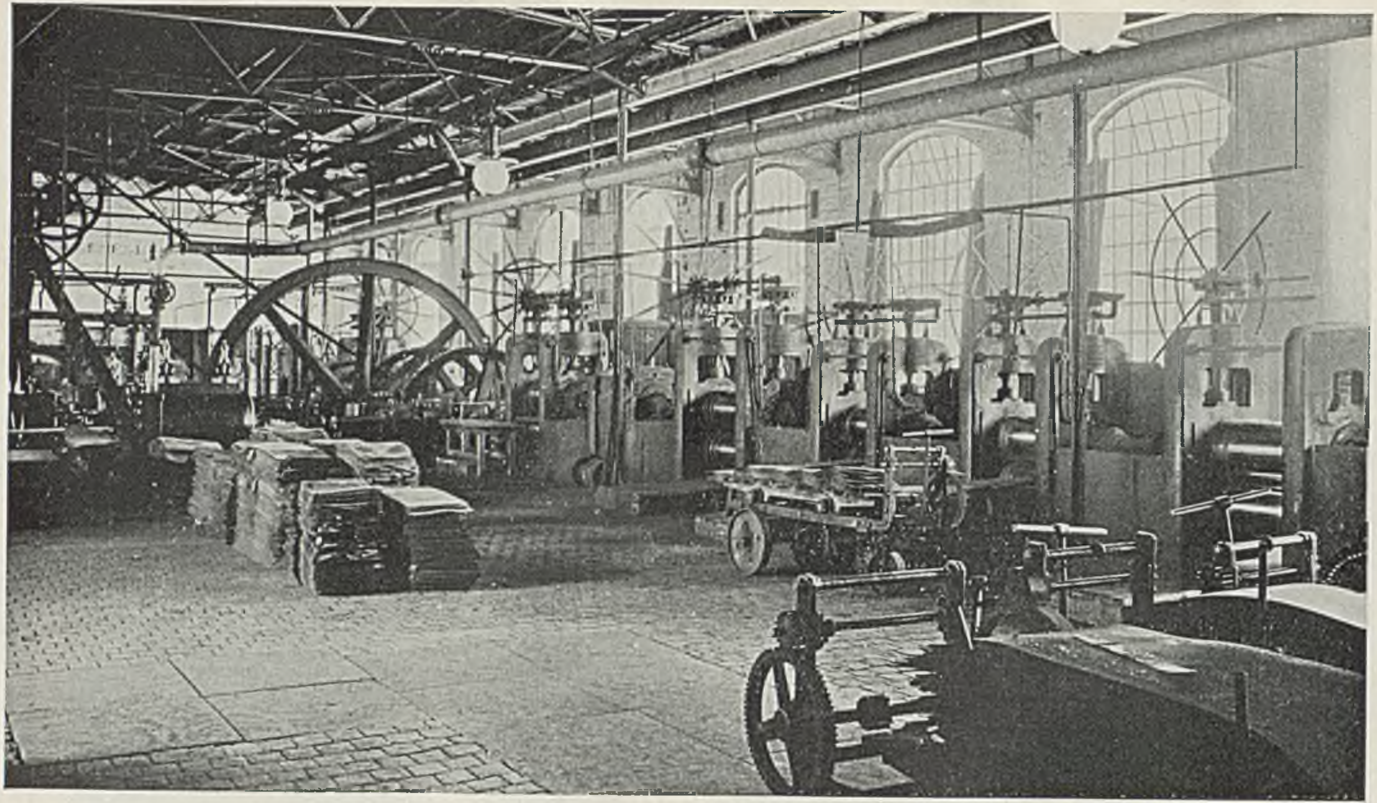

FIG. 5.—A " Train-Driven " Mill Erected about 1900 (Steam Power). Note Flywheel and Open Gearing. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

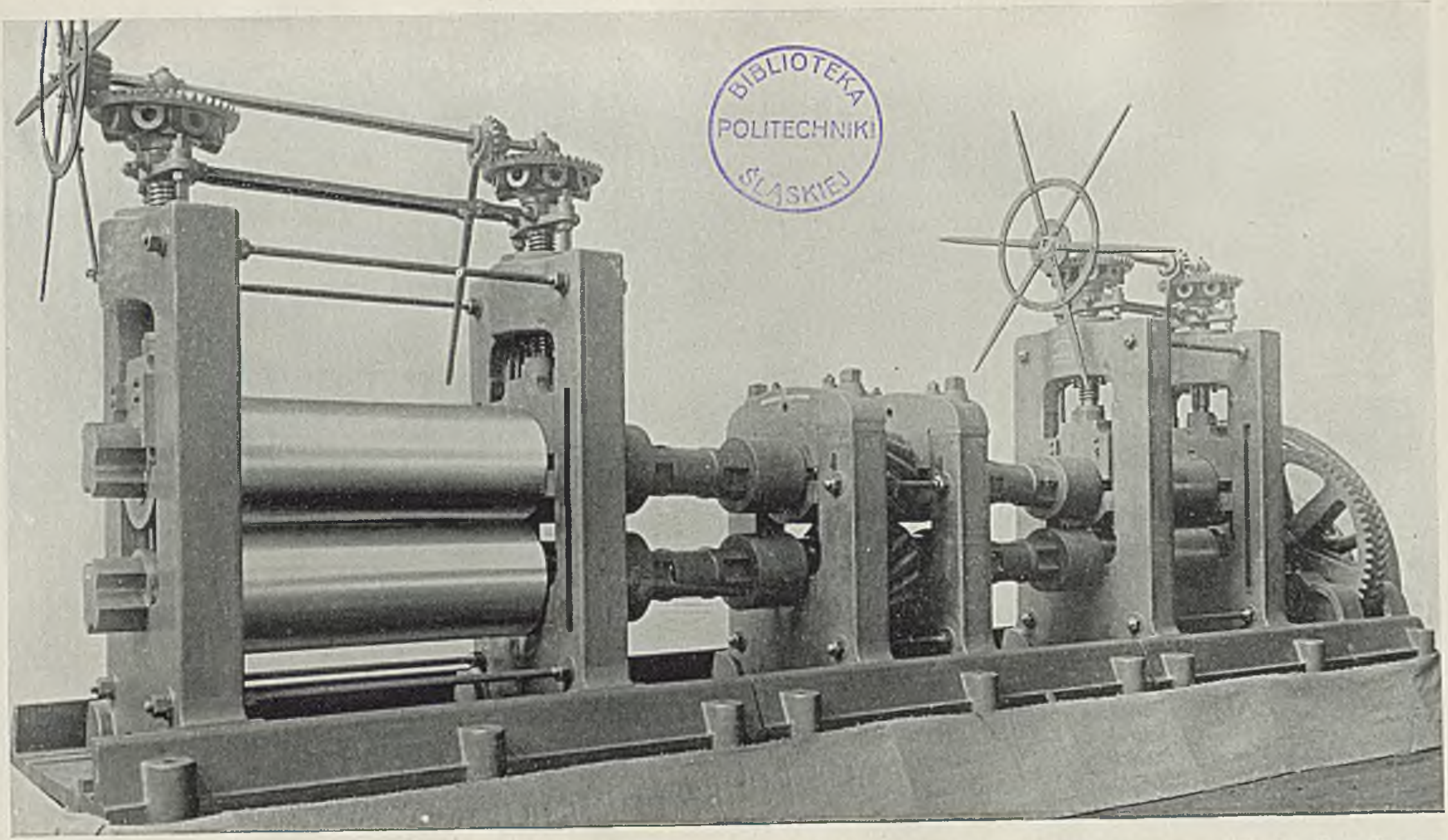

FIG. 6.—A Two-High "Train" Mill Erected in the Nineties. Note (right) Large Drive Wheel of Cast Steel and Unmachined Angular Teeth. Open Gearing.

(By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.)

PLATE VI.

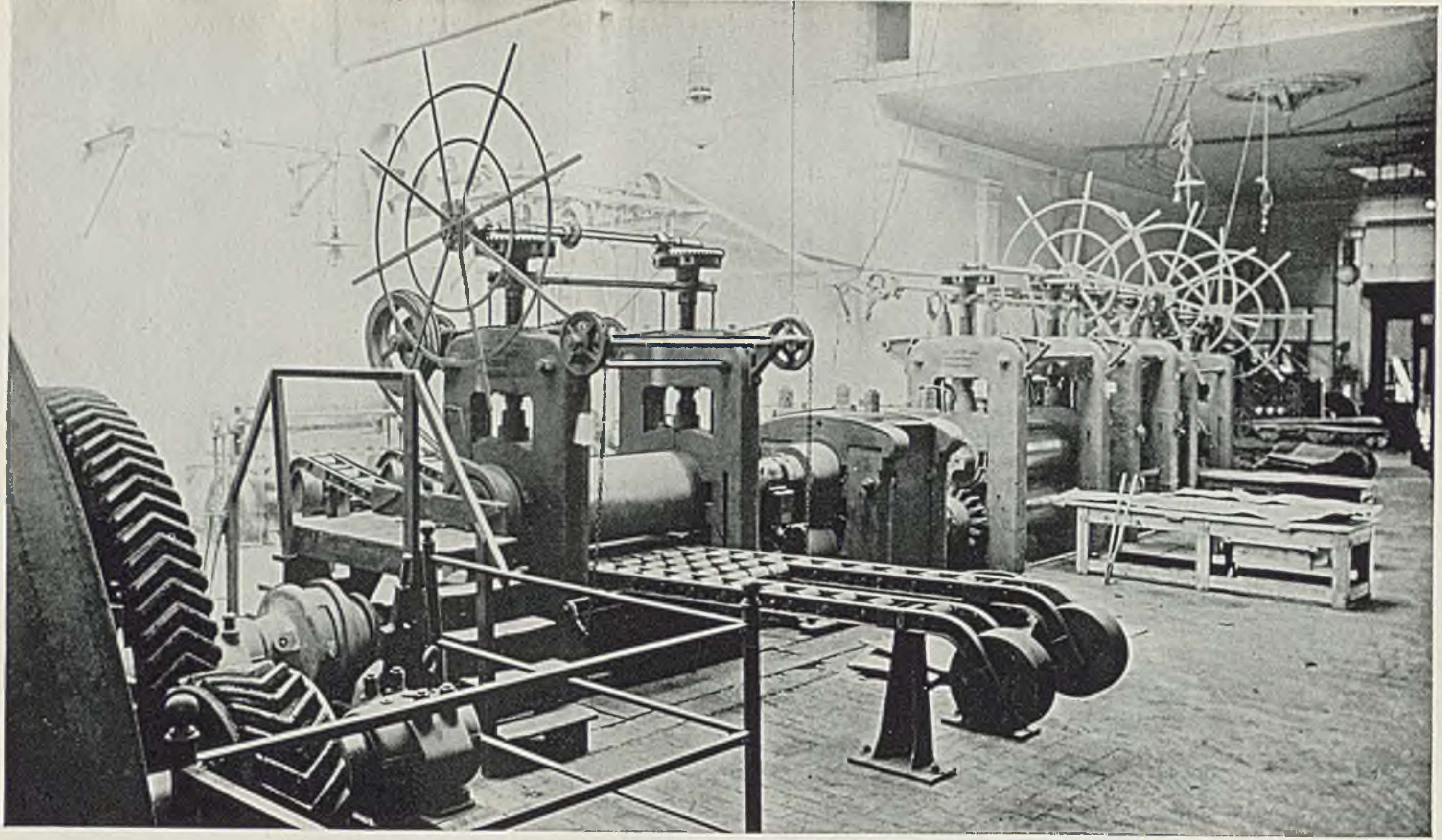

FIG. 7.—Rolling Mill for Copper, Brass, and Aluminium (1908). Note Unmachined Gear Wheels and Crude (Hand-Operated) Lifting Tables. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

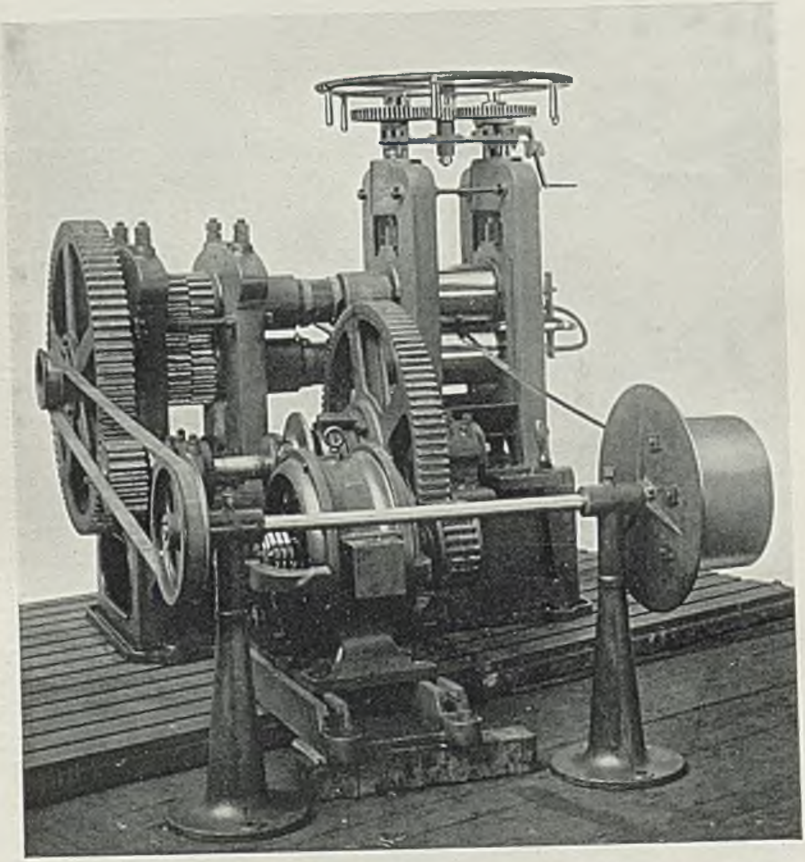

FIG. 8.—A Two-High Strip Mill of 1905. An Early Example of Electrically-Driven Strip Mill. Open Design Pinion Housing. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

PLATE VIII.

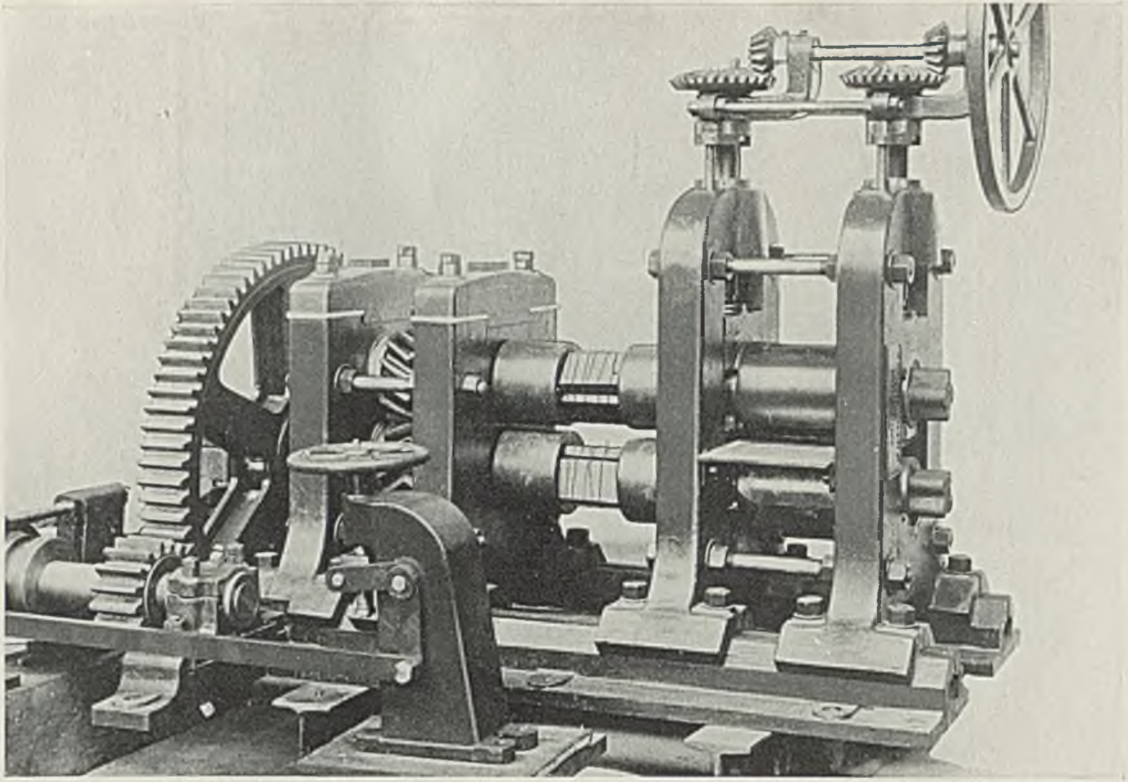

FIG. 9.—A British Two-High Mill of Pre-1908 Build. Individually Driven, Open Unmachined Gearing. (*By courtesy of W. H. A. Robertson & Co., Ltd., Bedford, England.*)

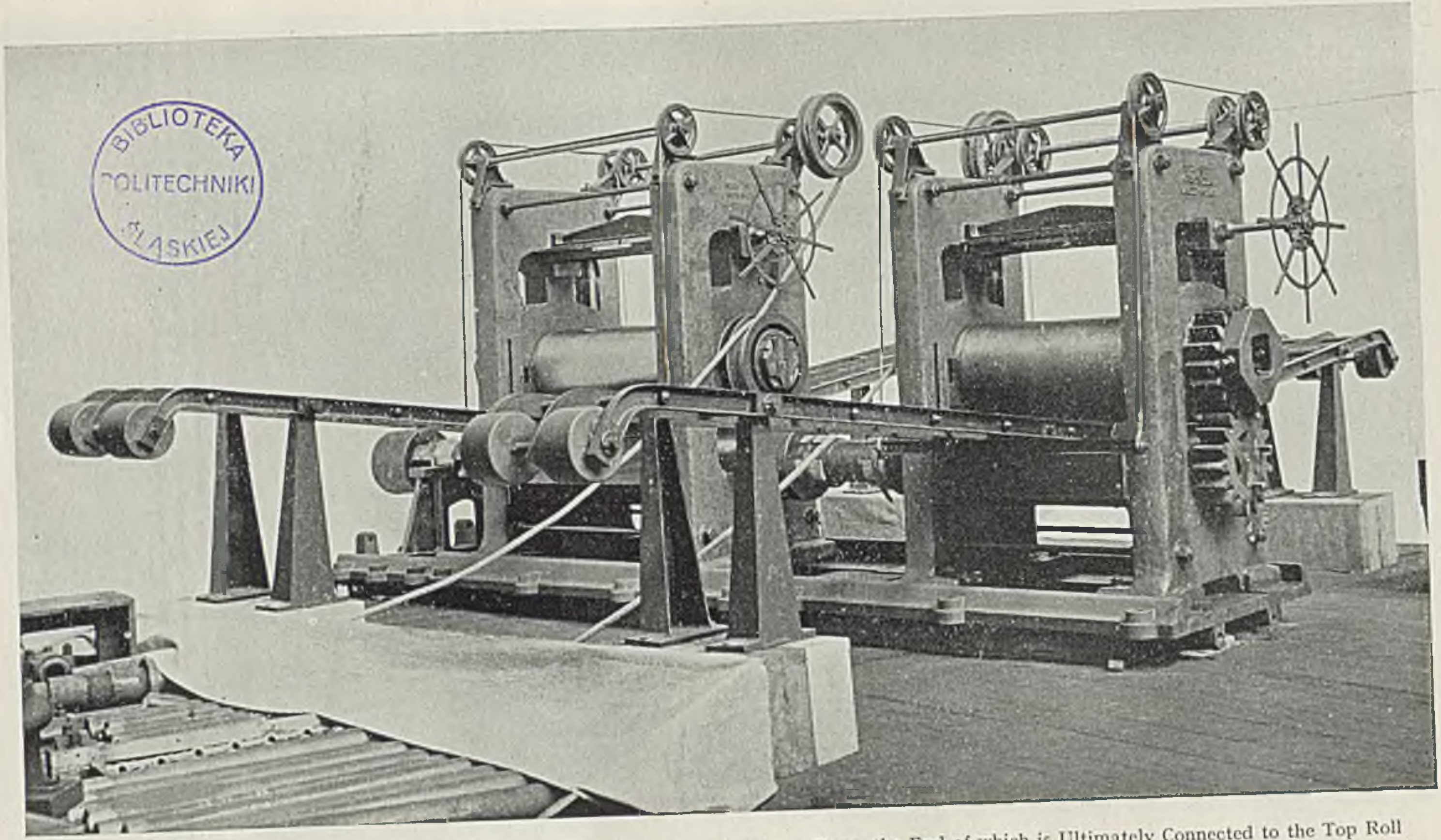

FIG. 10.—Copper Rolling Mill of 1907. Lifting Tables are Operated by Drawing a Rope, the End of which is Ultimately Connected to the Top Roll Journal. Top Roll Driven by a Pair of Friction Coupling Wheels. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

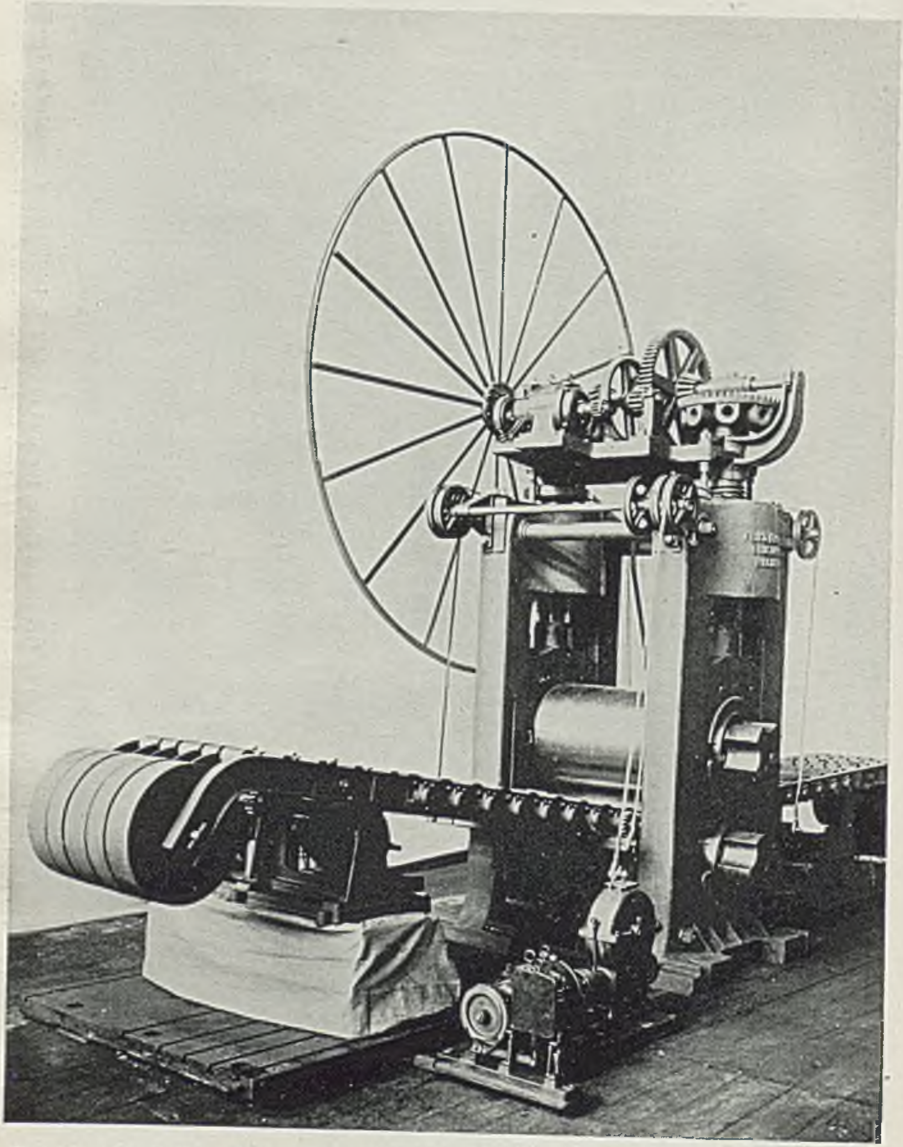

FIG. 11.—Hot-Rolling Mill for Sheets. Note Advance on Fig. 10. Covered Gear Wheels. Lifting Tables Still Worked by Ropes but from an Electric Motor. Also Motor Driven (Supplementing Hand) Screw-Down Gear. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

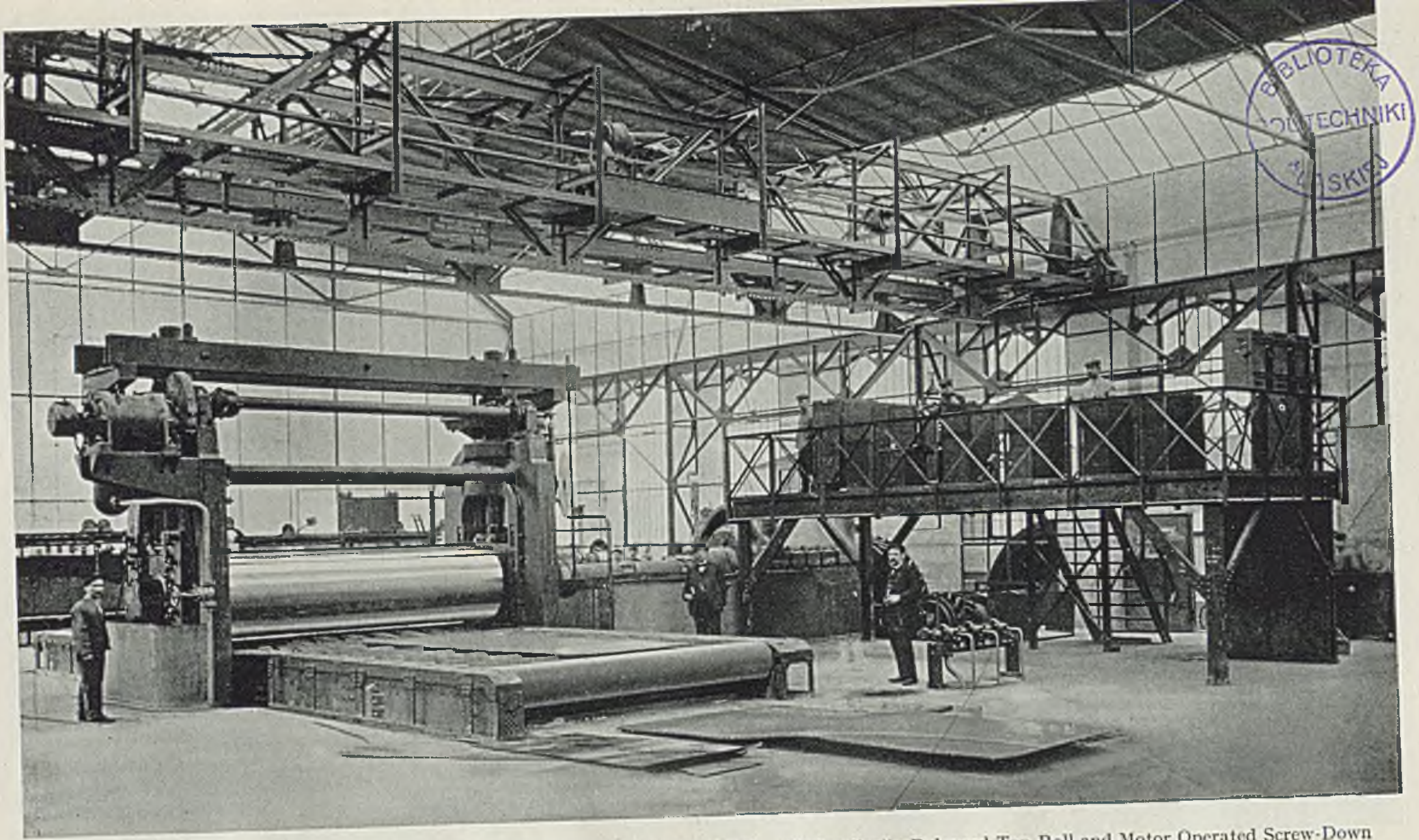

FIG. 12.—Reversible Two-High Hot-Rolling Mill for Copper Firebox Plates (1909). Hydraulically Balanced Top Roll and Motor Operated Screw-Down Totally Enclosed Pinions. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

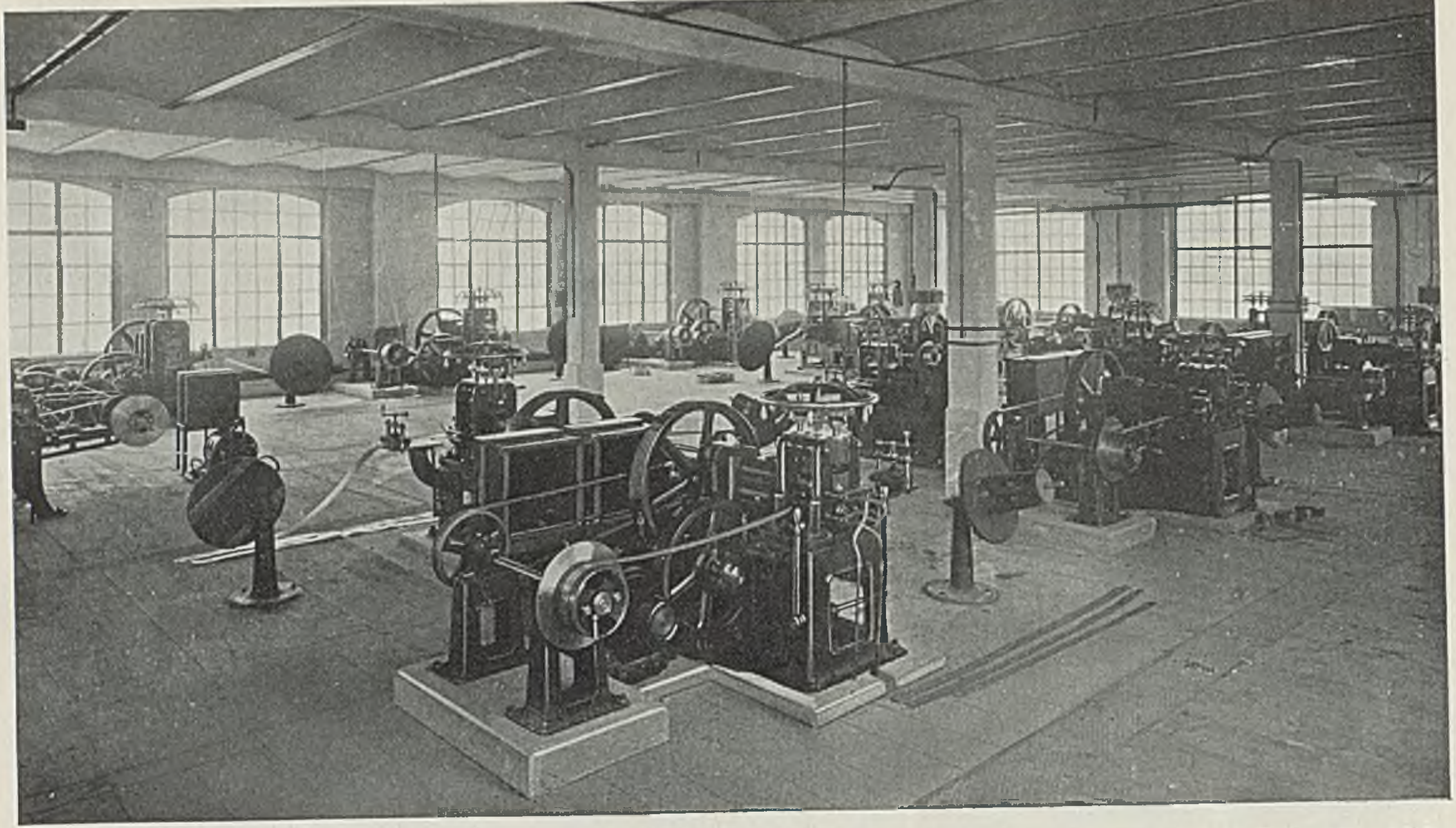

FIG. 13.—An Early Continental Installation (1909-1910) of Individually Driven Precision Strip Mills. (*By courtesy of August Schmitz Walzmaschinenfabrik G.m.b.H., Düsseldorf, Germany.*)

PLATE XIII.

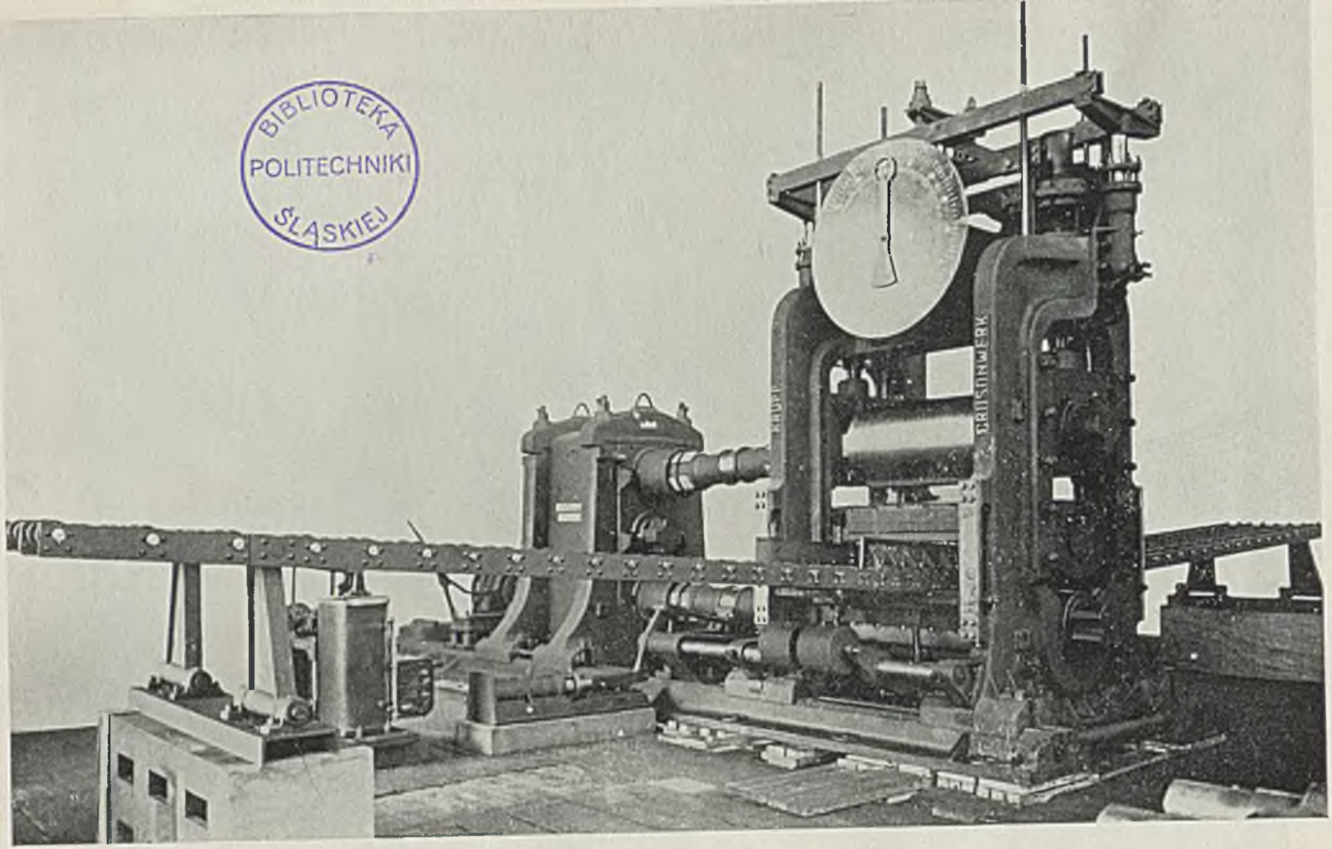

FIG. 14.—Three-High Sheet Rolling Mill of 1911. Top Roll Balanced and Centre Roll Lifted Hydraulically. Enclosed Pinions. Lifting Tables also Operated Hydraulically. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

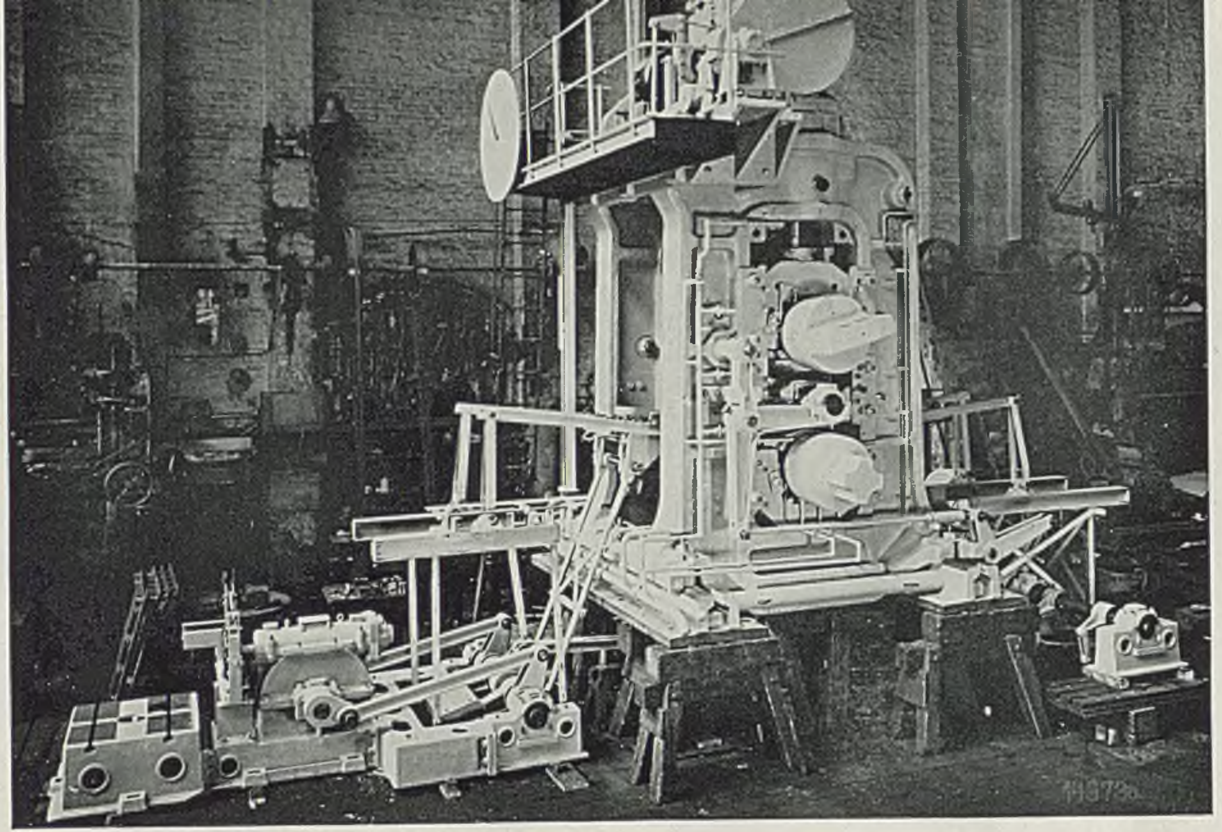

FIG. 15.—Three-High Hot-Rolling Mill with Electrically Operated Screw-Down Gear and Electrically-Driven and Controlled Tilting Tables. Note Operation of Top Roll by "Mesta" Joint Coupling System. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

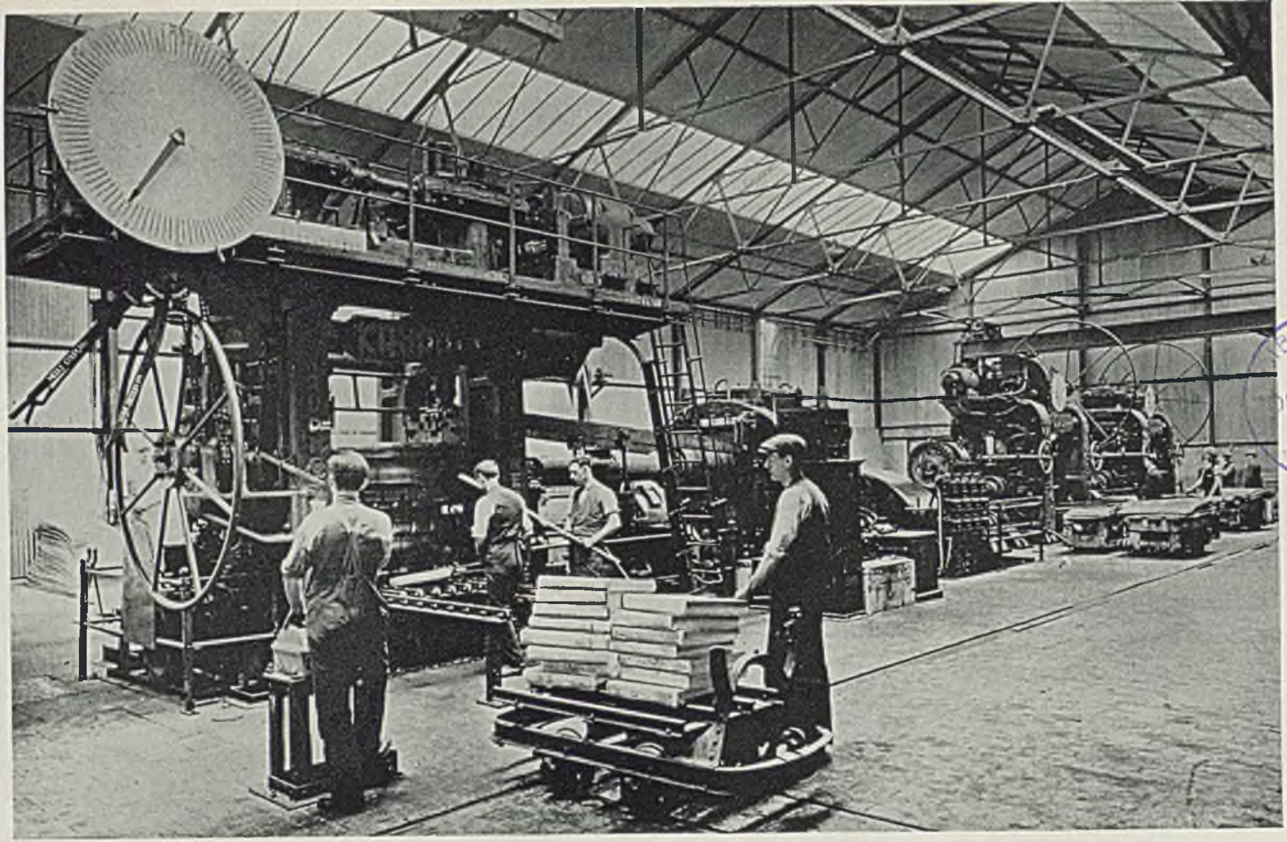

FIG. 16.—Sheet Rolling Mill for Aluminium—Comprising Three-High Breaking-Down and Intermediate Stands and Two-High Finishing Mill. Screw-Down Gear Operated both by Hand and Electrically. Precision Gearing. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

PLATE XVI.

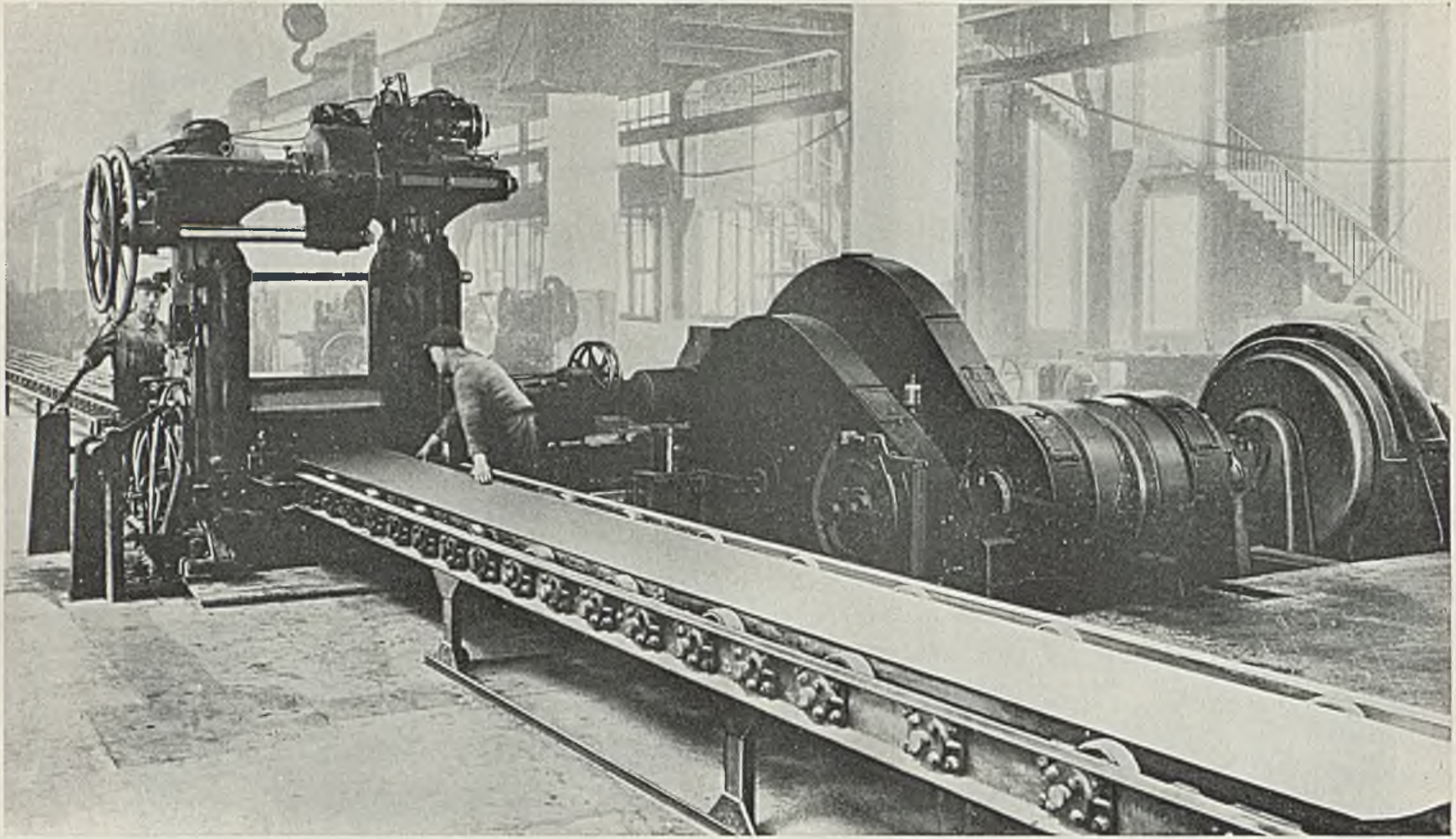

FIG. 17.—Reversing Mill for Heavy and Wide Strips. Note Totally-Enclosed Pinion and Reduction Gear. Adjustment of Roll by Hand and Electrically. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

PLATE XVII.

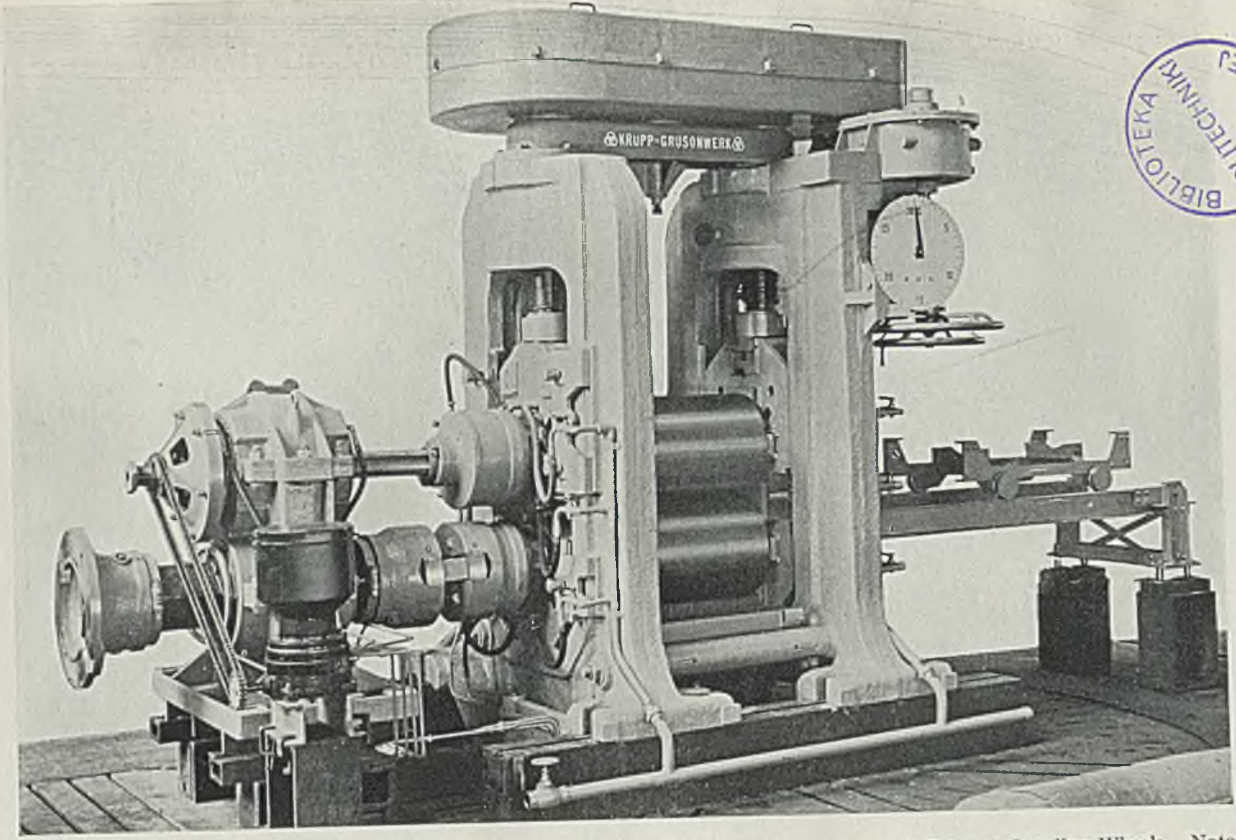

FIG. 18.—Two-High Breaking-Down Mill Illustrating a Modern Top Roll Drive by means of Friction Coupling Wheels. Note also Roll Dismantling Device (right) and Central Lubrication. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg,*

PLATE XVIII.

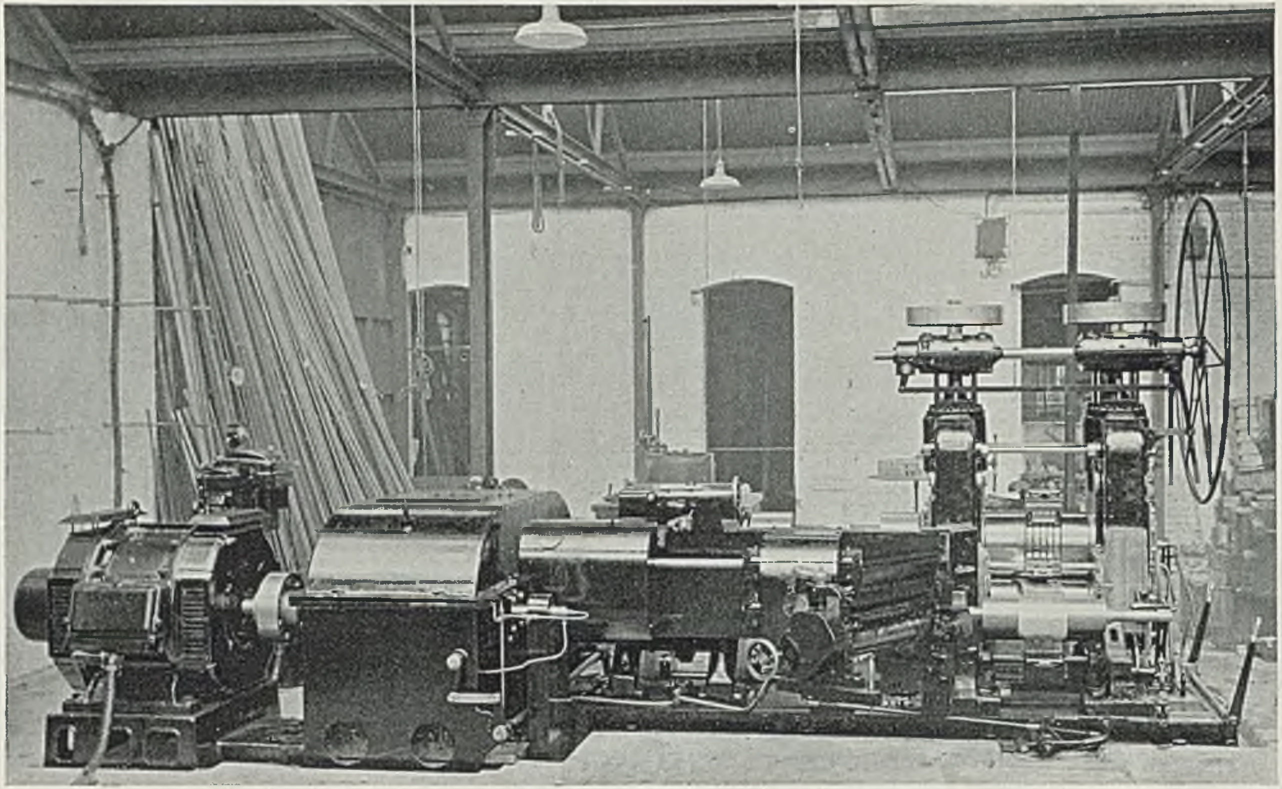

FIG. 19.—Modern Two-High Mill (British). Totally Enclosed Gearing, Flood Lubrication. (*By courtesy of W. H. A. Robertson & Co., Ltd., Bedford, England.*)

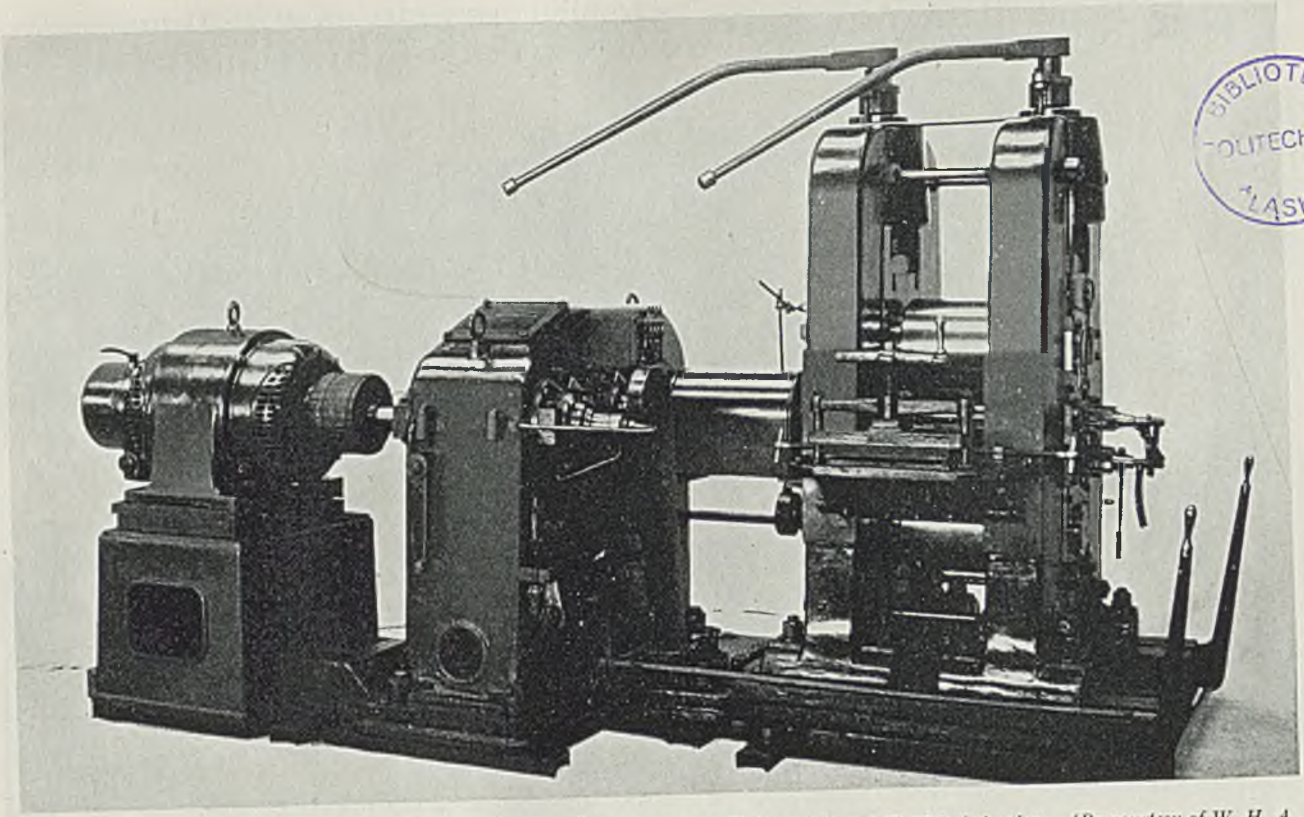

FIG. 20.—Modern Four-High Mill (British). Totally Enclosed Gearing and Pinions. Forced Feed Lubrication. (*By courtesy of W. H. A. Robertson & Co., Ltd., Bedford, England.*)

PLATE XX.

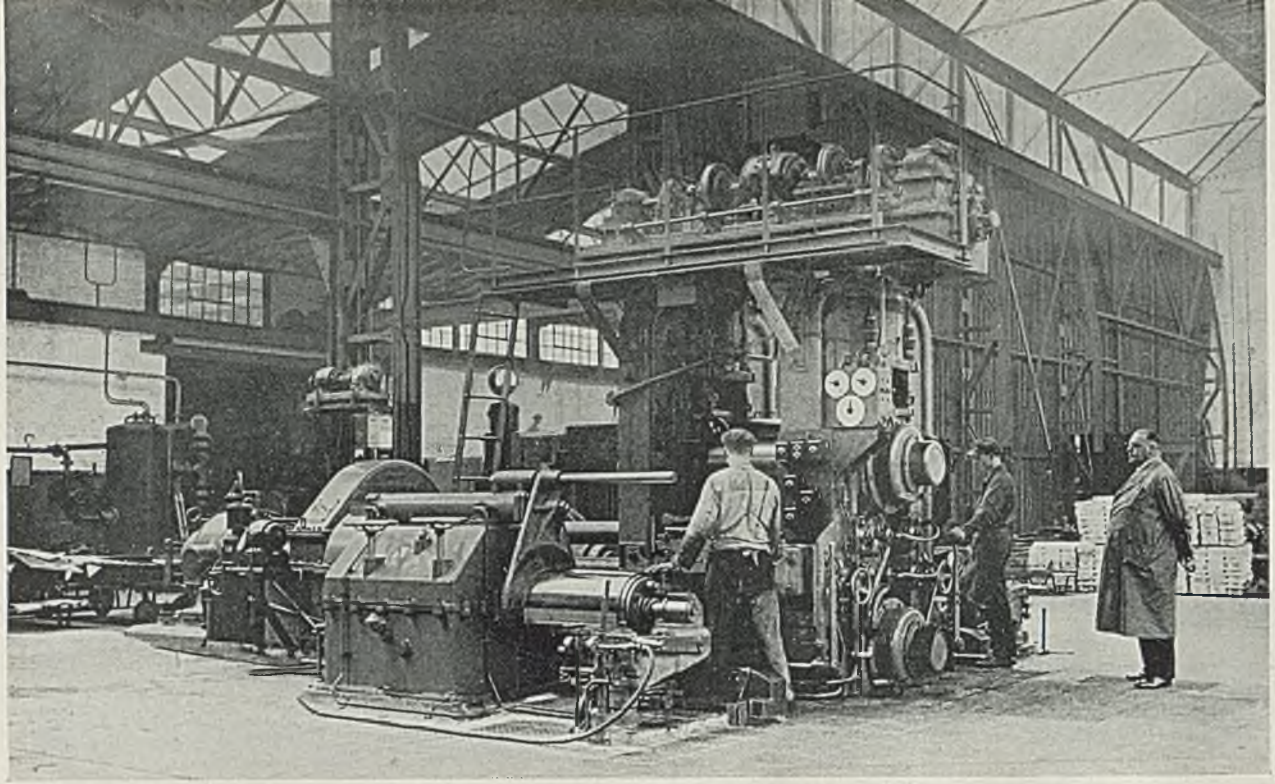

FIG. 21.—Four-High Mill (Reversible) for Strip up to 28 in. wide. Totally Enclosed Drive. Pneumatically Operated Band Brakes and Shearing Attachment. Electrically Operated Screw-Down Gear. The Pinion Housing Drives the Working Rolls by means of Coupling Spindles Running Quietly and Without Shocks. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

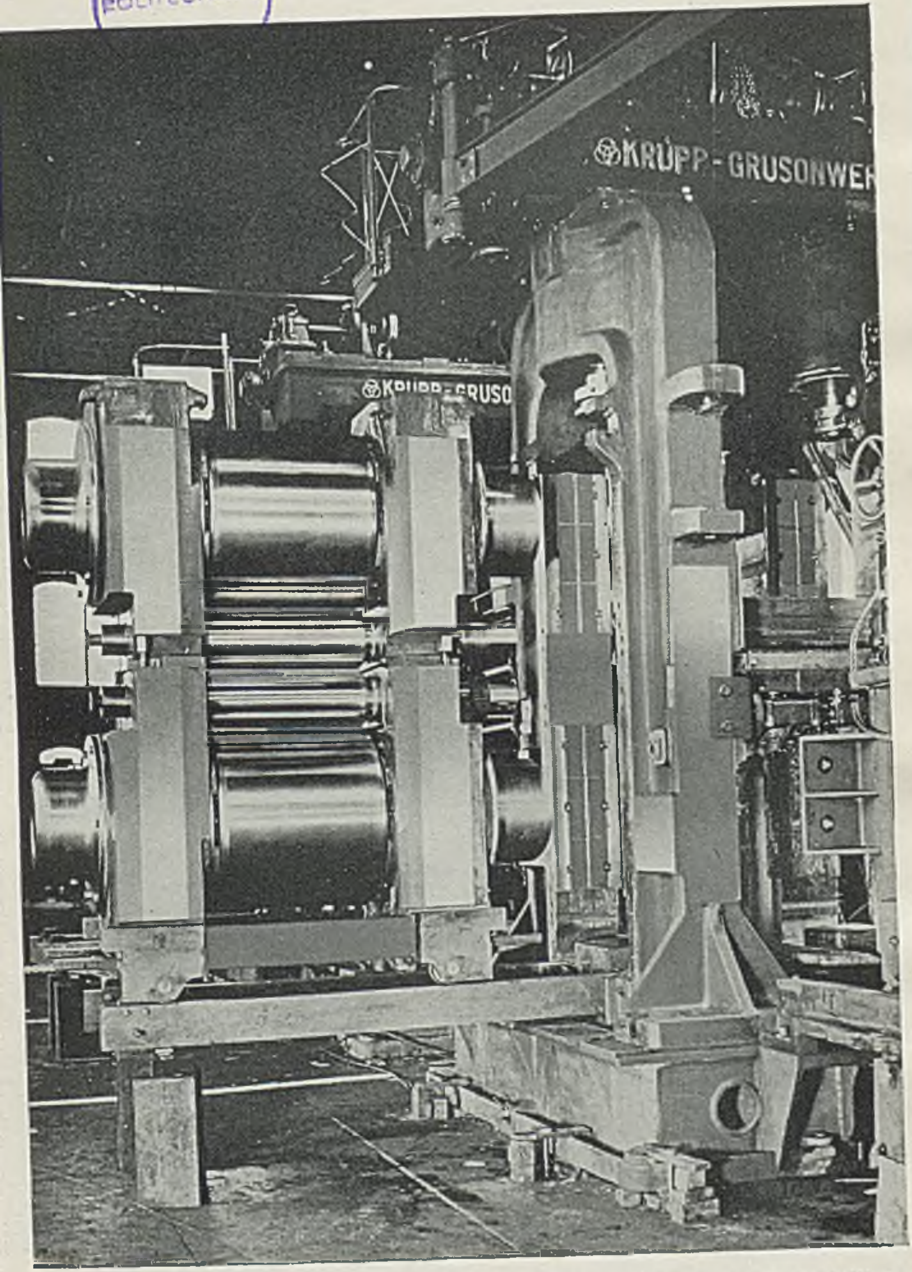

FIG. 22.—Section of Modern Four-High Mill Showing Roll Dismantling Device for Both Working and Backing-Up Rolls. *(By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.)*

PLATE XXII.

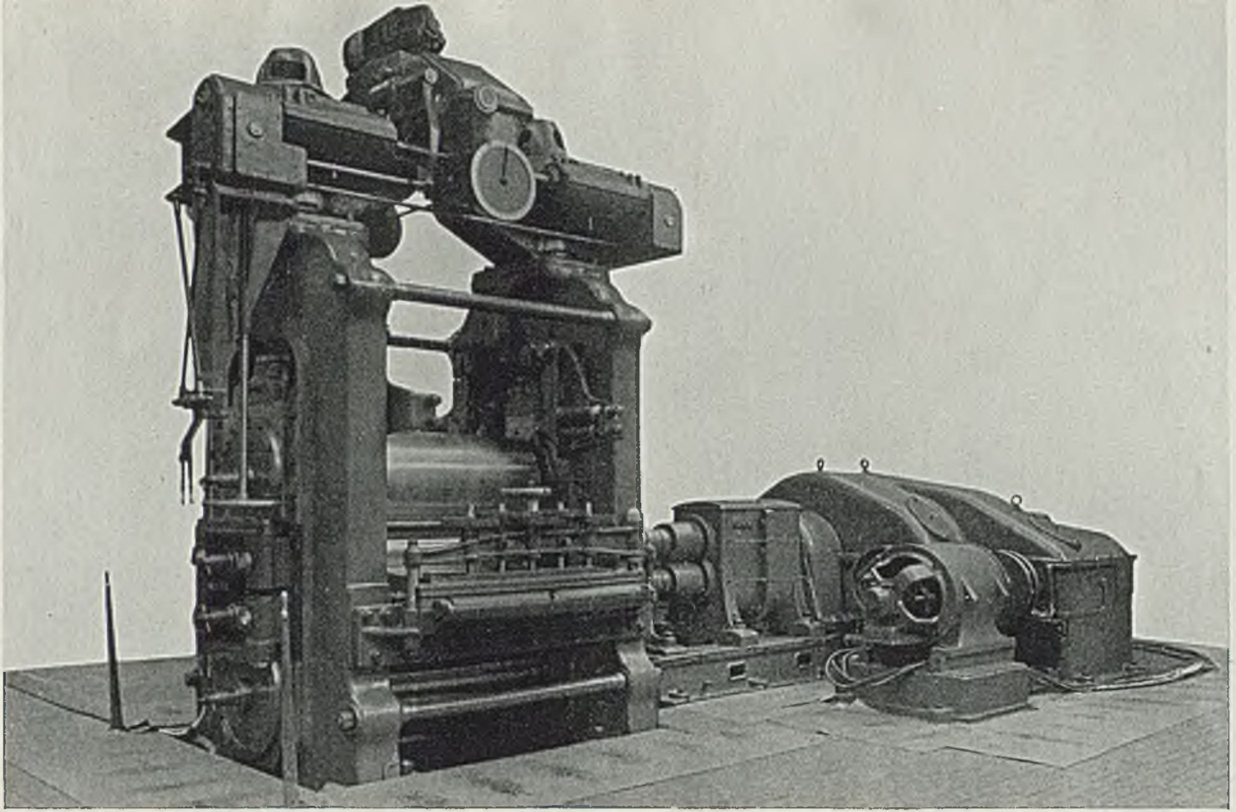

FIG. 23.—Modern Four-High Mill for Sheets up to 5 ft. in Width. Built by Schmitz, Düsseldorf, for the International Nickel Co., Inc., Huntington, U.S.A. Gearing, Pinions, and Screw-Down Gear Totally Enclosed. (*By courtesy of August Schmitz Walzmaschinenfabrik G.m.b.H., Düsseldorf, Germany.*)

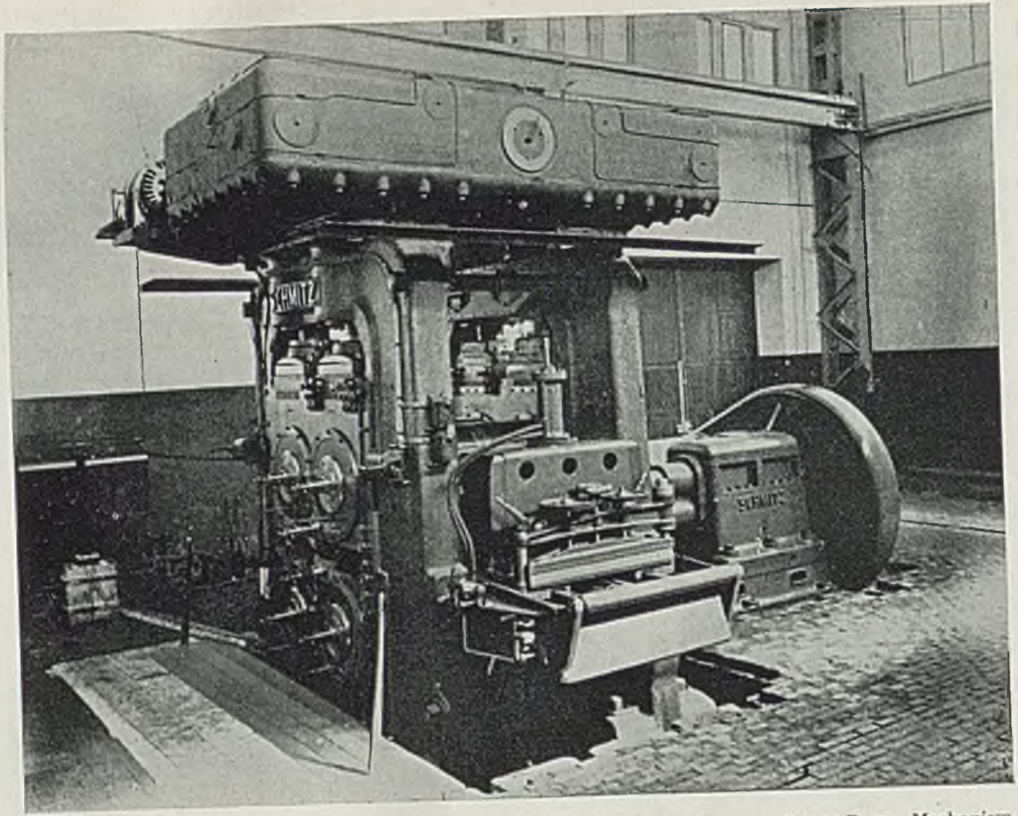

FIG. 24.—Modern "Cluster" Mill (Six-High). Totally Enclosed Gearing and Screw-Down Mechanism. Pneumatic Arrangement fitted for Feeding the Strip. (*By courtesy of August Schmitz Walzmaschinenfabrik G.m.b.H., Düsseldorf, Germany.*)

PLATE XXIV.

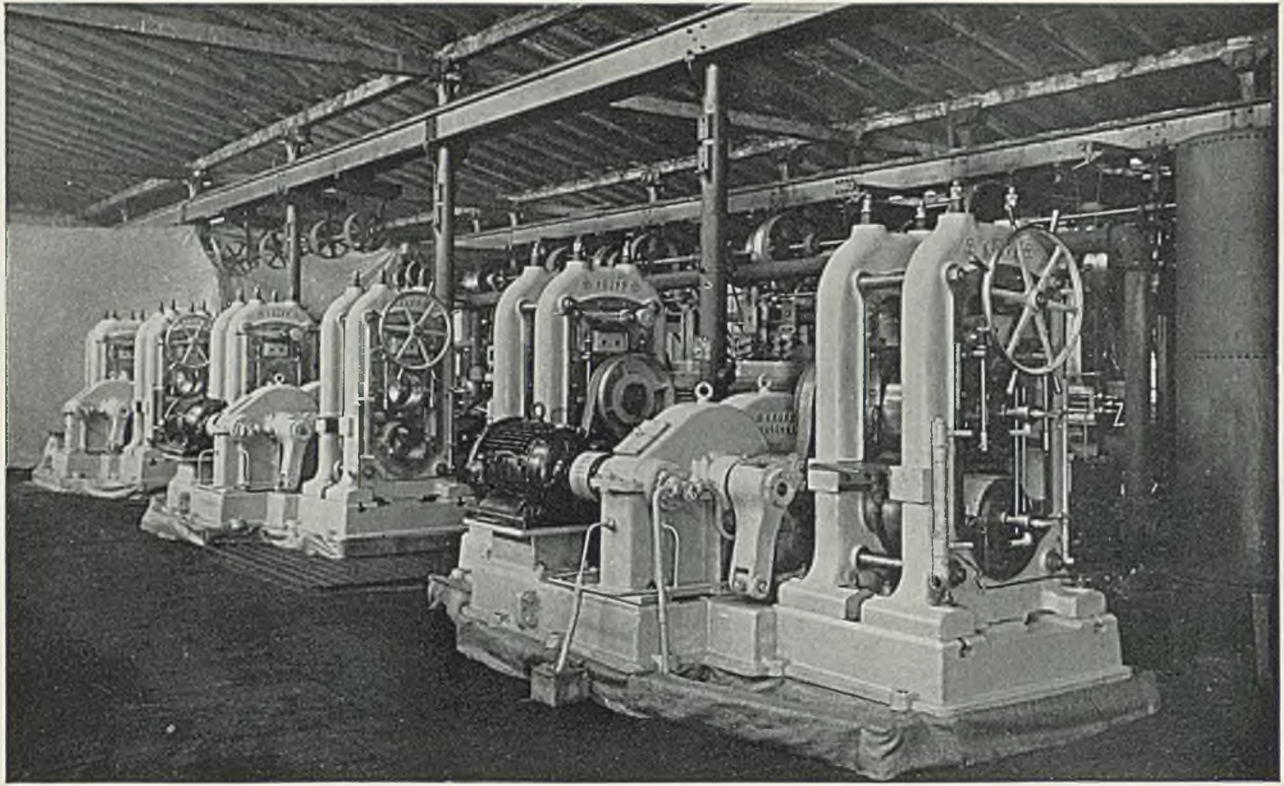

FIG. 25.—Group of Modern Equalising Mills designed to Roll Strip of Uniform Thickness to a Precision of 0·00008 in. Length of Roll Barrel 12 in × diam. of 20 in. Motor Driven by Precision Gearing—Top Roll by Belt from Bottom Roll. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

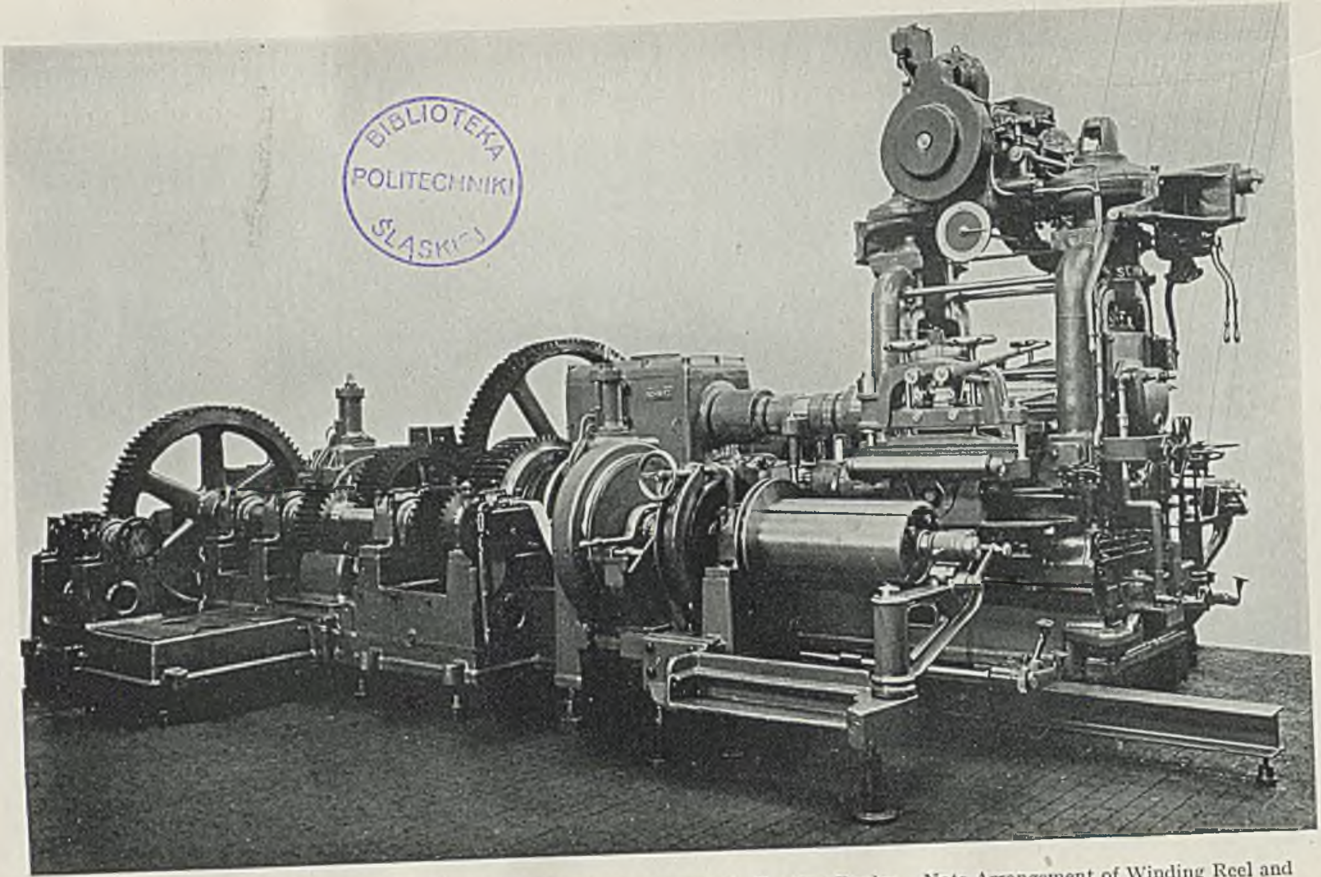

FIG. 26.—Modern Four-High Mill for Strip Rolling Fitted with Pneumatic Feeding Device. Note Arrangement of Winding Reel and Drive. (*By courtesy of August Schmitz Walzmaschinenfabrik G.m.b.H., Düsseldorf, Germany.*)

PLATE XXVI.

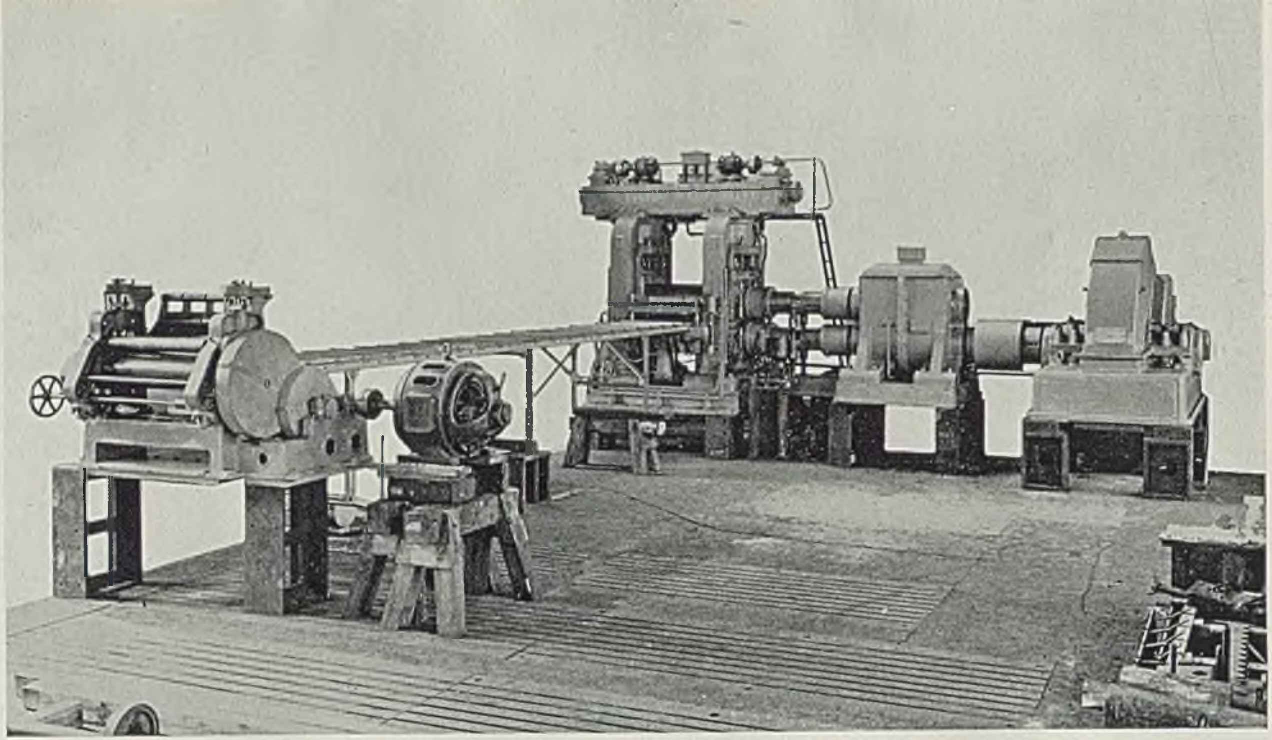

FIG. 27.—Modern Reversing Mill for Rolling Strip up to 40 in. wide. Pneumatic Band Brakes. Special Arrangement for Lubricating Bearings from Separate Grease Chambers. Water-Cooling Throughout. Screw-Down Gear Operated by Separate Motors but Connected so that Both can be Run Concurrently (note Coiler at End of Rolling Tables). (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

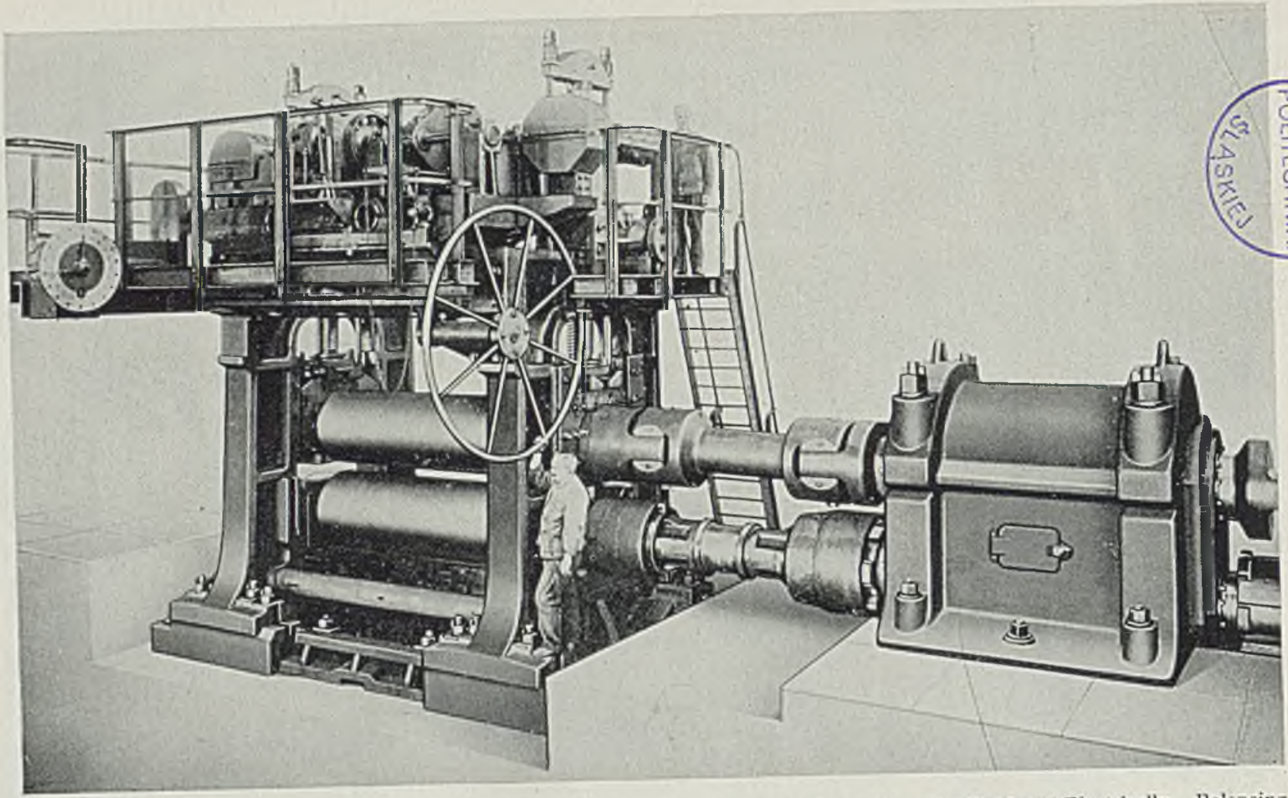

FIG. 28.—Large Two-High Reversing Mill. Rolls 9 ft. wide × 30 in. in diameter. Screw-Down by Hand and Electrically. Balancing of Top Roll Connected with Screw-Down Gear from Control Pulpit. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

PLATE XXVIII.

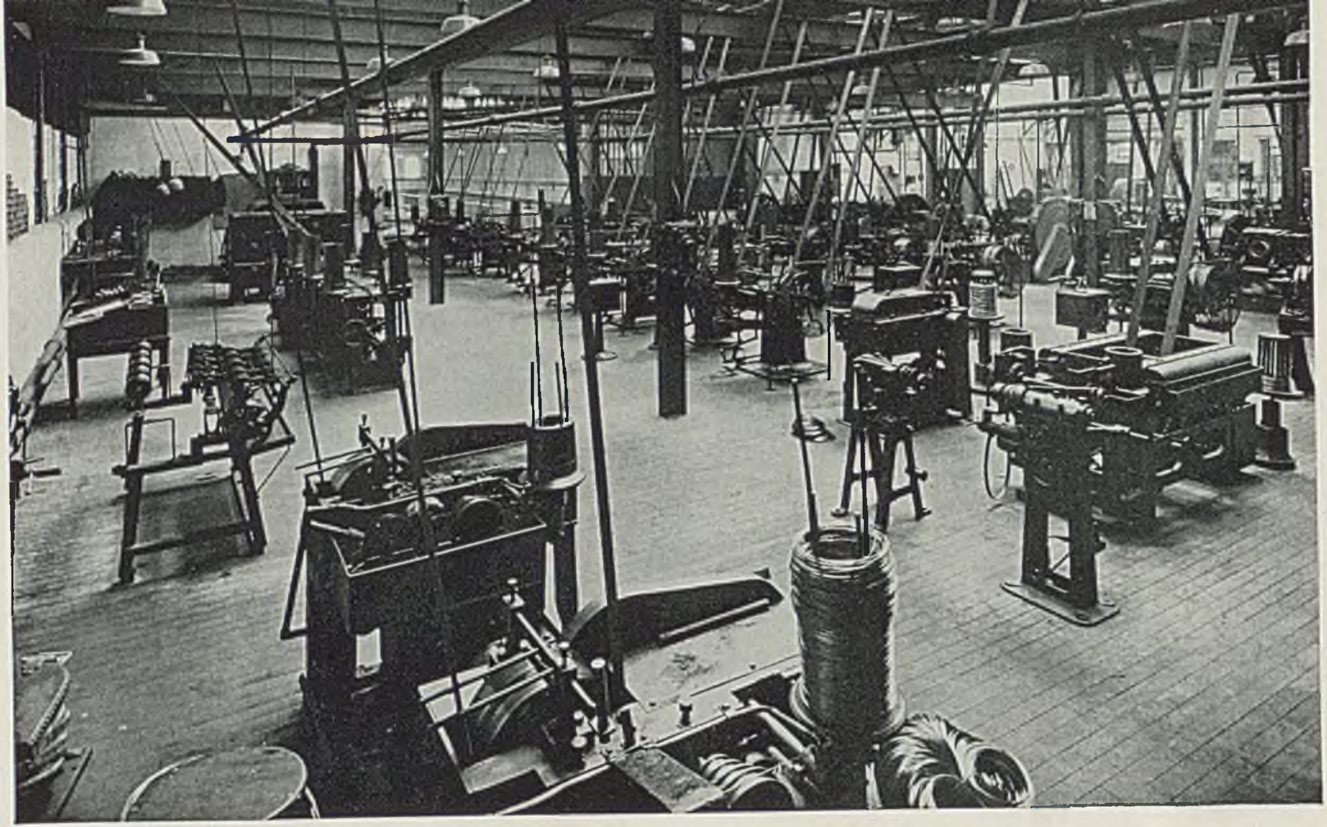

FIG. 29.—Modern Wire Mill Installation for Multiple Drawing through Diamond Dies. Note Automatic Spooling Equipment. (*By courtesy of Henry Wiggin & Co., Ltd., Birmingham, England.*)

PLATE XXIX.

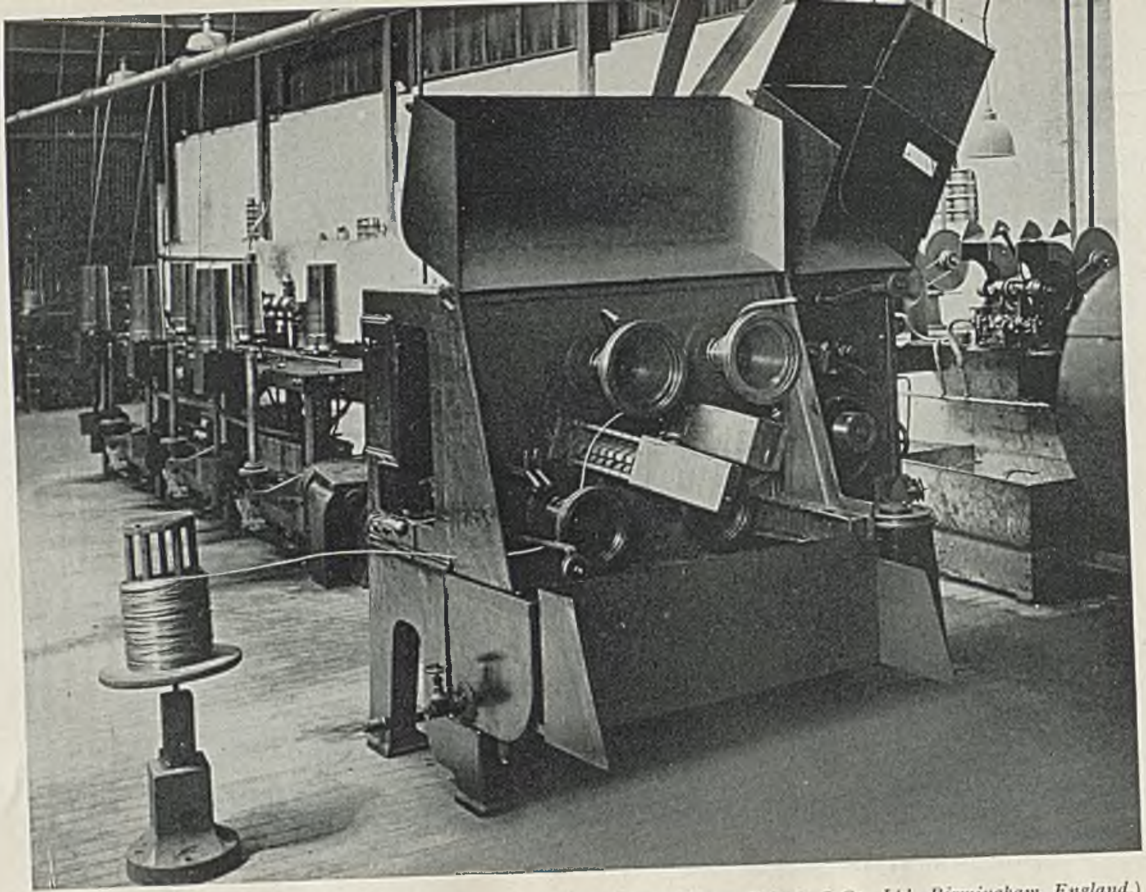

FIG. 30.—Multiple Wire-Drawing Machine by Breguet. (*By courtesy of Henry Wiggin & Co., Ltd., Birmingham, England.*)

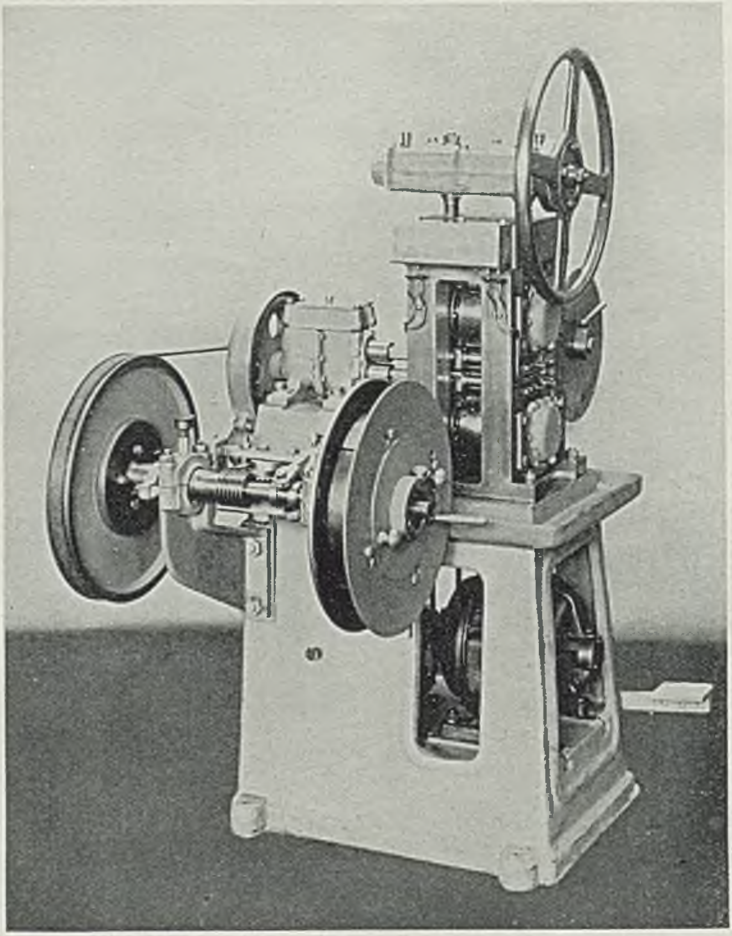

FIG. 31.—Modern Four-High Tape Mill for Rolling Tape or Ribbon from Round Wire. Working Rolls 1½ in. in diameter, Backing-Up Rolls 4¾ in. in diameter, Length 2⅜ in. Note Drive from Motor Arranged Inside Mill Supports. A Particularly Compact Design. (*By courtesy of Fried. Krupp Grusonwerk A.G., Magdeburg, Germany.*)

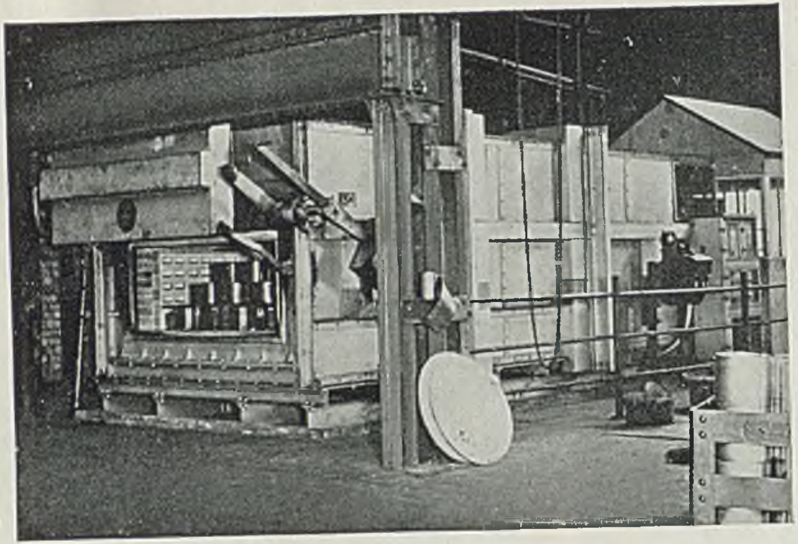

FIG. 32.—Electric Furnace for Batch Annealing of Brass Strip. Note Heating Arrangement Fitted to Door. (*By courtesy of Birmingham Electric Furnaces, Ltd., Birmingham, England.*)

PLATE XXXII.

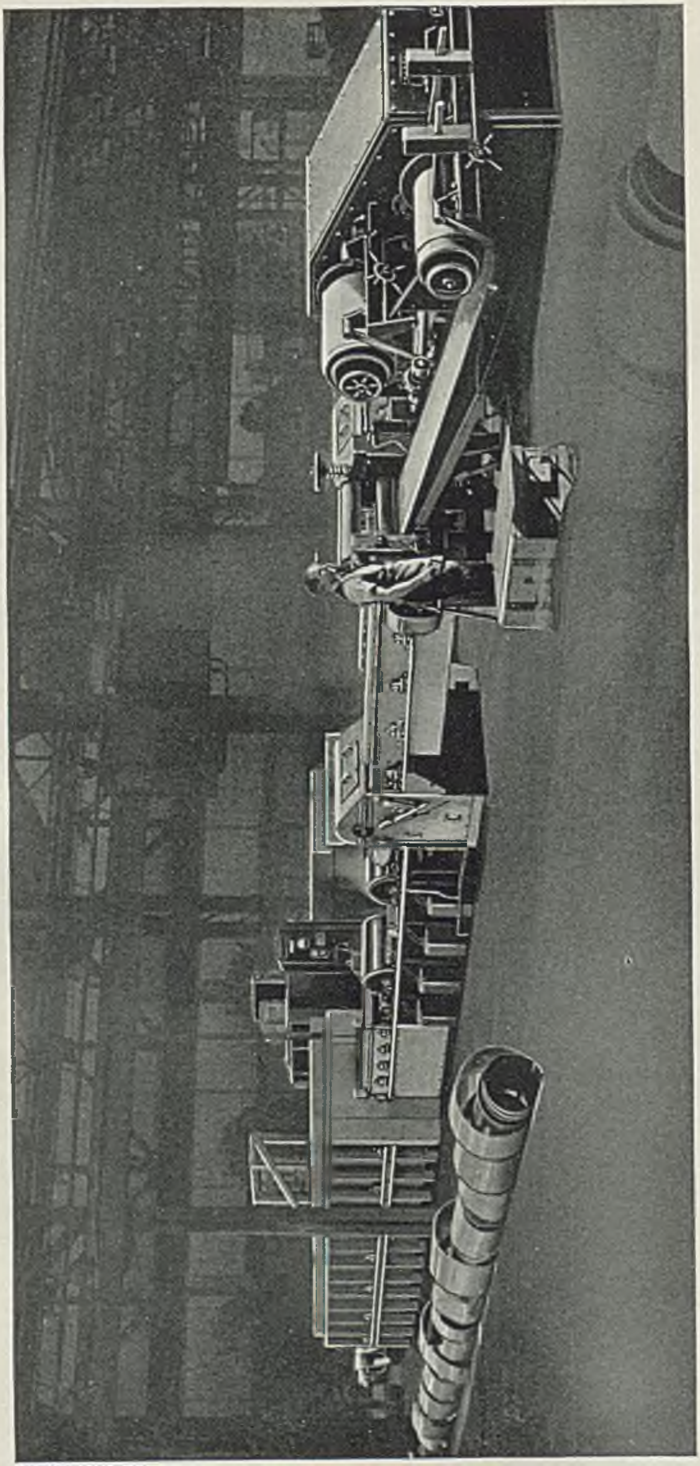

FIG. 33.—Electric Furnace for Continuous Annealing of Brass Strip Connected to Cleaning and Coiling Equipment. (*By courtesy of Birmingham Electric Furnaces, Ltd., and I.C.I. Metals, Ltd., Birmingham, England.*)

the operations of both rolling and drawing, and in both these sections improvements in the design of equipment have been effected. The modern rod- and wire-rolling mill, while not widely departing in fundamental principles from earlier designs, has been so greatly improved in detail of construction that it can be not unfairly compared with the improvement in the two-high rolling-mill. One of the latest installations illustrating this improvement in modern plant is the copper rod rolling-mill of the Phillips Electrical Works at Rockville, Ont., Canada. The designers and builders of this mill have taken full advantage of modern engineering improvements in running machinery, including roller bearings and modern helical pinion gearing. In building this mill, special attention has also been paid to the very important factor of lubrication, a feature which was conspicuously inferior in the older type of rolling-mill. The plant also embodies the use of vertical pinch rolls in the earlier stage of wire-bar rolling. A fairly complete description of this mill has been recently published.*

On the subject of wire and rod rolling, I must not omit to refer also to the very interesting work of Dr. W. J. P. Rohn of the Heraeus Vacuumschmelze A.G., Hanau a. M., Germany.† Dr. Rohn is an esteemed member of this Institute, and lectured some little time ago to our London Local Section on the subject. Every student of the development of metallurgical equipment should study the interesting and ingenious design of Dr. Rohn's mills.

The improvements effected in wire-drawing machinery are considerable and important. Exigencies of time and space prevent me from dealing with these at such length as I would like, and I must confine myself to generalities rather than to details. I am glad to be able to say, however, that British engineers have been active in this field, and some of the wire-drawing machines produced by British manufacturers compare very favourably indeed with those on the Continent; I am the more happy to say this here since it was scarcely possible to say it twenty-five years ago. (Fig. 29, Plate XXVIII.)

It is interesting to note that these improvements have not been primarily in connection with details of design but have arisen from what may be termed "the greater realization by engineers of what is required by metallurgists." The essential principle in wire-drawing is to obtain absolute uniformity of cold-work throughout the cross-section of the

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* R. C. Lewis, "Copper Rod Rolling Mill of Eugene F. Phillips' Electrical Works, Ltd.," *Wire and Wire Products*, 1933, 8, 5–8, 25.

† W. J. P. Rohn, "Anwendung kleinster Walzendurchmesser und Fortbildung von Mehrrollenwalzwerken" (Use of Small Diameter Rolls and Improvements in Multiple Rolling-Mills). *Stahl u. Eisen*, 1932, **52**, 821–825. W. J. P. Rohn, "Walzwerke mit dünnsten Arbeitswalzen," *Heraeus Vacuumschmelze, 1923–1933*, **1933**, pp. 381–387; and also W. J. P. Rohn, "Gleitlager an Walzwerken" (Gliding Bearings on Rolling Mills), *Z. Metallkunde*, 1931, **23**, 76–86.

wire being drawn. The requirements, therefore, are obviously that the wire shall enter the die at exactly the proper angle, in order to meet the bevel of the die with mathematical accuracy round the surface to be drawn. In the past, this point has not been by any means universally realized by designers and manufacturers of wire-drawing machinery, and there can be no doubt that improvements in this respect constitute the most important modifications of the modern machine.

On the other hand, detailed improvements such as that of effecting a large number of reductions in one continuous series of drafts has also led to no inconsiderable increase in efficiency and economy. One of the most typical examples of what may be called the multiple-die or continuous wire-drawing machine is that manufactured by Breguet in Switzerland (Fig. 30, Plate XXIX). In this class of machine, wire passes successively through as many as eighteen or twenty or more dies, and very considerable reductions are effected. I am omitting figures of gauge reductions obtained, since these vary in accordance with the particular alloy being worked and the speed of running. Reductions, for example, which can be effected in drawing copper or soft brass are not comparable with those needed for an 80 : 20 per cent. nickel–chromium alloy or alloys in that class.

Although not coming strictly under the head of wire-drawing machinery, I think that it is necessary to refer briefly to the development of dies during this period, and particularly to composition dies of the "tungsten-carbide" type. These have to some extent replaced both diamond dies and steel dies, and their use has certainly led to great improvements in the life of dies, better service, and more accurate gauge. The bugbear of the wire-drawer is, of course, the fault known as "pulling out," that is to say, the change in section effected in the hole of the die by irregular wear. The very much harder surface obtainable from these composition dies as compared with the older steel dies is a considerable factor in the progress made in this direction.

IV.—AUXILIARY EQUIPMENT, ANNEALING FURNACES, AND GENERAL.

In this final section of my review of development, I propose to deal briefly with a few auxiliary items of non-ferrous metal mill equipment, and also with the subject of annealing furnaces.

Improvements of importance, both in principle and detail, have been effected in appliances for the machining and preparation of ingots for rolling; in the shearing and flattening of sheets; and particularly in the bright finishing and polishing of sheet and strip metal. On the former subject special mention should be made of the introduction of the square turning lathe, by Waldrich of Siegen in Germany, which has been adapted for the machining of square ingots, and of the greatly improved milling machines by Herbert of Coventry and other English makers which are now available for this class of work.

Some improvements in detail have been made in design and construction of shearing, stretching, and roller flattening machines, but there is still much scope for progress in this class of equipment.

We have witnessed also during the last few years a remarkable advancement in polishing machines, which, while scarcely involving new principles, has yet led to appreciably wider applications of rolled sheet and strip metal. The surface finishing of metal has unquestionably been given much greater attention during the last few years than previously, and the product of "mirror finished" rolls on the one hand and modern grinding and polishing equipment on the other has brought into being an entirely new standard of finish of metal surfaces; indeed, the technique of surface finishing of rolled strip and sheet metal is to-day on a far higher level than it was even so recently as three to five years ago. The use of rolls with mirror finish is now very widespread, particularly on the Continent, and it is worth while to mention that experience in the use of these rolls has directed attention in greater degree than ever before to the subject of the surface quality of metals.

The obvious limitation of mirror-finished rolls in the production of sheet metal is that some amount of "work-hardening" is inevitable, and if dead-soft metals are required, the material must subsequently pass through an annealing process.

This point leads directly to the subject of annealing, for there is no doubt that the far higher standards demanded to-day in surface finish have stimulated serious and often anxious inquiries into the possibilities of improvement in the annealing process. It is of little use to attain a high standard of surface finish on metal products if such finish is to be immediately destroyed by the operations of annealing and pickling. It is perhaps too much to claim that the problem of bright-annealing of non-ferrous metals has been solved within the period of our present survey, but at least it may be said that it is well on the way to solution. Outstanding problems relate mainly to the working out of the most economical methods of technique.

A movement towards the construction of more efficient annealing furnaces had begun in the period between 1910 and 1915, and furnaces built on the semi-producer gas-fired principle came into use about that time in several newly constructed works and extensions. It was really this movement which started the evolution of the modern annealing furnace, since for almost the first time in the construction of annealing furnaces for non-ferrous metals a systematic study was made of methods for securing uniformity of temperature and efficiency in fuel consumption. That the ideal annealing furnace is not yet an accomplished fact does not in any way detract from the testimony due to the intensive efforts of furnace engineers during recent years.

One can scarcely withhold the term "revolutionary" from the contrasts between the coal- or coke-fired annealing furnaces to be seen in every non-ferrous metal works in the immediate pre-war period and the well-designed and constructed annealing furnaces of to-day, whether heated electrically or otherwise. I refer particularly at this point to the electric annealing furnace, since such furnaces were almost unknown and scarcely conceived of in ordinary works' practice when this Institute was founded, whereas to-day no new works can claim the description "modern" unless electric annealing furnaces form part of its equipment. I need not here enlarge on the advantages of these furnaces, their ease of control, uniformity of temperature and cleanliness, and general convenience of operation, but I may perhaps direct attention to two points, the importance of which is not always realized, namely, that (1) electric annealing furnaces can be much more readily fitted into the "flow of operations" of the modern works than can furnaces involving the use of solid, gaseous, or liquid fuels with their requirements of feed pipes, combustion chambers, flues, &c., consequently considerable "invisible" economics are effected; (2) by using electricity as a source of heat, the shape and general design of furnaces can be much more closely adapted to specific requirements. In other words, the furnace can be made exactly to "fit the job," and in laying out new works particularly it is often a distinct economy to instal a batch of several furnaces of different shapes and sizes dealing with specific types of product rather than to adopt the older and more conventional method of using one or two furnaces for all products. Figs. 32 and 33 (Plates XXXI and XXXII) show a type of furnace suitable for annealing strip in batches (Fig. 32) and a furnace for continuously annealing the same class of product (Fig. 33). These are popular types, but by no means represent all the numerous variations of design which during the last few years have been applied to the non-ferrous industry.

For the annealing of strip or wire or rod in coil form, furnaces of the cylindrical type have come into considerable favour. Such furnaces adapt themselves readily to the use of special atmospheres, and are as a rule economical in power consumption. In cases, however, where a very high degree of uniformity of temperature is required, and particularly where special gases are being used for reducing surface oxide, the continuous type of furnaces present distinct advantages. Bright-annealed wire, for example, is now almost exclusively produced from continuous furnaces.

While the development of electric annealing furnaces * is certainly the most remarkable and symbolic of our times, tribute must be paid to the work of gas and oil engineers in improving enormously the efficiency and reliability of annealing furnaces heated with these fuels. A similar remark applies to developments in the design of furnaces using powdered coal. In this field, as in others, competition has been healthy, and has certainly been of inestimable advantage to the non-ferrous industries at large.

There are yet many further developments of the last twenty-five years which deserve passing mention, but time does not permit. I cannot close, however, without referring briefly to the subject of the extrusion of metals. It can scarcely be claimed that the extrusion press itself has undergone any considerable transformation, at least so far as fundamental principles are concerned, but extrusion presses of recent design and construction are as a rule much more powerful and convenient of control than those of twenty or twenty-five years ago, and they are also equipped with auxiliaries which make for greater efficiency and economy in operating. The range of extruded products has consequently been greatly widened, although part of the credit for this should be given to improvements in the quality of die steels and tools used as well as to the process itself.

A point that I wish to emphasize particularly, however, is that the non-ferrous engineer and metallurgist has during recent years entered into a much fuller appreciation of the value and potentialities of the extrusion process, not only as a method of direct production, but also as a hot-working process of definite metallurgical value.

Extrusion has during recent years become more than a means for producing a special type of product. It has begun to occupy an important place in the "flow of operations" of mills producing metals in forms other than extruded sections themselves. A case in point which will occur to you at once is the important part played by extrusion in the production of special alloy tubes. Wider possibilities are also opening out, and I have seen extrusion presses in some degree taking the place of hot-rolling mills in the production of strip metal by the attractive method of extruding, *e.g.* a rectangular brass section of say 3·5 in. or 4 in. wide, 0·25 in. thick, and afterwards cold-rolling it to bright finished strip. The relative accuracy of gauge and width obtainable in such an extruded product renders it a very attractive proposition for the modern high-speed precision mill. One is tempted

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* For description of some modern installations see H. C. Kloninger, G. Keller, and H. Meuche, *J. Inst. Metals*, 1931, 46, 537–559; and also A. G. Lobley, "Electric Resistance Furnaces in Great Britain," advance proof, Sectional Meeting of World Power Conference, Scandinavia, 1933.

to visualize in the not too distant future important extensions of the application of this idea.

I have in the course of a lecture of an hour or so tried to review twenty-five years' progress; an immense task, yet well worth attempting, for I am sure that however superficial this survey may be it must inspire some measure of admiration for the work of the generation now rapidly passing. I beg you for a moment to look behind the bare record of plant and process improvements, and endeavour to realize something of the human qualities which have been the prime movers in this story of progress. The restless search after knowledge, the courageous attempts to do what had never been done before, the "dreaming of dreams" and the "seeing of visions," and the grim resolve to make the dreams come true and the visions attain reality. Such are the raw material out of which the achievements here outlined have been built up. The workers of these years have had many disappointments, made many mistakes, and often failed when they hoped most to succeed, but on the whole their story is a very impressive one. We have travelled a long way in these industries since 1908, and as I have attempted to re-visualize the period and to recall the years between, I have become the more convinced an admirer of my contemporaries.

The metallurgist-historian of the future will assign a notable place to these twenty-five years.

ACKNOWLEDGMENTS.

Acknowledgments of the loan of illustrations are made in the text, and I much appreciate the readiness and courtesy with which my requests for these have been responded to.

I wish, however, here especially to record my gratitude to the Directors of the Fried. Krupp Grusonwerk A.-G., Magdeburg, Germany, and in particular to the Director of their Rolling-Mill Department, Dipl.-Ing. E. Kugel, for the time and trouble expended in searching records and securing photographs illustrating various stages in rolling-mill design for both hot and cold operations.

My thanks are due also to Dr. Peter Schmitz of August Schmitz Walzmaschinenfabrik G.m.b.H., Düsseldorf, Germany, who himself has contributed in no small measure to progress in rolling-mill construction, for his collaboration and loan of illustrations.

I must also thank Messrs. Campbell and Gifford and Mr. A. G. Lobley for the loan of some excellent lantern slides.

SOME STEPS IN METALLURGICAL PROGRESS, 1908–1933 * †

By WALTER ROSENHAIN,‡ B.A., D.Sc., F.R.S.,
FELLOW and PAST-PRESIDENT.

SYNOPSIS.

The paper is a brief review of some of the more important steps in metallurgical progress during the twenty-five years of the existence of the Institute of Metals. The matters touched upon are those which have been of particular interest to the author and have been in some degree associated with the Institute of Metals. They include the following: Age-hardening and the development of new alloys capable of improvement by heat-treatment; "Y"-alloy and other casting alloys capable of benefiting by heat-treatment; the "modification" of alloys; aluminium-bronzes and brasses, the Durville and other special methods of casting ingots or billets; metals of very high purity; alloys for cutting tools—Stellite and sintered tungsten carbide; removal of gases from molten metals and alloys; the mechanical behaviour of metals—slip, fatigue, plastic deformation; the study of metals by X-rays and by electron diffraction; recent vindication of Beilby's hypothesis of "amorphous" metal; corrosion and the differential aeration theory; the protective surface film and its isolation; corrosion-fatigue.

THE occurrence of an anniversary naturally leads to retrospection, so that some attempt at a review of metallurgical progress during the twenty-five years which have elapsed since the first meeting of the Institute of Metals in Birmingham appears appropriate.† The preparation of such a review, however, if any attempt were made at completeness, would be an extremely formidable task, which the writer is unable to contemplate. He proposes, therefore, to confine attention to some of the steps which have formed part of the metallurgical history of the past quarter-century. Different individuals, in looking back upon the same history, would perhaps choose different aspects and different steps; no claim is made that those here selected are either the most important or the most interesting, but they are those which, for one reason or another, appeal most directly to the writer.

While it would be too much to claim that the Institute of Metals is responsible for most of the progress which has been achieved, yet a certain claim is justified on the ground that the Institute, from its formation, provided for the first time the means of adequate publication

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† This paper has been prepared at the request of the Council, and was not thrown open to discussion.—*Ed.*

‡ London.

and discussion not only for the results of research, but also for progress in practical developments in the non-ferrous industries. In this respect the Institute undertook a pioneering task, and although in various countries organizations have subsequently been developed for providing facilities of a similar nature for their own metallurgists and engineers, the Institute of Metals has, fortunately, been able to maintain its place not only in this country, but throughout the world. The sphere of the Institute of Metals has been intentionally confined on the one hand to the metallurgy of the non-ferrous metals, to the exclusion of steel, and on the other hand has excluded the whole field of the production of metals from their ores—in both cases with the deliberate purpose of avoiding overlapping with previously existing Institutions, yet there can be no doubt that, in regard to the scientific aspect of metallurgy, the Institute has provided a centre for publication and discussion which has stimulated research throughout the whole field of metallurgy and far beyond the immediate scope of the Institute itself. It may fairly be claimed that nowhere else do the scientific aspects of the subject receive an equal amount of attention. In thus emphasizing the value of the work of the Institute of Metals on the scientific side, the writer does not wish in the slightest degree to under-rate the great importance of the practical questions which the manufacturing and engineering members of the Institute bring forward; on the contrary, it is the function of the Institute as the meeting-ground of all three types of members that lends it a special character and greatly increased importance. If the scientific members of the Institute have played a very active part in its work, that should not be taken as discouragement by the manufacturers and users; on the contrary, it is for them to rival their scientific colleagues in their activities. A greater number of papers and contributions to discussions on the part of engineers and manufacturers would be welcomed by none more than the scientific members of the Institute.

It is not perhaps unnatural for the writer, in commencing the present review, to refer to the first paper which he had the honour to communicate to the Institute of Metals at its initial meeting in Birmingham in 1908.[1] In that paper he criticized the methods of studying the equilibrium diagrams of alloys as then carried out, for exploratory purposes, by Professor Tammann and his pupils. The need for a more exhaustive study of alloy systems and for more accurate determinations of equilibrium diagrams has since been almost universally recognized, and indeed the measure of accuracy and completeness which the writer advocated in 1908 has now been considerably exceeded.

With regard to Professor Tammann, the writer had the privilege, as

President of the Institute, of informing that eminent metallurgist of his election as Honorary Member of our Institute, and subsequently of welcoming him personally to the meeting in Düsseldorf in 1929. The events of many years ago have not detracted from the mutual respect and friendship which have sprung from that personal contact.

The subject of that early paper, however, has proved to be of fundamental importance in the progress of non-ferrous metallurgy, and not only on the purely scientific side. It was pointed out there that the very approximate equilibrium diagrams with which certain investigators were contenting themselves at that time were inadequate, and that much closer and more accurate study was required by means of methods of greater refinement. Some of these methods the writer was privileged to develop, with the aid of his colleagues in the Metallurgy Department at the National Physical Laboratory.[2, 3] At the same time, other methods of high accuracy have been developed elsewhere in this country and abroad. As a result, at the present day the technique of determining equilibrium diagrams has attained a degree of accuracy which could scarcely be contemplated in 1908. In that development the use of the methods of X-ray analysis, to which further reference will be made, has played a very important part. The value of equilibrium diagrams, however, was for a long time regarded with a good deal of scepticism by those who were not intimately acquainted with their possibilities. In his presidential address to the Institute in 1928, the writer endeavoured to explain on broad lines, and in the simplest possible way, the meaning and value of equilibrium diagrams and their importance for practical purposes. It is, therefore, unnecessary to go into this subject again, and only one particular aspect need be mentioned, because of the immense practical importance to which it has risen.

One of the points in regard to which the earlier "equilibrium" diagrams were particularly deficient—and this deficiency is still to be encountered in some published work—was the determination of limits of solid solubility at the boundaries of different phases, and especially of the limits of solid solubility of other metals and metalloids in the pure or nearly pure metals themselves. At first this appears to be a matter of academic interest only, but the invention of Duralumin presented the metallurgical world with a new problem, since the inventor of age-hardening (Wilm) admittedly had no idea of its mechanism or nature. It might have been thought that a knowledge of the processes by which age-hardening occurs in Duralumin was a matter of minor importance in view of the fact that for practical purposes Wilm had discovered an alloy which has maintained its place in the front rank of heat-treated aluminium alloys to the present day; fortunately, however, the scientific investigator cannot help regarding a mysterious process of this sort as a challenge. This challenge was taken up by two groups of investigators —namely, those at the Bureau of Standards in America, under the immediate leadership of Dr. P. D. Merica,[4] and at the National Physical Laboratory here.[5, 6, 7] Both groups of investigators arrived at what is now universally admitted to be the true solution of the problem. Their solutions differed in detail, and there are still differences of opinion about certain aspects of what occurs, but a broad generalization was reached. Wherever the curve of solid solubility in an equilibrium diagram is of such a shape that the solid solubility is appreciably higher at a high temperature than it is at lower temperatures, it is possible by quenching after heating at the higher temperatures to produce a supersaturated solid solution. Such a solution may subsequently undergo decomposition either at room temperature or at somewhat higher temperatures. The result of this decomposition is what is now widely known as "age-hardening," although the term, as Professor A. Portevin[8] has recently pointed out, is unsatisfactory. The statement made ascribing hardening in such cases to the decomposition of the supersaturated solid solution will scarcely be disputed by any scientific metallurgist. The exact process which occurs in this decomposition, however, is much more difficult to establish. The so-called "precipitation" theory, according to which the hardening is due to the separation of a very large number of extremely minute particles or groups of atoms in the early stages of precipitation of a dissolved substance, is widely but not universally accepted, whilst there is also a divergence of view whether these separated particles produce hardening by distortion of the lattice in which they are interposed (the writer's theory) or by acting as "keys" which prevent mutual slip of layers of the crystals (Jeffries' slip interference theory).[9] These points, and many of the scientific difficulties still connected with them, have received an immense amount of investigation, and constitute problems which still stimulate further research and, consequently, further discoveries. Meanwhile, however, a recognition of the fact that alloy systems in which certain kinds of solubility lines have been found are capable of age-hardening has proved of the greatest practical interest. It must be remembered that prior to the discovery of Duralumin by Wilm, steel was the only known material which could be hardened by heat-treatment. Since the principle of age-hardening was elucidated, an ever-increasing number of alloys has been discovered and developed which are capable of improvement by heat-treatment, in many cases to a most remarkable extent. Apart from alloys of aluminium itself, perhaps the most interesting example is that of the alloy of copper and a small percentage of beryllium, in which a degree of hardness can be obtained approaching that of hardened steel. Even among the alloys of iron itself, similar facts have been discovered, as, for example, in the alloys of iron with molybdenum and with tungsten which are capable of age-hardening, and the ageing effects which can be produced by nitrogen, and probably by oxygen and carbon, in mild steel at quite moderate temperatures. The range of such alloys is steadily widening at the present time, and is placing at the disposal of the manufacturer and of the user a whole series of products of a novel and valuable nature. These can be placed definitely to the credit of scientific investigators, and in particular to the more accurate study of the equilibrium diagrams such as had been advocated by the writer in his paper of 1908.[1] In this direction the Institute of Metals has perhaps been more helpful than in any other, since it has furnished scope and encouragement for the writers of papers on what might otherwise have been regarded as abstruse and academic subjects.

Although it is not possible to enter into details of the modern development of aluminium alloys, there are one or two features which it is perhaps desirable to mention. For some time after the discovery of Duralumin it was believed that the improvement of properties by quenching and ageing could be obtained only with alloys which had undergone mechanical working, such as forging or rolling, and the application of heat-treatment to castings was not considered feasible. An understanding of the principles involved in the heat-treatment of light alloys, however, immediately led the writer and his colleagues to the conclusion that such treatment should be applicable to castings. It seemed probable, however, that the time required for preliminary heating to secure complete solution of the second phase or constituent would be much longer for the cast material. Experiments quickly led to a verification of this view, and the result has been the development of a series of casting alloys capable of being very materially improved by heat-treatment. About the same time, it was realized that the best available alloys of aluminium lost their strength rapidly with increasing temperature, and a search was made, under the urgent stimulus of war conditions, for light alloys which would maintain their strength as far as possible at high temperatures, such as 250°–350° C., which are encountered in aeroplane and motor-car engines.

One result was the development of an alloy, since widely known and used especially for piston purposes, containing copper 4, nickel 2, and magnesium 1·5 per cent., which has come to be known, through accidental lettering used in the laboratory, as "Y" alloy. Although the full application of this alloy for practical purposes suffered a lag of something like ten years from the time when it was first described, it maintained its position for some time, and is still among the best of the aluminium alloys for its particular purpose, *i.e.* for use at high temperatures, whether as castings or forgings.

More recently, alloys have been produced which, while largely based in constitution and mode of treatment on "Y" alloy, are capable of attaining still better properties, a result which they owe in part to the incorporation of a small amount of titanium. These, although similar in type to "Y" alloy, offer certain marked advantages, and it is to be hoped that still other developments and improvements will follow. The resistance offered by industry to the introduction of new alloys is fortunately much less to-day than it was ten or fifteen years ago, and the threatened competition of magnesium and its alloys will probably serve as a further stimulus to those interested in the alloys of aluminium.

Mention has already been made of the use of X-ray methods in the study of alloy systems, but this application of modern physics is proving so valuable that more than passing reference is required even in the present review. While the proper use of the microscope can and does carry our knowledge far into the minute structure of alloys, there are definite limits, due to the wave-length of light itself, which make it impossible to carry magnification beyond a definite degree. Even if this is placed at so high a value as 10,000 diameters, whilst the orthodox view places it nearer 2,000, it yet leaves us very far from the possibility of studying the arrangement of the atoms in the crystals of our metals. Fortunately, however, the use of X-rays, which may be described as a variety of light having a wave-length about a thousand times shorter than that of yellow light, makes it possible to observe phenomena known as the diffraction of X-rays in crystals which give the key to the arrangement of the atoms themselves. Thanks to the work of a series of brilliant investigators, among whom Bragg, Laue, Mark, Polanyi, Schmid, Bernal, Bradley, Westgren, van Arkel, and others may be mentioned, not only the experimental technique, but also the methods of interpreting results have been developed to an amazing extent. It is now possible, not only to determine with remarkable accuracy the dimensions of the crystal lattice of any given sample, but also to correlate these with the concentrations of solid solutions and with the formation of intermetallic compounds. The result is that many of the phase boundaries of alloy systems can now be determined with great accuracy by these means. They enable us to go further, however, by showing the arrangement of the individual atoms in the lattice. Some of the lattice structures which have been described, such as those of the so-called gamma type of alloy phases, appear to be formidably complicated and difficult to understand. The writer [10] has put forward the view that some of these structures can best be explained by supposing that a certain type of intermetallic molecule is formed which cannot be readily packed together so as to fill space in a satisfactory manner. Since the leaving of gaps in such a structure would entail the storage of a large amount of energy, it is suggested that these gaps are filled by atoms of either component metal (whichever happens to be present in excess), these additional or "filling" atoms behaving much like the water of crystallization in a crystal of copper sulphate or similar substance. Some objections have been raised to this view, but the writer thinks that these are not insuperable, and would commend it to the consideration of those who study these apparently complex bodies.

The advance of our insight into the structure of alloys is of value, however, not only because of the more accurate determination of equilibrium diagrams, but also because it is providing the material for a much better understanding of the nature of the metallic state and of the laws which govern the formation of intermetallic phases and the constitution of alloys in general. It is not perhaps too much to hope that in the near future the general laws governing alloy constitution and behaviour will be discovered, and will bring order and understanding into the rather varied and troublesome collection of equilibrium diagrams with which the metallurgists have to deal at the present time. When this result is achieved, the practical consequences are likely to be important, and manufacturers and users will have occasion once again to thank not only the scientific investigator for his patient pursuit of abstruse and difficult subjects, but also the Institute of Metals for the encouragement and support which it consistently gives to such work.

Whilst the application of age-hardening to a wide variety of alloys has been responsible for some of the most important advances in non-ferrous materials, interesting developments have taken place in other directions independent of the age-hardening processes. It is interesting to note in this connection that whilst age-hardening was discovered in connection with the aluminium alloys and has hitherto been more widely exploited in that field than elsewhere, a whole group of new materials, consisting mainly of aluminium, has been developed, which owe their value mainly to an entirely different treatment. These are the so-called "modified" alloys, of which the well-known materials containing from 10 to 14 per cent. of silicon are typical. These and their properties are so well known that it need only be pointed out that here also we have an empirical discovery which has led to very important results, but that, even to-day, after much investigation, it cannot be definitely stated that the mechanism of the process is fully understood. A number of papers have appeared in the *Journal of the Institute of*

Metals dealing with the "modification" of alloys; the work of Gayler showed the close connection between "modification" and super-cooling.[11] She was able to show the relation between the microstructure and freezing temperatures of the modified alloys and the limiting temperatures of the "labile" super-cooled state. Whilst this has furnished some degree of insight into the mechanism of modification, it seems that our knowledge is still insufficient to allow us to enunciate a general principle which would make the extension of the process to other materials a fruitful line of progress. Gwyer and Phillips [12] have shown that modification phenomena can be produced in other types of alloys, but even this indication has as yet failed to produce any alloys other than those of aluminium which are improved to a marked degree by similar means. It may well be that when the mechanism of the process comes to be as well understood as that of age-hardening, a similar fruitful development may occur. Possibly there may be an intimate connection between "modification" and the factors which govern the grain-size of an alloy.

During the period of twenty-five years under review there have naturally been many other developments of new alloys, some of which have proved of permanent importance, whilst others, for which great claims were made, have failed to find or hold a place in industry. Among those which have succeeded, in varying degrees, in attaining large-scale importance, a number of alloys of nickel must be mentioned. Some of these are proprietary and well known. The alloys of copper and nickel, generally known as cupro-nickel, were extensively studied during the War, and have since received increasing application, especially for condenser tubes, where a high degree of resistance to corrosion is more important than low price. In the same connection, the alloys of copper with aluminium, the aluminium content varying from 2 to 10 per cent., have also proved important. The "aluminium-bronzes," although known for many years previously, were particularly studied by Carpenter and Edwards [13] and by Lantsberry and the present writer,[14] but found application only very slowly, so that even at the present time, although a number of alloys of this type and their derivatives containing nickel and other elements are finding some large-scale applications, the writer considers that they are not utilized as extensively as might be expected from their remarkable properties. One of the latest developments in this direction is the aluminium-brass which has resulted from one of the researches carried out for the British Non-Ferrous Metals Research Association.[15] This alloy, containing about 2 per cent. of aluminium, is intended especially for condenser tubes. The aversion to aluminium as a constituent of brass, and, in fact, to its mere presence in a brass foundry or brass works of any kind, is well known to practical men; the reason for it has not been apparent, except that it is recognized that a very small percentage of aluminium (0·1 per cent. or even less) present in ordinary brass may be markedly deleterious. Since, however, with proper casting methods an alloy containing 2 per cent. of aluminium gives highly satisfactory results, there is here need for investigation.

The casting methods used for alloys containing aluminium, such as the "aluminium-bronzes" which have been used in France for coinage purposes, have also undergone important developments. A most interesting process, well known under the name of "Durville," has introduced a new method into foundry practice by showing the value of filling a mould, more especially an ingot or billet mould, by the slow and steady flow of the metal. The process is one which has been used, in the first instance, only for alloys containing aluminium, and it is believed that its success depends on the formation of a tough surface skin on these materials. It seems likely, however, that similar methods of casting, subject to suitable modification, may be applicable to many other materials.

Among other new materials which are still in course of development, one of the most interesting groups is that of the alloys of beryllium, especially with copper and nickel. Reference has already been made to these in connection with age-hardening, since they can be made in that way to develop remarkable properties. They are of interest also from the point of view that they embody the first approach to practical application of what is, for industrial purposes, a new metal—beryllium. Much attention has been devoted to the study of this metal, both in Germany [16] and in this country.[17] The German investigators have devoted themselves mainly to the use of the metal as an alloying element, and have produced remarkable alloys. An appreciation of the possibilities of the metal itself as a basis material has led to attempts in this country to produce it in a state of high purity. This has proved remarkably difficult, owing to the persistence with which it combines with practically every element with which it comes into contact, including nitrogen and oxygen. None the less, the material has been obtained in a sufficient degree of purity to demonstrate the fact that it is essentially ductile, although, in the form ordinarily produced, it appears to be brittle. It does, however, even in the impure condition, combine a high degree of strength and a relatively high melting point with a very low density. The investigation of this and similar more or less rare metals is not only justified, but important, because it has been found again and again in the past that a rare metal which is a laboratory curiosity has in a few years become a commercial product. Aluminium and tungsten are perhaps the most striking examples of this kind, and it is not likely that we have come to the end of the list.

Although the present review relates in the first place to the non-ferrous metals and alloys, and can deal with these only at a few selected points, there is a group of novel materials which are so important, and differ so widely from anything formerly available, that mention must be made of them in spite of the fact that they are perhaps on the borderline of the ferrous field. These are the modern materials of very great hardness which have been developed for cutting purposes. The development of the high-speed cutting steels took place to a large extent before the foundation of the Institute of Metals, although great progress has been made in these also. A step in another direction was taken when alloys of great hardness and of sufficient strength to be used as cutting tools were developed, in the first instance, in America. These alloys could not be softened, and were used in the state obtained by casting, any subsequent shaping being effected solely by grinding. These alloys, of which Stellite is perhaps the best known, have achieved some measure of importance, particularly on the Continent. More recently, however, materials consisting mainly of tungsten carbide have been developed. These are prepared by methods which had formerly been followed mainly in the production of tungsten and other filaments of high-melting metals for electric lamps. The process is well known as that of sintering and swaging. In the case of the carbides, however, swaging is not used, but, on the other hand, a binding substance is added which generally consists of cobalt. Carbide and cobalt are mixed together in a finely-divided state, pressed into moulds of any desired shape, and are then heated in an atmosphere of hydrogen at a sufficiently high temperature to produce a solid sintered material. Cutting tools made in this manner are now widely used, and yield results exceeding anything that can be obtained with high-speed steels or other cutting alloys. The hardness and cutting power of tungsten carbide produced in this manner does not fall far short of that of the diamond, which, it may be mentioned, has also come to be used as a cutting tool. Whether or not materials produced in this way (sintering) can be called alloys, and whether—since they do not contain more than a very small proportion of iron or none at all—they may be included in the non-ferrous field, are matters which may be left open.

Reference has been made above to the development of novel methods of casting, of which it has been possible to mention only one. For the production of sound castings, however, the condition of the metal is of very great importance, and much attention has been given in recent years by investigators to the problems arising from the presence of dissolved gases in metals and to the means for their elimination. A series of papers on this subject has been communicated to the Institute of Metals from the National Physical Laboratory [18, 19] and from the University of Birmingham.[20] The removal of dissolved gases from aluminium alloys, in particular by such processes as "pre-solidification," the passage of nitrogen, of the vapours of volatile chlorides such as titanium tetrachloride and carbon tetrachloride, and of mixtures of these with nitrogen, have all been studied. The use of dry nitrogen itself has also been advocated. Mention must also be made of the development by Tullis [21] of the use of chlorine and of boron chloride. The use of titanium tetrachloride for the removal of gas inevitably introduces a small amount of titanium into the alloy, and it is a curious coincidence that this fact should have been studied and published at about the same time as the use of small amounts of titanium in these alloys for grain-refining purposes was developed. This whole question of the grain-refining effects of certain elements when added to alloys in sometimes quite small proportions appears to be a matter requiring much further investigation. It is being increasingly realized that control of the size and type of crystal structure not only in castings which are to be used as such, but also in ingots and slabs intended for subsequent mechanical working, is a matter of first-rate importance, and may determine the success or failure of a given piece of material. The various casting processes, including the use of water-cooled moulds, vacuum casting as developed by Rohn,[22] the recently described "R.W.R."* process of the German "V.A.W." Company,†[23] all embody features which bear strongly on this point, and mark a development which has followed on the recognition of the part which the internal structure of alloys plays in their practical behaviour during manufacture and use.

Whilst the importance of purifying metals and alloys from undesirable contaminations with gas is becoming increasingly recognized, the necessity for eliminating other impurities is also being appreciated. The important effects which the presence of small quantities of impurities may produce in the behaviour and properties of a metal have come to be realized in recent years. The result has been, on the one hand, an effort to prepare metals of very high purity in the laboratory for purposes of a detailed study or on a large scale for practical applications, while, on the other hand, a detailed study of the effects of impurities has been renewed and carried to greater detail and over a wider range than had formerly been attempted. Of the latter, a series of researches carried out at the National Physical Laboratory for the British Non-

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* Roth-Wende-Rüttel. † Vereinigte Aluminium Werke.

Ferrous Metals Research Association on the effect of impurities in copper may be mentioned. This work has thrown much light on the combined effects of some of the more important impurities which are to be found in varying degrees in all fire-refined copper. The great importance of these investigations has become emphasized by conditions affecting the British copper industry as a consequence of decisions taken at the Ottawa Conference, and it is to be hoped, therefore, that these important researches will be continued, and that the high standard which has been achieved hitherto will be fully maintained. The problems which have to be faced become more and more difficult as the research progresses, but fortunately the increasing experience of the investigators enables them to cope with their difficult task.

With regard to the preparation of pure metals on a commercial scale, we have two examples from America in the preparation of high purity zinc by the New Jersey Zinc Company and of aluminium of great purity by the Hoope process. So far as this country is concerned, efforts have been mainly made in the laboratory, and these have been most successful in regard to the preparation of high-purity manganese [24] and iron.[25] Recently, however, the methods developed for the production of high-purity manganese (vacuum distillation) have been successfully used at the National Physical Laboratory in the production of magnesium of very high purity.[26] Whilst it is not suggested that these materials, which necessarily entail great expense in their production, are likely to be of direct practical use, yet their preparation and study are necessary if the true effects of the impurities present in commercial material are to be properly understood. The study of these very pure materials is also of fundamental importance in the establishment of correct equilibrium diagrams. In the field of the aluminium alloys and in regard to the differences of opinion which exist on the subject of age-hardening, the study of alloys made of high purity metals has become particularly important.

When the Institute of Metals was founded in 1908, it might almost have been said that the study of the structure of metals and alloys was still in its infancy. The great pioneers of the subject—Sorby, Roberts-Austen, Osmond, Martens, and Howe—had completed their work, but the battle for the recognition of the value of the methods for which they had laid the foundation had still to be won. To-day the widespread use not only of metallographic methods, but also of still more abstruse ways of studying the inner structure of materials, shows clearly that the battle has been won. Some of the fruits of victory have been discussed above. The study of alloys in regard to their constitution and behaviour has advanced very rapidly indeed, because it promises immediate results. The study of the mechanical properties of metals in relation to their crystalline structure, on the other hand, for a time made only slow progress. The first account of the discovery of the mechanism of plastic deformation in metals by the process of slip was published in 1899.[27] For nearly twenty years the matter remained very much where that work had left it, and it is, indeed, only in quite recent years that it has been advanced, but fortunately that advance has been rapid and great. It is due in part to the fruitful application of X-ray methods to the study of the phenomena of deformation, an application initiated largely by the work of Taylor and Elam [28] and carried further, especially in connection with the phenomena of fatigue, by Gough.[29] Many continental workers have also contributed to the subject in other directions.[30] In the second place, the study of the phenomena of deformation and fatigue in metals has been rendered much easier by the development of methods for producing large single crystals of metals, and even of some alloys. One of the first steps in this direction was the preparation, by a process of critical strain and critical annealing, of large single crystals of aluminium by Carpenter and Elam.[31] Subsequently a variety of methods have been developed for the production of single crystals, first in the form of comparatively thin rods or wires, and later in massive pieces, during the solidification of metal from the liquid state. It is difficult to sum up briefly the results which have been achieved by these investigations. In the first place, it may be said that whereas the work of Ewing and Rosenhain had shown that deformation occurs by slip along certain planes in metallic crystals, it has now been possible to show precisely on which planes it occurs in crystals of different types both when a steady load and an alternating load is applied. It has also been shown more definitely than was possible by purely microscopic means that the crystalline character of the material is not destroyed, or even seriously impaired, by plastic deformation. The writer, however, thinks that it is now clear, in the light of these investigations, that the lattice structure of a crystal which has undergone deformation is to some extent distorted and locally damaged, and that this damage and distortion account for the hardening which the metal undergoes as a result of cold-working. The modern methods of investigation have led to a further discovery which had escaped earlier microscopic observers; this is the strong tendency for the crystals to assume a common orientation, such that a particular axis of a crystal tends to lie in the direction in which the metal has been elongated. This "preferred" orientation, and the manner in which it behaves when the metal is subsequently heated and annealed, offers a series of discoveries and problems of the most interesting kind. Practical applications of these discoveries have not yet been developed except in a few isolated instances, but it seems probable that our increasing understanding of the nature and process of plastic deformation will materially affect our methods of working metals and the results which we can achieve thereby.

The subject of cold-working and plastic deformation recalls the work of an eminent Past-President of the Institute of Metals, the late Sir George Beilby. His beautiful work on the surface films produced in the polishing of metals, and his extension of this idea to that of the production of similar flowed films on the surfaces within the crystals where slip had occurred, appeared to offer a satisfactory explanation of many of the phenomena in question. The use of the word "amorphous" by Beilby and by some of those, including the present writer, who endeavoured to support and extend his theory, was perhaps unfortunate, because it led to much opposition of an unnecessary sort. As a result of this opposition, both Beilby's theory of a flowed surface "amorphous" layer and the writer's theory of an "amorphous" intercrystalline layer have been for many years somewhat discredited. It is interesting to note, however, that recent researches in which the structure of surface films on polished metal specimens has been studied by means of the latest method of physical investigation [32]—electron diffraction—have gone to show that the surface films, if not truly "amorphous," contain only slight traces of crystal structure, so that they closely approach the ideal "amorphous" condition. On the other hand, it has been shown that substances which are regarded as truly "amorphous," such as glass and vitreous silica, also show under X-ray examination distinct signs of crystal structure. It would seem, therefore, that whatever definition we may adopt for the term "amorphous," the description of flowed films of metal as "vitreous" is to a considerable extent justified. With regard to the internal surfaces on which slip has occurred, it is now clear, in the writer's opinion, that here also the crystalline structure must be, to some extent, broken down. Without entering into any lengthy discussion of this point, however, it is sufficient to call attention to recent researches on the heat absorbed or rendered latent during plastic deformation. The work of Farren and Taylor [33] carried out on tensile test-pieces has clearly shown that heat is absorbed in these circumstances and has given an indication of the amount. This has been, to some extent, confirmed by the more recent work on wire drawing carried out by the writer and V. H. Stott.[34] It can be shown that the amount of heat absorbed is greater than can be accounted for by the storage of energy by internal elastic stresses, so that something essentially akin to phase change must take place to a small extent during plastic deformation, and this, in the writer's opinion, is due to breakdown of the lattice at and near surfaces of slip.

Closely associated with this aspect of scientific metallurgy is the study of the laws of the metallic state based on our knowledge of lattice structure and the changes of that structure. Much important work on this subject has recently been carried out by Hume-Rothery.[35] The writer, some years ago,[36] put forward certain theories on lattice distortion resulting from the presence of atoms of an alloying element. Exceptions to some of the generalizations put forward in that theory have since been discovered, but it seems that these are due to the fact that the theory in question was an attempt to explain metallic structures and properties on a geometrical basis, and that the term "lattice distortion" originally used in reference only to geometrical distortion will have to be interpreted in the light of our increasing knowledge of the arrangement of the electrons in the lattice.

It is impossible to complete a review of this kind, however sketchy and imperfect, without some reference to corrosion. Research on corrosion has always formed an important activity of the Institute of Metals, and a large number of reports and papers on the subject are contained in its *Journal*. A year or two ago, it would probably have been said in this review and elsewhere that on the theoretical side the long-drawn-out controversy as to the mechanism of corrosion had been settled, and that the electrochemical theory as developed on the principle of "differential aeration" was widely if not universally accepted. From one point of view it is unfortunate that more recent work appears to throw some doubt on the validity of "differential aeration" as the true explanation in all those cases where it has become customary to invoke it. Disturbing as such a change in our ideas might be, it should be welcomed, since a fuller recognition of the truth, and an understanding of the mechanism of one of the important phenomena with which metallurgists have to deal, cannot but lead to progress and the overcoming of difficulties which had not yet been mastered. While, therefore, we must recognize the important services which the existing theory of corrosion and of "differential aeration" has rendered in explaining many of the complicated phases of the process, we look forward with interest to further developments and to the formulation of a more complete theory which will, no doubt, be built up by a combination of the older and the new knowledge.

Whatever theory of corrosion may ultimately find general acceptance, there is at least one discovery which has been gradually established over a period of years which not only explains many of the phenomena of corrosion, but is also a valuable means for providing certain metals and alloys with protection against chemical attack. This is the discovery of the important part played by the surface film which is formed on most metals, if not on all, either by the action of atmospheric oxygen or of moisture or of both. The existence of such a film in the case of aluminium was always recognized, and it was a logical consequence of this view that those engaged in an attempt to combat the corrosion of aluminium and its alloys should seek to utilize that protective surface film and to thicken and to strengthen it. This has been very successfully done by the anodic oxidation process developed by Bengough and Stuart,[37] both of whom were workers for the Corrosion Research Committee of the Institute of Metals. The use of " anodized " aluminium is now widespread and successful, the film serving even better as a basis for a protective pigment or enamel than as a complete protection in itself. Since the publication and patenting of Bengough's and Stuart's methods, certain other ways of producing anodic films on aluminium and its alloys have been developed, some of them with interesting results. The demonstration that a protective film really exists has, in recent years, been given by the actual separation of the film both by Evans,[38] by Sutton and Willstrop[39] at the Royal Aircraft Establishment, Farnborough, and by Withey and Millar[40] at the National Physical Laboratory. The important function of a film of this type, presumably consisting mainly of chromium oxide, for the protection of rust-resisting steels from corrosive attack, is also fully recognized. Even in cases, however, where the surface film is not sufficiently strong or chemically resistant to serve as a complete protection against corrosion, its presence and nature materially affect the way in which corrosion occurs and the circumstances which favour its progress or inhibition.

It is believed, in many quarters, that it is the repeated rupture of such a film, even when not of a highly protective nature, which leads to the comparatively rapid failure of metals under alternating stress when exposed at the same time to mildly corrosive influences. An immense amount of work on this subject has been done by D. J. McAdam, jr., in America, but it is interesting to note that one of the earliest, if not the earliest, record of the influence of corrosion on fatigue resistance was made by B. P. Haigh in a paper read before the Institute of Metals in 1917, whilst subsequent work on the subject has been fully described by Gough in his Autumn Lecture to the Institute in 1932.

In thus glancing backwards over twenty-five years of metallurgical progress, the writer, whilst seeking to summarize as briefly as possible some of the achievements of those years, cannot help looking forward in almost every instance to the future developments which the present situation of our knowledge suggests. It has sometimes been said that the rate of progress which the application of science has brought about during the last thirty or forty years cannot possibly be maintained. The younger workers in such a field are sometimes heard to express their envy of those who worked thirty or forty years ago, " when so much still remained to be discovered." This, however, the writer regards as a state of mind which must have existed for hundreds of years—it certainly existed in his own mind thirty years ago. So far from believing that the field of discovery and advance is approaching exhaustion, he feels satisfied that if world conditions remain favourable to the development of scientific thought and scientific methods and to their application to the practical problems of mankind, then discovery and progress are certain to continue at an increasing rate. Whether or not these conditions can be maintained, however, must depend on the use which man contrives to make of the materials which research and industry together place at his disposal. If they are used for destructive competition, whether in war or in commerce, progress cannot be maintained, and even our existing status must crumble.

REFERENCES.

The number of publications directly or indirectly referred to in the present paper is very large. No attempt has been made to furnish a complete list of references, but those given will, it is hoped, be sufficient to serve as a general guide to the literature of the various branches of this subject.

[1] Rosenhain, *J. Inst. Metals*, 1909, **1**, 200–226.
[2] Rosenhain, *J. Inst. Metals*, 1915, **13**, 160–183.
[3] Rosenhain, *J. Inst. Metals*, 1929, **42**, 31–68.
[4] Merica, Waltenberg, and Scott, *U.S. Bur. Stand. Sci. Paper* No. **347**, 1919.
[5] Hanson and Gayler, *J. Inst. Metals*, 1921, **26**, 321–355.
[6] Gayler and Preston, *J. Inst. Metals*, 1929, **41**, 191–234.
[7] Gayler and Preston, *J. Inst. Metals*, 1932, **48**, 197–208.
[8] Portevin, May Lecture, *J. Inst. Metals*, 1933, **51**, 315–356.
[9] Jeffries and Archer. " The Science of Metals." New York : **1924**.
[10] Rosenhain, *Z. Metallkunde*, 1930, **22**, 73–78.
[11] Gayler, *J. Inst. Metals*, 1927, **38**, 157–184.
[12] Gwyer and Phillips, *J. Inst. Metals*, 1926, **36**, 283–324.
[13] Carpenter and Edwards. " Eighth Report to the Alloys Research Committee of the Institution of Mechanical Engineers on the Properties of some Alloys of Copper and Aluminium," *Proc. Inst. Mech. Eng.*, **1907**, 57–269.
[14] Rosenhain and Lantsberry. " Ninth Report to the Alloys Research Committee of the Institution of Mechanical Engineers on the Properties of some Alloys of Copper, Aluminium, and Manganese." *Proc. Inst. Mech. Eng.*, **1910**, 119–292.
[15] Genders, *J. Inst. Metals*, 1930, **43**, 163–192.
[16] " Beryllium : its Production and its Application." (Published by the Zentralstelle für Wissenschaftlich-Technische Forschungsarbeiten des Siemens-Konzerns.) New York : **1932**.
[17] Sloman, *J. Soc. Chem. Ind.*, 1929, **48**, 309–316T ; *J. Inst. Metals*, 1932, **49**, 365–388.
[18] Archbutt, *J. Inst. Metals*, 1925, **33**, 227–239.
[19] Rosenhain, Grogan, and Schofield, *J. Inst. Metals*, 1930, **44**, 305–318.
[20] Hanson and Slater, *J. Inst. Metals*, 1931, **46**, 216–227.

[21] Tullis, *J. Inst. Metals*, 1928, **40**, 55–62.

[22] Rohn, *J. Inst. Metals*, 1929, **42**, 203–214.

[23] Kessner, *Metallwirtschaft*, 1932, **11**, 583–584.

[24] Gayler, *J. Iron Steel Inst.*, 1927, **115**, 393–411.

[25] Tritton and Hanson, *J. Iron Steel Inst.*, 1924, **110**, 90–121.

[26] *Annual Report of the National Physical Laboratory*, 1932, p. 245.

[27] Ewing and Rosenhain, *Phil. Trans. Roy. Soc.*, 1899, [A], **193**, 353; 1900, [A], **195**, 279.

[28] Taylor and Elam, *Proc. Roy. Soc.*, 1925, [A], **108**, 28–51.

[29] Gough, *Proc. Roy. Soc.*, 1928, [A]. **118**, 498–534; Gough and Cox, *ibid.*, 1929, [A], **123**, 143–167; Gough and Cox, *ibid.*, 1930, [A], **127**, 431–453, 453–479.

[30] E. Schmid, *Metallwirtschaft*, 1928, **7**, 1011–1015; *Physikal. Z.*, 1930, **31**, 892–896; *Z. Elektrochem.*, 1931, **37**, 447. Schmid and Wassermann, *Z. Physik*, 1928, **48**, 370; *Metallwirtschaft*, 1930, **9**, 698–702 ; *Metallwirtschaft*, 1931, **10**, 735–736; *Z. Metallkunde*, 1931, **23**, 87–90.

[31] Carpenter and Elam, *Proc. Roy. Soc.*, 1921, [A], **100**, 329–353.

[32] French, *Proc. Roy. Soc.*, 1933, [A], **140**, 605–652.

[33] Farren and Taylor, *Proc. Roy. Soc.*, 1925, [A], **107**, 422–451.

[34] Rosenhain and Stott, *Proc. Roy. Soc.*, 1933, [A], **140**, 9.

[35] Hume-Rothery, "The Metallic State: Electrical Properties and Theories." London: 1931.

[36] Rosenhain, May Lecture, *J. Inst. Metals*, 1923, **30**, 3–26; Miers, May Lecture, *J. Inst. Metals*, 1927, **37**, 331–350; Rosenhain, Cantor Lectures, *J. Roy. Soc. Arts*, 1925.

[37] British Patents 223,994 and 223,993 of Aug. 2, 1923; Department of Scientific and Industrial Research Report, 1926. London: H.M. Stationery Office.

[38] Evans, *J. Chem. Soc.*, 1927, 1020–1040.

[39] Sutton and Willstrop, *Nature*, 1927, **119**, 673–674.

[40] Withey and Millar, *J. Soc. Chem. Ind.*, 1926, **45**, 170–174T.

CORROSION-FATIGUE CHARACTERISTICS OF AN ALUMINIUM SPECIMEN CONSISTING OF TWO CRYSTALS.*

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Synopsis.

An aluminium specimen consisting of two crystals has been tested under alternating torsional stresses in a slow stream of tap-water; the main object of the experiment was to investigate the effect of an intercrystalline boundary on failure by corrosion-fatigue. The boundary was not attacked by the corrosive medium, nor did it influence in any visible manner the method of failure of the specimen, which took place primarily by the formation of cracks in areas undergoing heavy plastic deformation. On the surface of the specimen these cracks were generally parallel to the traces of the operative slip-planes; in several cases they had their origin at holes situated in the most highly stressed regions; of the origin of these holes no definite evidence is available.

Whilst general attack in the form of oxide film and small pitting occurred throughout the duration of the experiment (about 6 weeks), this did not, to any appreciable extent, contribute to the failure of the specimen.

I.—Introduction.

Although a great deal of research work has been devoted in several countries to the problem of corrosion-fatigue, such investigations have been almost entirely confined to the determination of the corrosion-fatigue resistance of various metals and alloys, the effect of heat-treatment, different corrosive environments and frequencies, and similar aspects. Apart from the examination of failures in practice due to corrosion-fatigue, very little metallographic work has been done. Accordingly, when in 1929 a programme of research on corrosion-fatigue, for the Department of Scientific and Industrial Research, was drawn up, one of the main items included for investigation was a study of the changes in microstructure which occur in a specimen (or machine component) while undergoing alternating stress in the presence of a corrosive environment.

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Two questions appeared to be of particular importance—the point of initiation of a corrosion-fatigue crack and its subsequent course. As to the former, it was thought that a corrosion-fatigue experiment on a single crystal, in affording an opportunity of correlating the observed micro-structural changes with the applied stresses and the crystalline structure, would provide interesting information. The material selected for the purpose was aluminium, and the corrosive medium a slow stream of tap-water. The main results of this first experiment may be briefly summarized as follows:* (1) The specimen failed after about 24 million reversals of a range of stress ($\pm$ 0·6 ton/in.^{2} resolved shear stress) which would not have produced fracture in a similar crystal tested in air. (2) Failure was due primarily to preferential corrosion along the site of previously formed slip-bands, leading to the formation of a large number of cracks following the traces of the operative slip-planes. (3) Small pits occurred over the whole surface, their distribution bearing no relation to the stress distribution in the specimen. These, during the 6 weeks occupied by the tests, had not developed to such an extent as to contribute materially to the failure of the specimen. (4) Larger holes also occurred, again unrelated to the stress distribution. These likewise did not seriously affect the fracture.

This experiment did not yield any information as to the effect of intercrystalline boundaries. The present paper describes the results of a similar test carried out on an aluminium specimen consisting of two large crystals separated by a boundary, the principal object being to determine whether more intense corrosion occurred at the boundary and, if so, whether its effect would be sufficient to produce an intercrystalline fracture.

II.—DESCRIPTION OF SPECIMEN AND METHOD OF TEST.

The specimen (test-mark AL12A) used in the present test was prepared by Carpenter and Elam's critical strain and heat-treatment method. It consisted of two large crystals separated by an irregular boundary. From this bar a cylindrical specimen was machined, having a central test portion 0·5 in. in diameter by 1·2 in. long, joined by fillets of large radius to enlarged ends 0·75 in. in diameter, these latter being gripped in the chucks of the testing machine. The length of the test portion was so chosen as to include the whole of the boundary separating the two crystals.

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* H. J. Gough and D. G. Sopwith, "The Behaviour of a Single Crystal of Aluminium under Alternating Torsional Stresses while Immersed in a Slow Stream of Tap-Water," *Proc. Roy. Soc.*, 1932, [A], 135, 392.

The type of stressing system adopted was alternating torsion, which possesses two advantages for the present purpose, *viz.* the absence, even at fracture, of any large amount of distortion of the specimen as a whole, and the variation of resolved shear stress round the specimen. The Stromeyer alternating torsion machine was used, the specimen acting as a coupling between an oscillating shaft and a heavy flywheel.

The corrosive medium employed was the ordinary laboratory tap-water, an analysis of which showed that it contained 28·16 parts per 100,000 of solid matter, mainly $CaCO_3$ (18·10 parts). The specimen was enclosed in a rubber water-jacket fitted with inlet and outlet water tubes about $\frac{1}{8}$ in. diameter (Fig. 1). The average rate of water flow was about 10 lb. per hour, the actual rate varying somewhat owing to pressure fluctuations in the mains. The tests were conducted throughout at the comparatively low speed of 400 stress reversals per minute. These conditions were precisely similar to those employed in the case of the single crystal previously tested, as was also the stress applied throughout the tests, *viz.* $\pm$ 0·615 ton/in.^{2} nominal shear stress, equivalent to a value of $\pm$ 0·6 ton/in.^{2} maximum resolved shear stress. The previous test had shown that, provided the boundary produced no very marked effect, this stress would lead eventually to failure; also, the adoption of the same stress value would enable further evidence to be obtained regarding the corrosion-fatigue phenomena exhibited by each constituent crystal.

III.—X-RAY AND STRESS ANALYSIS.

After machining, the surface of the specimen was etched to remove any disturbance due to the machining; the specimen was then subjected to X-ray analysis at each end of the test portion. The results of the corrected X-ray analyses are shown plotted in the stereographic diagram (Fig. 2).

In order to check whether any relation existed between the orientations of the two crystals in this specimen, the spherical co-ordinates of the 112 and 123 planes were also calculated; it was found that the two crystals did not possess any common planes of the types 100, 111, 110, 112, or 123. The two crystals thus appear to be at a completely random orientation.

The resolved shear stresses due to torsion on one octahedral plane in the direction of its intersection with another have been shown * to be given by :—

$$S_r/S = A \cos (\lambda - \alpha)$$

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* *J. Inst. Metals*, 1926, 36, 185.

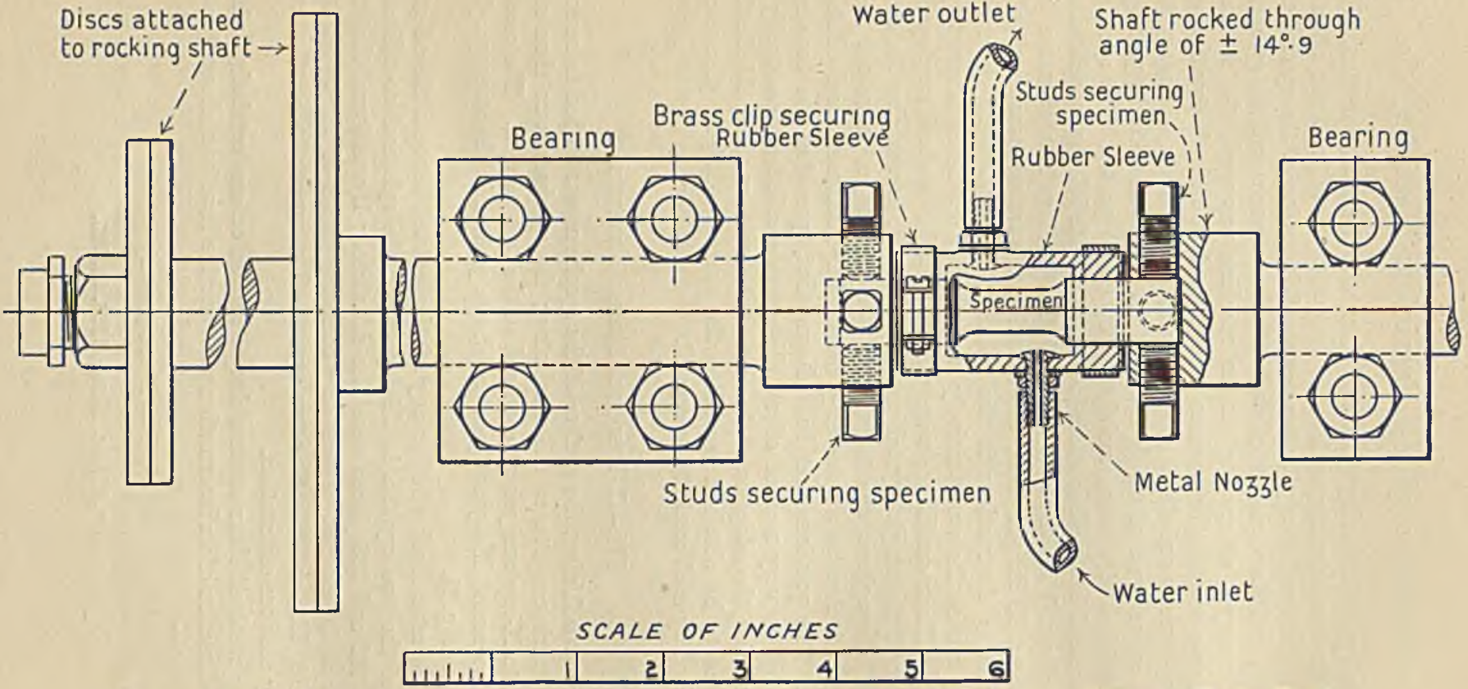

Fig. 1.—Corrosion-Fatigue of Aluminium Boundary Specimen AL12A. Arrangement of Specimen in Alternating Torsion Machine.

where S_r = resolved shear stress $\Big\}$ at surface of specimen.
S = nominal ,, ,,
λ = angular distance between reference plane and point under consideration.
A, α = constants derived from the orientations of the two octahedral planes.

Table I gives the calculated values of the constants A and α for all the twelve possible slip planes and directions in each crystal. The symbols used follow the usual conventions,* single symbols indicating the octahedral planes, and double symbols the intersection of two of these planes.

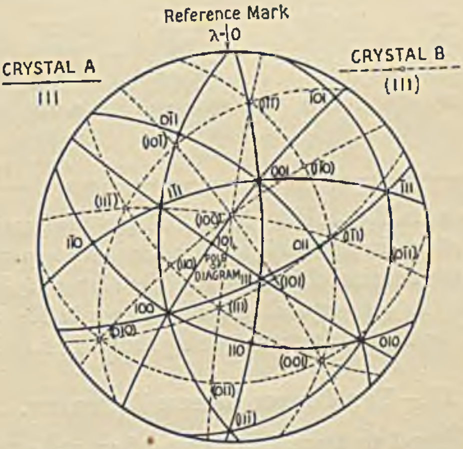

FIG. 2.—Corrosion-Fatigue of Aluminium Boundary Specimen AL12A. Stereographic Diagram showing Position of Principal Planes with respect to Axes of Specimen.

The resolved shear stress curves are shown in Fig. 3 (Plate XXXIII) (for both crystals A and B). The required maximum resolved shear stress value being ± 0·6 ton/in.^{2} as for the previous single crystal specimen, and the maximum stress factor (from Table I) being 0·975 (on plane 3 in direction of intersection with plane 1, crystal A), the required value of nominal shear stress S was $\pm 0{\cdot}6/0{\cdot}975 = \pm 0{\cdot}615$ ton/in.^{2}. This value has been adopted throughout the experiment, the necessary torque being calculated in the usual way from the formula

$$S = 2T/\pi r^3$$

where T = torque applied,
r = radius of specimen.

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* *J. Inst. Metals*, 1926, 36, 185.

TABLE I.—*Values of Constants in Resolved Shear Stress Equations.*

Octahedral Plane.	Contained Direction.	Crystal A.		Crystal B.	
		A.	*a*°.	A.	*a*°.
0	01	0·684	288° 5′	0·805	167° 2′
	02	0·900	230° 48′	0·550	137° 8′
	03	0·782	183° 27′	0·428	206° 45′
1	12	0·572	2° 47′	0·716	273° 53′
	13	0·926	199° 12′	0·772	72° 18′
	10	0·411	222° 20′	0·283	4° 24′
2	23	0·273	70° 2′	0·561	285° 8′
	20	0·680	58° 34′	0·514	255° 42′
	21	0·415	51° 2′	0·278	351° 2′
3	30	0·307	200° 36′	0·502	108° 12′
	31	0·975	267° 8′	0·529	344° 56′
	32	0·670	90° 12′	0·491	43° 37′

The stress curves (Fig. 3, Plate XXXIII) give the numerical values of resolved shear stress in the various directions, corresponding with the above value of the nominal shear stress. The slopes of the traces of the octahedral planes in both crystals are also shown in Fig. 3, the trace of the operative slip-plane at any point being shown in full lines.

IV.—THE COURSE OF THE BOUNDARY.

As it was desired to trace the course of events at the boundary throughout the test, and it was also desirable that the surface of the specimen should be highly polished for the actual tests, the position of the boundary was mapped before the final polishing. After the specimen had been machined, it was etched in order to remove the disturbing effect of the machining on the structure, the etching being somewhat deeper than usual in order to bring up the boundary. The boundary was then surveyed under the miscroscope, using a 40 mm. lens with oblique illumination, and its course plotted. The central section of Fig. 3 shows the developed surface of the parallel portion of the specimen, with the course of the boundary. The latter is quite irregular and cannot be correlated with the traces of any of the crystallographic planes; it lies completely within the parallel portion of the specimen. The resolved shear stress curves and slope diagrams are also shown in Fig. 3, alongside the crystals to which they refer (*viz.* crystal " A " nearer the reference end, and crystal " B " at the other end). The position of a point on the surface will be referred to by its two co-ordinates (λ, *d*), where λ is the angle between reference plane and axial plane through point, and d is distance in mm. from a plane perpendicular to the axis passing through the mid-point of the specimen (reckoned positive towards the right, *i.e.* towards crystal " B " and away from reference end).

V.—DETAILS OF THE EXPERIMENT.

The details of the various tests and intermediate examinations are most concisely stated in tabular form (Table II).

TABLE II.—*Details of Tests and Examinations.*

Reference Number of Test.	Resolved Shear Stress, Tons/in.^{2}.	Number of Reversals (millions).	Total Number of Reversals (millions).	Details of Examination, &c.	Treatment before Next Test.
1	± 0·4 throughout	1·022	1·022	Slip distribution mapped, photographs and panorama taken	Surface lightly cleaned
2		2·001	3·023	Two cracks visible, slip and cracks mapped, photographs and panorama taken, also panorama of crack 1	Surface lightly cleaned
3		1·977	5·000	Slip and cracks mapped, photographs and panorama of crack 2 taken	None
4		7·005	12·005	Test stopped on account of slight increase in range of strain. Photographs taken.	Surface lightly cleaned
5		5·763	17·768	Cracks mapped	None
6		11·525	29·293	Cracks mapped and photographs taken. Test discontinued	Cross-section cut and polished
...	...	...	...	Cross-section—cracks and boundary mapped and photographs taken.	

VI.—CHANGES IN MICROSTRUCTURE DURING TEST.

(*a*) *General Attack; Oxide Film and Pitting.*

On removal from the machine after the first test (one million reversals) the surface of the specimen was found to be dull grey in colour with some brighter streaks roughly parallel to the axis, particularly at about $\lambda \doteqdot 40^\circ$ and 300°, *i.e.* approximately symmetrical about the water inlet (the water entered vertically upwards at $\lambda \doteqdot 0^\circ$ near the reference end of the specimen, in all the tests). The position of the inlet was marked by a ring of oxide colours about ⅜ in. in diameter, this being the only trace of oxide coloration visible to the naked eye. The outlet (at the other end of the specimen at $\lambda \doteqdot 180^\circ$) was indicated by a slightly brighter ring and a roughly triangular area with its base on the fillet and apex at about $\lambda \doteqdot 180^\circ$. This triangle was somewhat lighter than the surrounding surface, probably due to water at either side moving towards the inlet, so that less water flowed over this area.

Under the microscope the surface was seen to be entirely covered by a film of oxide of varying colours, the background being usually fairly bright yellow, with varying amounts of small patches of other colours, mostly green or brown. On the whole, the film was very much more uniform than was the case at the same stage in the previous single crystal specimen, probably on account of the larger water spaces in the type of water-jacket used since the first test on the latter specimen.

The depth of the film as judged from its colouring could not be related to the stress distribution, and was apparently affected only by the varying water velocity at different points of the surface.

The only evidences of pitting at this stage were some minute dots visible at various points on the surface. There were at many places appearances as of larger pits, but on closer examination it was seen that these consisted in most cases of small patches of oxide, and were often red or green, and not black or grey. Examination under higher magnification showed that these were certainly not depressions. It must be concluded, therefore, that these spots were not pits, except in a few cases which could be accounted for as polishing pits. Owing to the extremely minute size of the pits—only about one-tenth the (linear) size of the first unmistakable pits on the single crystal (after 10^7 reversals)—no quantitative estimate of their frequency of occurrence has been attempted.

After a further two million reversals, the specimen was found to have cracked, there being two cracks visible to the naked eye. One of these was about ½ in. long, and the other, close to it, about half that length. Both cracks, particularly the larger, had masses of yellowish-white deposit on them. This deposit also occurred at the junction of the fillets and the enlarged ends, probably being trapped there when washed away from the parallel portion. The surface was again greyish-black in colour, and rather more uniform than after the first test. The ring of oxide colours at the inlet was still present. Under the microscope the general appearance was much the same as after the first test, a photographic panorama of the surface taken near the centre-line from $\lambda = 180^\circ$ to 360° showing very much the same coloured patches as the previous panorama of the same areas. The only noticeable difference was the disappearance of some vaguely defined dark areas previously observed. A few larger pits were observed at this stage. (See *e.g.* Fig. 4, Plate XXXIV.)

At several points on the surface, especially near the shoulders, black

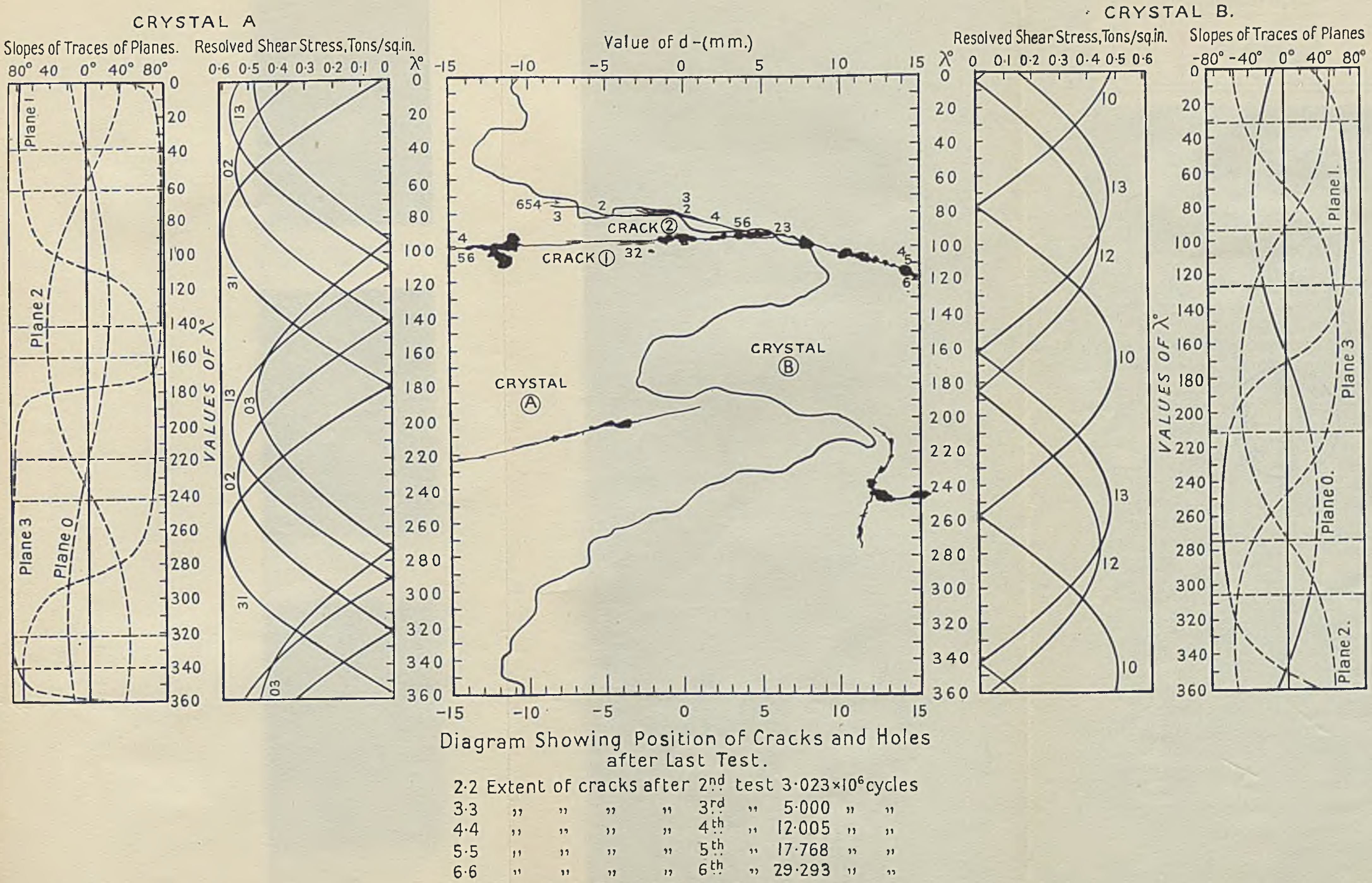

FIG. 3.—Corrosion-Fatigue of Aluminium Boundary Specimen AL12A.

[*To face p. 64.*

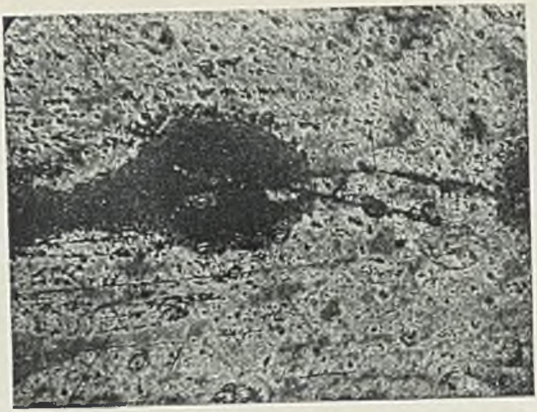

FIG. 4.—Crack 1 crossing boundary (after second test). ($\lambda = 93{\cdot}5°$, $d = 5{\cdot}4$). × 100.

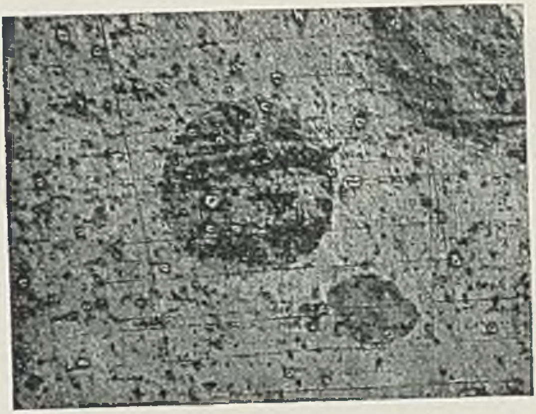

FIG. 5.—Typical slip (after second test). ($\lambda = 86{\cdot}5°$, $d = -11{\cdot}2$.) × 100.

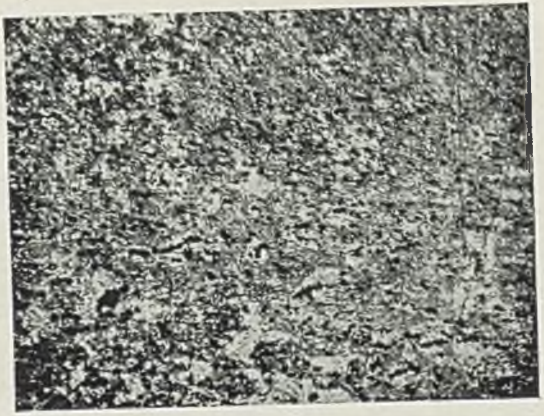

FIG. 6.—Merging of small pits (after third test). ($\lambda = 15°$, $d = -8{\cdot}3$.) × 100.

All reduced by $\frac{1}{3}$ in reproduction.

FIG. 7.—Preferential corrosion on slip band (after second test).
($\lambda = 259{\cdot}5°$, $d = -9{\cdot}4$.) × 100

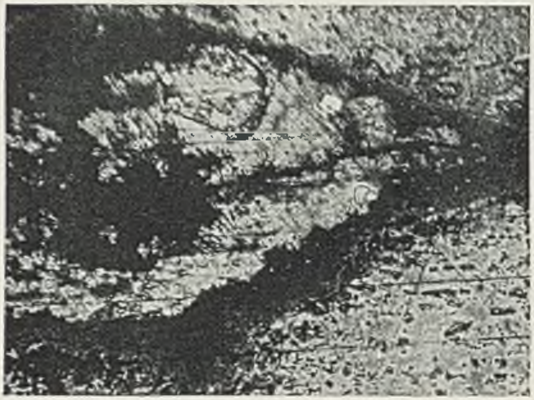

FIG. 8.—Large hole on crack 1 (after second test).
($\lambda = 95°$, $d = 3{\cdot}5$.) × 100.

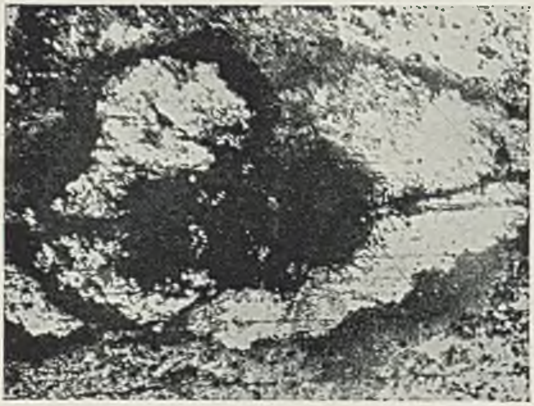

FIG. 9.—Same hole as Fig. 8 (after third test).
($\lambda = 95°$, $d = 3{\cdot}1$.) × 100.

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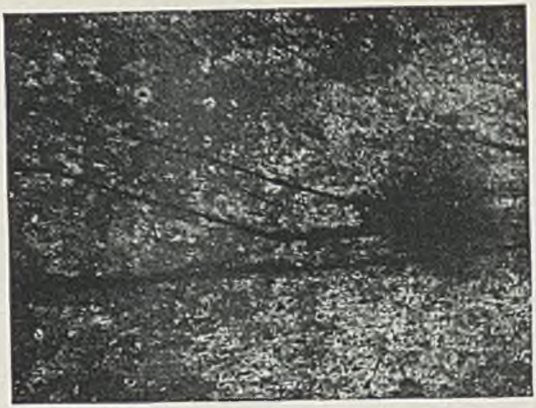
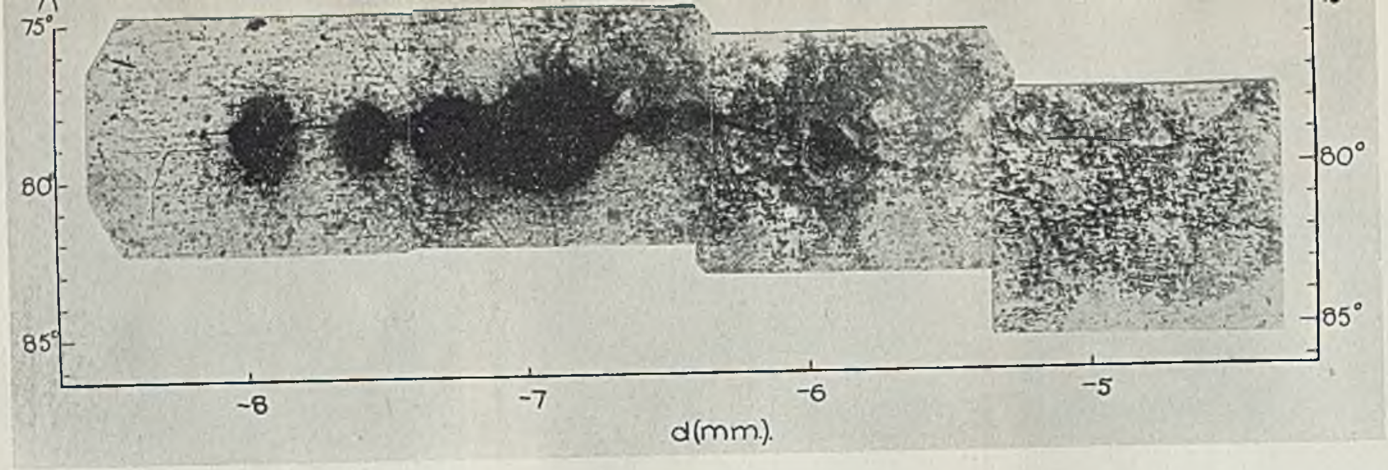


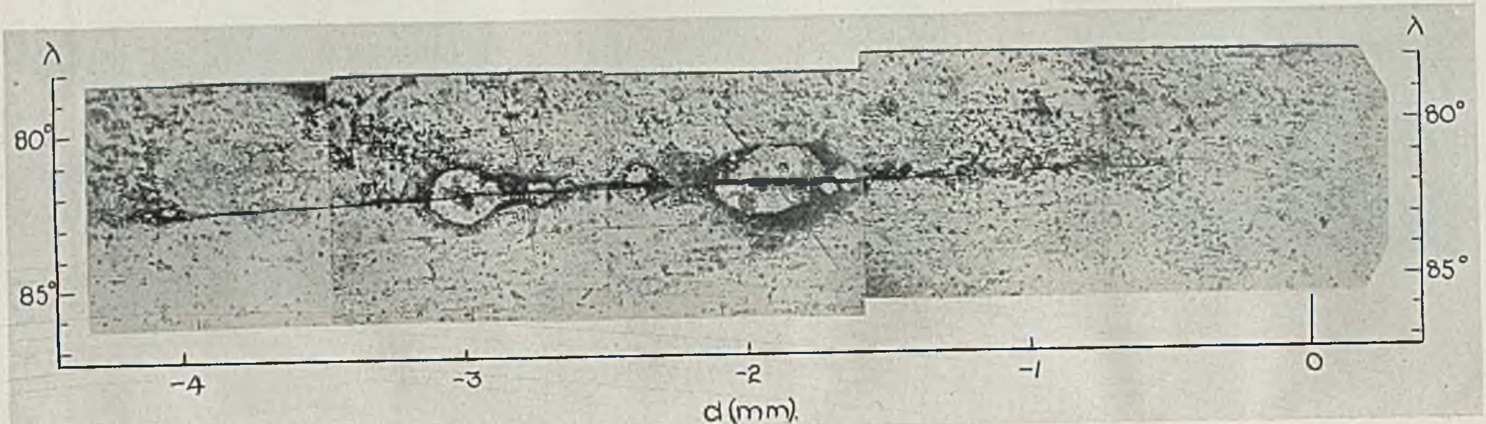
FIG. 10.—Cracks crossing boundary (after final test). ($\lambda = 81°$, $d = -1{\cdot}3$.) × 100.

FIG. 11.—Branching of crack 1 (on cross-section). × 330.

FIG. 12.—Crack 1 and boundary (on cross-section). × 100.
All reduced by $\frac{1}{3}$ in reproduction.

PLATE XXXVII.





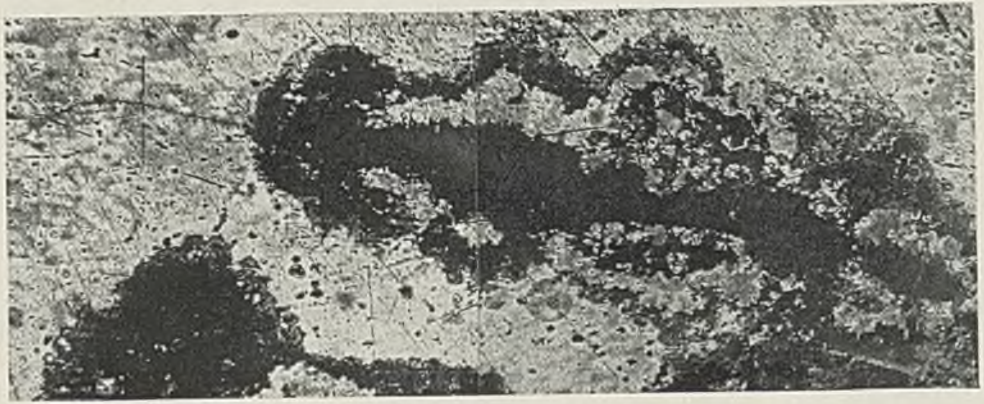


FIG. 14.—End of crack 2 (after fourth test).
($\lambda = 84°$, $d = 0{\cdot}3$.) × 100.
Reduced by $\frac{1}{4}$ in reproduction.

dots surrounded by bright white or yellow rings occurred. The surrounding material was at first thought to be a deposit of corrosion products, but closer examination, together with a comparison of the appearance before and after lightly cleaning the surface, showed that the rings were of comparatively uncorroded material. Some of these dots will be seen in Fig. 5 (Plate XXXIV). Merging of small pits (Fig. 6, Plate XXXIV) occurred to some extent in isolated places during the third test (total five million reversals). These were positions of high resolved shear stress; this is in agreement with the occurrence of joining up of pits in the previous single crystal specimen but the amount of such joining was, however, too limited for any general conclusions to be reached at this stage. The pits were rather more numerous and more evenly distributed, no relation between the number and the resolved stress being noticeable. The ringed pits were still in evidence, showing no change since the previous test.

During the remainder of the tests, the general appearance of the surface became gradually darker, making it increasingly difficult to observe such features as pits and slip bands. So far as could be judged from the lighter areas, no great increase in the size or number of pits occurred. In fact, the number of pits appeared to decrease, confirming a previous opinion that some of the apparent pits were really patches of darker oxide film, and not actual depressions. No further merging of pits was observed.

(*b*) *Slip Bands and Cracks.*

The number and distribution of slip bands on this specimen were very similar to those observed in fatigue tests on single crystals conducted in air. Both were in good agreement with the resolved shear stress distribution (calculated on the assumption that the boundary had no effect on the stress conditions), the agreement becoming even closer as the test proceeded. Little slip occurred after the third test (five million total reversals). Typical slip is shown in Fig. 5 (Plate XXXIV) (after second test).

In the previous test on a single crystal, slip production had ceased some time before a definite crack appeared, and before the intermediate stage of preferential corrosion along previous slip-bands became apparent.

In the case of the present specimen, however, very little of this intermediate stage was observed, the only example being that shown in Fig. 7 (Plate XXXV) (taken after three million total stress reversals). No further progress occurred in this region up to the end of the experiment (a total of twenty-nine million reversals). On the other hand, after the second test, two definite cracks were present. The positions of these are shown on the map of the cracks after the completion of the tests (Fig. 3, Plate XXXIII). This figure indicates the positions and extents of the cracks and holes present on the surface of the specimen after the final test. The portions of the cracks which were visible at this stage were those of the upper two cracks (at $\lambda = 80°$ and $95°$ approximately) included between the figures 2 . . . 2. Both these cracks have occurred near the boundary and, even at this stage, the larger crack crosses the boundary once, and the smaller twice. This position is near one of the two largest stress maxima in the specimen (crystal "A," direction 31, $\lambda = 87°$ or $267°$), and is the one of these two positions in which the greater part of the test portion of the specimen is occupied by crystal "A"; the stress in crystal "B" in this region is considerably less than in crystal "A." The direction of the cracks agrees extremely well with the traces of the operative slip-plane, and a very definite change in slope takes place where they cross the boundary, *e.g.* Fig. 4 (Plate XXXIII) which shows the larger crack (referred to below as crack 1) crossing the boundary at $\lambda = 93{\cdot}5°$, $d = 5{\cdot}4$. After crossing into crystal "B," both cracks stop; this probably reflects the relative stress distributions in the two crystals.

Crack 1 was found, on removing the specimen from the machine, to be covered with deposit over most of its length. This was mapped before cleaning the specimen lightly, and the surface as then revealed compared with the map. It was found that a large mass of deposit usually indicated the presence of a hole, of smaller size than the mass, the outline of which was marked by a ring of material darker in colour than the remainder of the surface. The surface between these holes and rings was much less heavily corroded, as is shown in Fig. 8 (Plate XXXV).

Except for a very slight extension at each end, crack 1 did not change during the third test. This crack was covered by fresh deposit. Crack 2, on the other hand, had extended about 3 mm. towards the left, cutting the boundary again for the third time. A panorama of this crack was taken at this stage and is reproduced as Fig. 13 (Plate XXXVII). It shows the three points at which this crack crosses the boundary and also several holes and corroded rings as previously described. This crack was accompanied by less deposit than the larger crack 1. One of the larger holes on crack 1 had extended considerably. A comparison of Figs. 8 and 9 (Plate XXXVII) (after second and third tests respectively) suggests that this extension has taken place in two ways—by the extension of the original hole and by the formation of a new hole slightly to its left. There are two points which support this suggestion—the corroded ring surrounding the left-hand part of the hole and running into it near the centre of the original hole, and the fact that possible traces of the original surface are discernible between the old and new portions of the hole.

Both cracks extended during the fourth test, crack 1 to the fillet at either end of the test portion of the specimen, and crack 2 only a short distance at each end. The extent of both is indicated in Fig. 3, (4 . . . 4).

The new parts of crack 1 were comparatively free from large holes, but the right-hand extension showed heavily corroded areas. The smaller crack 2 extended further into crystal " B ", the new portion consisting of a narrow hole following the trace of the operative slip-plane. This hole is therefore probably the result of heavy corrosion on a continuation of the crack (Fig. 14, Plate XXXVIII; $\lambda = 84°$, $d = 0{\cdot}3$). It will be noted that this test was of much longer duration than the previous tests.

After the final test two new cracks were found, and crack 2 had extended to meet crack 1. The position of these cracks at this final stage is shown in Fig. 3 (Plate XXXIII). In addition, two smaller cracks had started from crack 2 at a point near one of the places where it crossed the boundary; these are shown in Fig. 10 (Plate XXXVI) ($\lambda = 81°$, $d = -1{\cdot}3$). These cracks also change slope when crossing the boundary, and run parallel and close to crack 2, finally running into an extension of the sloping part of crack 2 at about $\lambda = 80°$, $d = -0{\cdot}7$. The end of this extension can just be seen at the right-hand side of the photograph, slightly above the main crack.

Apart from the above, little change had taken place in cracks 1 and 2. More holes had formed, particularly on the portion of crack 1 in crystal " B," the whole of which was considerably widened into a groove of irregular width. At none of the places at which these two cracks crossed the boundary (five in all) could any signs of preferential corrosion either at the junction of the crack and boundary, or along the latter, be detected. Cracks 1 and 2 join at a point where crack 1 approached the boundary very closely and where there is a hole (present after the fourth test).

Cracks were found to have commenced from both ends of a large hole at $\lambda = 201{\cdot}5°$, $d = -4{\cdot}4$, which was present after the fifth test. The long, narrow portion of this hole had developed into a definite crack, which, after proceeding about half-way towards the left-hand fillet as a groove, or series of irregular holes, continued to the fillet as a fine crack, with occasional interruptions. The crack proceeding to the right from the hole was of narrow width throughout, and stopped before the boundary was reached. The two portions of this crack on either side of the hole were not collinear, but both agreed well with the operative slip direction in this region, which represents the maximum of the 13 direction.

The crack in crystal "B" started at a large hole at $\lambda = 245°$, $d = 13{\cdot}4$, which was present after the fourth test, and proceeded in both directions, roughly along the root of the radius, in an irregular manner, and also up the radius. Most of this crack consisted of a series of holes joined by short cracks of no particular orientation, and its propagation has probably been decided rather by stress concentration at the root of the radius than by resolved shear stress considerations, as in the case of the other cracks.

(c) *Local Attack—Large Holes.*

By the term "large hole" is meant a definite hole of much larger size than the small pits previously described. The latter were never more than about 0·02 mm. in diameter, and usually very much smaller, whilst those holes described as large were at least ten times this (linear) size. No such holes occurred during the first test, but after the second test a large hole was found on crack 1, at $\lambda = 95{\cdot}5°$, $d = -1{\cdot}3$. The crack will be seen running from each end of the hole, the two branches being parallel, but not collinear. This suggests that the hole was present before the crack, and that it may indeed have been the point at which the crack originated. There were several smaller holes on crack 1 and on crack 2 (the holes on which were on the average smaller than on crack 1), and one and a doubtful second away from the cracks, at $\lambda = 175°$, $d = 6{\cdot}2$ and $\lambda = 80°$, $d = 9{\cdot}6$, respectively. The latter holes were considerably smaller and obviously shallower than those on the cracks, and no traces of cracks could be seen in their vicinity.

A fairly large hole was found after the third test, with no crack, at $\lambda = 102{\cdot}5°$, $d = -2{\cdot}0$. This is fairly close to the large crack 1, and indeed occurs within the comparatively uncorroded ring surrounding the largest hole on the crack. It is similar to the holes found on the cracks, but has no surrounding rings. The position is away from the boundary and in a region of high shear stress containing fairly heavy slip. No increase in the size of this hole occurred in the remaining twenty-four million reversals of the test.

The occurrence of other large holes has been referred to above in connection with cracks.

(d) *Effect of Boundary.*

In all the examinations of the surface, special attention was paid to the vicinity of the boundary. The observations may be summed up in the statement that no indication was observed of any effect exerted by the boundary on the corrosive action, either by preferential corrosion at the boundary or by changes in the oxide film, or by crack propagation along the boundary. The development of crack 2 shown in Fig. 13 (Plate XXXVII) shows this very clearly, the position of the boundary being indicated only by the three changes of slope of the crack.

VII.—EXAMINATION OF THE CROSS-SECTION OF THE SPECIMEN.

After the specimen had received twenty-nine million reversals, it was considered that no further useful information would be obtained by continuing the tests. The specimen was therefore mounted in fusible alloy and cross-sectioned at the centre of the test portion. The cross-section was then metallurgically polished and examined under the microscope, the position of the cracks being mapped. Afterwards the section was etched in order to render visible the intercrystalline boundary.

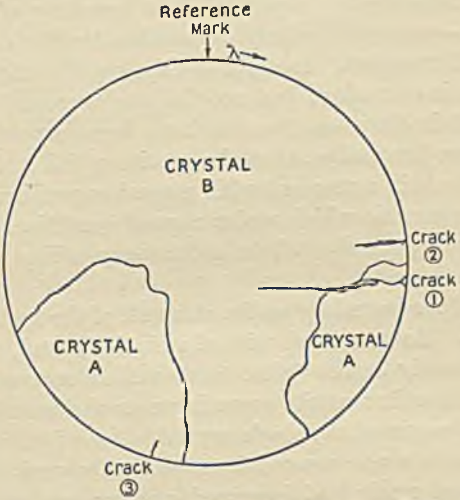


FIG. 15.—Diagram showing Traces of Cracks and Boundary on Cross Section.

The positions of the cracks and boundary are shown in Fig. 15, looking towards the end away from the reference end of the specimen. It will be seen that except for a very short distance along crack 1, the cracks show no tendency to follow the boundary. They appear to start parallel to the trace of the operative slip-plane, later becoming more or less radial. As shown in the diagram, most of the cracks were single, but in one place crack 1 branched out in a similar manner to that observed in several of the cracks on the single crystal specimen, this portion consisting of an intricate network of very fine cracks as shown in Fig. 11 (Plate XXXVI) (× 328). Fig. 12 (Plate XXXVI) shows the portion of the crack 1 which follows the boundary. Owing to the specimen having been deeply etched in order to bring up the boundary, the edges of the crack are very indistinct.

VIII.—General Discussion.

As regards the main object of the experiment, *viz.* the question as to whether more intensified corrosion would occur at the boundary and so lead to intercrystalline failure, the test shows quite conclusively that this is not the case in aluminium. The conditions—a specimen consisting of two large crystals separated by a boundary of a total length of about 3 in.—were particularly favourable for the development of such intensified corrosion. In spite of this, not the slightest evidence was found of this occurring; had not the cracks crossed the boundary and changed their direction it would have been impossible to detect, without previous knowledge, that the specimen did in fact contain a boundary. This is in agreement with general experience in corrosion-fatigue; even materials which under normal conditions fail by intercrystalline cracking usually fail in a trans-crystalline manner under corrosion-fatigue.*

The effect of the boundary on the strength of the specimen is somewhat indefinite. As compared with the single crystal, this specimen cracked considerably earlier (after three million reversals as against fifteen million), the first cracks occurring near the boundary. On the other hand, in the case of the single crystal, after a further nine million reversals, the surface was covered by a profuse system of cracks, and the total range of strain had increased greatly; whilst the boundary specimen withstood a further twenty-six million reversals after the cracks first appeared, at the end of which time only two new cracks had formed, and the strain, except for a slight temporary increase at about twelve million reversals, remained constant throughout the test. The boundary has also had extremely little effect on the stress-distribution as indicated by the slip, which agreed extremely closely with the calculated resolved shear stress: this is in agreement with similar two-crystal specimens tested in air.

Pitting, whilst generally similar to that in the single crystal, was rather less in extent, and joining-up of pits, although occurring in one or two areas of high resolved stress, was much less general. It can, however, be said quite definitely that the small pits had again no

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* See *e.g.* H. J. Gough, "Corrosion-Fatigue," *J. Inst. Metals*, 1932, 49, 70.

influence on the failure of the specimen. The pits, after reaching a certain very small size, appeared to develop only by joining up, and in no case did such joined-up pits develop into either a hole or a crack.

The behaviour of this specimen as regards the occurrence of large holes differed in some respects from that of the single crystal. The number of holes was much less, and in all cases they occurred near stress maxima, in many cases contributing largely to the failure of the specimen by the formation of cracks. These holes could be divided into three classes:—

(i) Holes from which cracks developed later, *e.g.*, those at $\lambda = 201{\cdot}5°$, $d = -4{\cdot}4$ and $\lambda = 245°$, $d = 13{\cdot}4$, and possibly that at $\lambda = 95{\cdot}5°$, $d = -1{\cdot}3$.

(ii) Holes occurring on cracks after these had been in existence for some time, *e.g.*, several of those on cracks 1 and 2.

(iii) Holes occurring away from cracks and not leading to cracks, *e.g.*, that at $\lambda = 102{\cdot}5°$, $d = -2{\cdot}0$.

Holes of class (i) in the single crystal specimen were quite exceptional, but in the boundary specimen the two holes mentioned were observed originally to have no traces of cracks proceeding from them, whereas cracks subsequently developed. The only hole of class (iii), which in the single crystal was very numerous, was one at $\lambda = 102{\cdot}5°$, $d = -2{\cdot}0$. It is noticeable that whereas the holes which occur on cracks, or which lead to cracks, progressively increase in size, this hole was not larger after twenty-nine million cycles than after five million.

Both specimens contain large numbers of holes of class (ii), these occurring on all the cracks in both specimens. These result from increased corrosion set up at the cracks, resulting first in the crack developing into a groove and later to local increases in breadth in the form of these large holes.

The hole at $\lambda = 95{\cdot}5°$, $d = -1{\cdot}3$ may be of either class (i) or (ii), but its appearance so closely resembles that of the one at $\lambda = 201{\cdot}5°$, $d = -4{\cdot}4$, that the probability is that this hole preceded the crack on which it is situated.

Whilst the initiation and growth of the class (ii) holes are easily explicable, the question of the initiation of those of classes (i) and (iii) is as yet unsolved. The opinion was expressed in the earlier paper that such holes might be due to etching pits, impurities, or inclusions. In the present case, all the large holes occur near resolved stress maxima. It is also quite clear that the boundary has played no part in their initiation; similarly, it appears highly improbable that they could have developed from the small pits, otherwise holes of intermediate size should have been observed.

The cracks on the single crystal specimen occurred, due to preferential corrosion, along the site of slip-bands previously formed, since the formation of slip had ceased some time before their appearance. In the boundary specimen, however, slip went on for some considerable time (at least two million cycles), and it thus appears more probable that, at least in the case of crack 2 which definitely did not originate at a hole, any preferential corrosion along slip-bands took place along *operative* slip-planes. In either case, the cracks occur in the regions of greatest plastic deformation, *i.e.* at stress-maxima, and follow the traces of the operative slip-plane. An exception to this is the isolated crack in crystal "B," the course of which is apparently controlled by stress-concentration at the root of the radius.

ACKNOWLEDGMENTS.

The experiment described forms an item of the research programme financed by the Department of Scientific and Industrial Research, and supervised by the Executive Committee of the National Physical Laboratory. The authors desire to express their appreciation to these bodies for the research facilities provided and for permission to publish the results. The authors' acknowledgments are also made to their colleagues in the Physics and Metallurgy Departments of the Laboratory, who kindly undertook the X-ray analysis and metallurgical polishing of the specimen; also to Mr. G. Forrest, B.Sc., of the Engineering Department for very considerable help rendered in the course of the experiment.

NOTES ON THE PREPARATION OF LEAD AND LEAD ALLOYS FOR MICROSCOPIC EXAMINATION.*

By BRINLEY JONES,† M.Met., MEMBER.

SYNOPSIS.

A method is outlined for the rapid preparation of lead and tellurium-lead for low- and high-power microscopic examination.

Time devoted to preliminary polishing is restricted, the true structure of the metal being revealed by chemical solution of surface layers. After the removal of recrystallized layers, sections may finally be prepared for high-power examination by a treatment of alternate polishing and etching, the final polishings being vigorous.

SINCE the presentation of the paper by W. Singleton and Brinley Jones on "Some Effects of the Addition of Tellurium to Lead," ‡ a number of inquiries has been received as to the methods adopted for the preparation of micro-sections of lead and tellurium–lead. In view of these requests, it has been deemed desirable to make this the subject of a separate contribution. The methods of preparation of micro-sections of lead and tellurium–lead used in connection with research work carried out by Singleton and Jones, are described below.

Two important features of any satisfactory method of preparing lead and lead alloys for microscopic examination are: (1) rapidity; (2) production of surfaces suitable for high-power examination.

Two photomicrographs taken from a section of lead pipe showing defects due to annular lamination are included in this paper. Approximately 35 minutes were spent in producing Fig. 1 (Plate I), an extra 10 minutes being required for Fig. 2.

The preparation of these photographs may be divided into four sections: (1) preliminary polishing; (2) preparation of the surface; (3) etching; (4) drying.

PRELIMINARY POLISHING.

Attempts to produce a perfectly smooth surface, by polishing alone, prior to etching, have been abandoned owing to tediousness and uncertainty, and as little time as possible is devoted to initial polishing. Saw-marks are first removed by filing, and the specimen is then gently rubbed on progressively finer grades of well-used emery paper. A saturated solution of paraffin wax in paraffin is used as a lubricant.

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† Research Laboratories of Goodlass Wall and Lead Industries, Ltd., Perivale, Middlesex.

‡ *J. Inst. Metals*, 1933, 51, 71.

The specimen is next rubbed for a short time on Selvyt cloth, which has been previously soaked with an emulsion of metal polish, soap, and the paraffin wax solution. It is quite sufficient at this stage to produce a surface free from unreasonably deep scratches.

PREPARATION OF THE SURFACE.

The next operation consists in removing a considerable surface layer of metal—recrystallized, scratched, and dirty—by vigorous chemical attack, and in accomplishing this without producing pitting. After cleaning with benzine, the section is treated with a solution of ammonium molybdate, such as is used for the determination of phosphorus. Drops of the reagent are repeatedly poured over the surface, which is continually washed with water, and to prevent irregular action, the specimen is frequently drawn across Selvyt cloth moistened with this solution. The true structure eventually begins to emerge, becoming more and more perfect as the dissolving and washing proceed. For low-power work, no further treatment is required, and the section may be washed, dried, and photographed. The grains are now revealed in contrast and with clarity, but high-power examination is not yet feasible. Fig. 1 (Plate XXXIX) illustrates a specimen treated in this way.

ETCHING.

After low-power examination, the specimen is again polished on the Selvyt cloth soaked with the emulsion previously described and then immersed in the following solution, recommended by Vilella and Beregekoff:* glycerol 4 parts, glacial acetic acid 1 part, conc. nitric acid 1 part. The nitric acid is added immediately before use, and the solution should be heated to a temperature of approximately 80° C. Alternate polishing and etching should now continue until the structure is satisfactory. An extremely bright, silvery appearance is soon obtained, and it is important to note that slow and delicate polishing is not now so necessary, since there is no longer a recrystallized layer of metal. The Selvyt cloth must be maintained in a soaked, slippery condition, so that the final polishing can be carried out with sufficient rapidity to give a perfectly flat surface. Fig. 2 (Plate XXXIX) illustrates a section after the final etching.

DRYING.

When it is certain that the structure has been completely developed, the specimen is dipped into boiling water and dried in an air blast so that evaporation of moisture is almost instantaneous. This is the simplest method which has been found to leave an unstained surface.

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* "Polishing and Etching Lead, Tin, and Some of their Alloys for Microscopic Examination," *Indust. and Eng. Chem.*, 1927, **19**, 1049–1052.

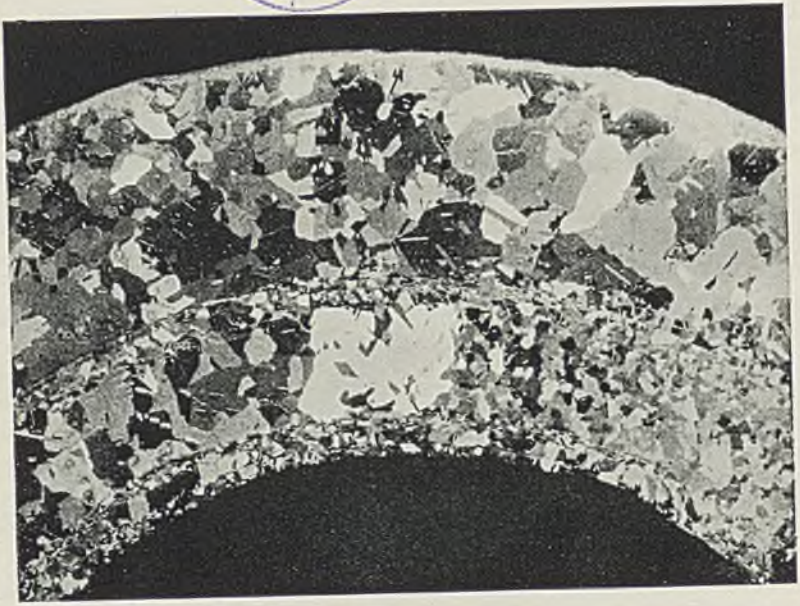

FIG. 1.—Lead Pipe Showing Defects due to Annular Lamination. Etched with Ammonium Molybdate Solution only. × 15.

FIG. 2.—Lead Pipe Showing Defects due to Annular Lamination. Etched with Ammonium Molybdate and followed by Glycerol Reagent. × 50.

AN INVESTIGATION OF THE HEAT-TREATMENT OF "STANDARD SILVER." *

By HUGH O'NEILL,† M.Met., D.Sc., MEMBER, G. S. FARNHAM,‡ B.A., M.Sc., MEMBER, and J. F. B. JACKSON,§ B.Sc.

SYNOPSIS.

The precipitation-hardening of quenched "Standard silver" (7·25 per cent. copper) has been investigated by Meyer hardness analysis.

Precision X-ray spectrograms obtained with Cu-radiation from thick disc specimens of the heat-treated alloy indicate that surface preparation may considerably affect the lattice parameter results. Polishing should be avoided in this work, and etching may have bad effects. Quenched "Standard silver" when reheated for 30 minutes in the 300° C. region is in a sensitive condition, and appears to precipitate completely when deformed. If precautions are taken, the lattice parameters indicate a normal progressive precipitation of copper constituent as the quenched alloy is reheated at increasing temperatures.

INTRODUCTION.

INCIDENTAL to a study of the hardness changes which accompany the reheating of quenched "Standard silver," certain inconsistencies were observed in X-ray work undertaken to reveal the corresponding variations of lattice parameter. In some cases, at least, these inconsistencies appear to be due to the method of preparation of the specimens. "Standard silver" quenched from 750° C. contains copper in supersaturated solid solution, the effect of this dissolved copper being to reduce the size of the cube edge (a) of the atomic space lattice of the silver. Progressive reheating of the quenched alloy followed by cooling should cause the copper constituent to be continuously rejected from the solid solution, and thus bring about a progressive increase of the solvent lattice parameter. This change was duly found in some series of observations, but different effects were noticed in others, whilst occasionally the X-ray spectra appeared to contain mixed lattices. Such factors as the polishing and etching of the specimens used, the attack of salt baths, and the possible heterogeneity of the alloy have all been considered in the course of this work.

HEAT-TREATMENT OF THE "STANDARD SILVER."

The alloy was originally cast by the makers in the form of ingots $1\frac{1}{8}$ in. thick, and supplied to the authors as hot-rolled plate 2·92 mm. thick, the

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analysis of which was silver 92·65, and copper 7·25 per cent. It was sawn into pieces, which were cleaned on emery paper, and then quenched and reheated for 30 minutes according to the particulars given in Table I. After reheating, the specimens were cooled in air, and in all cases except series 4, described below, they were rubbed on emery paper before reheating.

TABLE I.

Reference No.	Heat-Treatment.	Heating Bath.	Microstructure.	Brinell No. H1/10/30
O	Hot-rolled, as received	...	streaks of eutectic copper	72·5
Q	Soaked 30 minutes 750° C., quenched in cold water	$BaCl_2$, $CaCl_2$, NaCl	" austenitic "	50·5
T200	Quenched as above, reheated 30 minutes 200° C., cooled in air	paraffin	do.	60
T300	do. 300° C., do.	$55NaNO_3$, $45NaNO_2$	apparently " austenitic "	110
T500	do. 500° C., do.	"	" sorbitic "	83
T750	do. 750° C., do.	$BaCl_2$, $CaCl_2$, NaCl	" pearlitic "	72

TABLE II.—*Heat-Treatment and Strain-Hardening of "Standard Silver"* (7·25 *per cent. Copper*).

Heat-Treatment.	After Heat-Treatment.			After Subsequent Cold-Rolling (92 Per Cent. Reduction of Thickness).	
	Hardness.		n.	Hardness.	
	P_u, Kg./mm.^{2}.	Increase, Per Cent.		P_u^*, Kg./mm.^{2}.	Increase, Per Cent.
Quenched 750° C.	86 †	...	2·58	...	...
do.; aged 6 days	84	0	2·56	160	0
do.; reheated:					
200° C., 30 minutes	100	19	2·47	165	3
300° C. ,,	149	77	2·26	179	12
500° C. ,,	127	51	2·30	165	3
750° C. ,,	108	29	2·34	156	−3

* This value was obtained from a 10-kg. impression and the assumption that $n = 2·0$. The rolled metal was too thin to permit of indentation at various loads.

† Indentations completed within 12 minutes of quenching.

HARDNESS TESTS BY MEYER ANALYSIS.

The various specimens were indented with a 1 mm. ($D = 1$) steel ball at different loads, and the constants to the Meyer expression $L = ad^n$ were determined by logarithmic plotting. From these constants: $n =$ the *hardenability*; whilst the *hardness* $P_u = \frac{4a}{\pi} . D^{n-2} = 1{\cdot}273a_1$ (where $a_1 =$ a when $D = 1$). Hardness values in terms of P_u are strictly comparable, for they relate to ball impressions having always a constant angle of impression. The indentation results are given in Table II and plotted in Fig. 1.

It is evident from Fig. 1 that the hardness–reheating temperature curve for a progressive "precipitation" treatment passes through a maximum, whilst the n-reheating temperature curve has a corresponding minimum. Tempering beyond the hardness maximum leads to a softening associated with the "coarsening" of the precipitate, and this is accompanied by a slight steady rise in the n value.

The cold-rolling experiments make evident the differences in the hardenability of the alloy after the various reheating treatments. The general effect is to level out the peak in the hardness curve, as Norbury[1] has previously indicated. The specimen which showed maximum hardness on precipitation-treatment was still the hardest after 92 per cent. reduction, and the "pearlitic" specimen did not strain-harden as much as the "austenitic" (quenched) one.

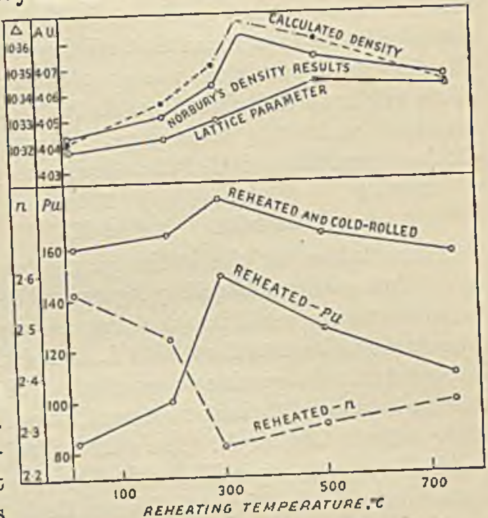

FIG. 1.—Quenched and Reheated "Standard Silver."

EXAMINATION BY X-RAYS AFTER VARIOUS SURFACE PREPARATIONS.

The technique employed to obtain X-ray spectrograms was a modified form of Dehlinger's "back-reflection" method using high-order planes such as the (511). The specimens, however, instead of being in powder form, were pieces of rather thick plate such as are suitable for small-ball hardness-testing and microscopic examination. The actual hardness-test specimens were used, and were fixed to a reciprocating mounting which the authors devised for attachment to the Hilger universal X-ray goniometer and which was operated by its clockwork mechanism.

Unfiltered Cu-radiation was employed from an X-ray tube working at 25–30 m.amp., and the time of exposure for silver alloys was generally 2–4 hrs. This soft radiation only penetrates such alloys to a very small depth—perhaps 0·001 mm. below the surface—and it is for this reason that surface preparation is so important.

Fig. 2(*a*) (Plate XL) shows a precision spectrogram of cast, pure silver which was annealed at 400° C. in a salt bath, after polishing. Whilst being X-rayed the specimen was stationary in this case, and the resolution is good. The same specimen after rubbing on "000" emery paper gave the result shown in Fig. 2(*b*), the lines being more continuous, but more diffuse, owing to the cold-worked surface layer. These spectrograms gave a lattice size for silver of $a = 4{\cdot}077$ A. which compares well with Owen and Yates' value of 4·0772 A.

As etching will rapidly remove the distorted Beilby layer, the authors were led to use etched specimens in the work which is described later. Actually it was then found that etching introduced troubles of its own. The first set of specimens was given a metallographic polish, etched in dilute sulphuric and chromic acids (as recommended by Norbury) and examined under the microscope. X-ray spectrograms subsequently obtained from them yielded the following results:

Series 1	Q.	T300.	T500.	T750.
a	= 4·064	4·072	4·064	4·061 A.

These values for the lattice parameter were most unexpected, as equilibrium results obtained by Ageew and Sachs [2] led the present authors to believe that a would increase progressively from about 4·03 A. in the quenched specimen to about 4·08 A. in a fully "pearlitic" one. It was suspected that the spacing values obtained in series 1 were unreliable, and this not because of the heat-treatment, since the Brinell tests corresponded fairly well with Norbury's. The authors' belief was that variations in the surface layer were responsible for the discrepancies. The peculiar danger of surface distortion in this particular case lies in the fact that strain-hardened metal reaches equilibrium more rapidly than unstrained metal; consequently in heat-treatments such as these, where time is known to have an effect, the outside layer may run ahead of the core of the specimen and yield X-ray values which are not representative, and do not necessarily correspond with hardness-test results. A second series of specimens was therefore prepared, which will be referred to as series 2.

Series 2 was treated as series 1, but no polishing was applied after final heat-treatment. When the metal had been taken from the hot bath and cooled, it was cleaned by etching in a solution of nitric acid 10, chromic acid 1, and water 89 per cent. The results for lattice parameter are reported in Table III, and neither agree with series 1 nor give the expected range of values. Specimen 2 (T300) gave two sets of lines. As specimens Q and T200 always etched slowly and the others relatively quickly, it was decided to prepare another series with only a slight etching attack.

Series 3 was treated similarly to series 2, *i.e.* no polishing was applied subsequent to heat-treatment, but in the first place it was accorded what will be designated as treatment (3α) and was given a flash etch of a few seconds' duration in an ammonium persulphate solution. This was applied to remove the slight effects of salt bath attack. The results reported in Table III for the three treated specimens seemed to be too high, and it was decided to dissolve away some of the surface and to re-test. Treatment (3β) consisted in the removal of a layer 0·0025 in. thick from the face of the specimen by attack with 50 per cent. nitric acid, followed by washing. As Table III shows, this treatment gave results similar to those for series 2, except that two of the specimens now showed double rings, *i.e.* two lattice sizes. It was suspected that the inner metal had a different chemical composition, and the specimen was therefore etched still further. Treatment (3γ) consisted of the removal of a further 0·0025 in. of alloy with nitric acid in the case of two of the specimens, Nos. T200 and T300. The uniform parameter results of 4·075 A. in both specimens (Table III) indicated that there was either heterogeneity in the alloy, or a breakdown of the supersaturated solid solution by the etching reagent, or a preferential solution and removal of copper by the etching reagent. An attempt was first made to prepare metal free from any possible heterogeneity, it being realized, for instance, that "inverse segregation" might give a silver enrichment in the core of the plate of about 0·3 per cent.

Series 4, therefore, aimed at a more thorough solution treatment and the avoidance of polishing before reheating. The alloy, as received, was cold-rolled to 1·68 mm. (43 per cent. reduction), soaked at 800° C. for 5 hrs., quenched, cold-rolled again to 1·04 mm. (38 per cent. reduction), and soaked at 800° C. for another hour before quenching.

Specimens (4α) were given a flash etch in ammonium persulphate and X-rayed. The quenched specimen gave a result (4·064 A.) similar to the quenched metal in series 1, and this was considered to be high and unrepresentative. The surface was therefore removed by etching.

Specimen (4β) was thus the same as quenched (4α) after 0·005 in. had been removed with nitric acid. It gave two spacings—4·038 A. and 4·075 A., the first of which seemed to approach the expected value.

Specimen (4γ) was (4β) etched until only 0·5 mm. thick, *i.e.* it was practically the core of the alloy. The X-ray spectrogram was surprising, being simply a collection of spots scattered over the film, together with a faint 4·075 A. spectrum. This indicates almost unbelievable heterogeneity or else mixed etching products.

Specimen (4δ) was specimen (4γ) after polishing and re-quenching from a further soak of 30 minutes at 750° C., followed by final polishing. The idea was to remove etching products and heterogeneity if these were present, and also to avoid etching effects by finishing in the lightly polished condition. This resulted in some blurring, but as etching seemed to introduce troubles of its own, a blurred film was still most likely to settle the question of the lattice size of the quenched alloy. The X-ray spectrogram of this specimen gave the result $a = 4{\cdot}038$ A. and this is believed to be the true value.

TABLE III.

Heat-Treatment.	Surface Preparation.	Parameters (A).		Film Reference.
		Ring 1.	Ring 2.	
Q750° C., Q800° C.	Series 1 polish + etch	4·064	...	...
	,, 2 etch	4·056	...	...
	,, 4α flash etch	4·064	...	...
	,, 4β deep etch	4·038	4·075	...
	,, 4γ very deep etch	scattered spots	4·075	Fig. 4
	,, 4δ requenched and polished	4·038	...	Fig. 3
Q750° C., T200° C.	Series 2 etch	4·042	...	Fig. 3
	,, 3α flash etch	4·061	...	...
	,, 3β deep etch	4·042	4·075	Fig. 4
	,, 3γ very deep etch	4·042 (faint)	4·075	...
	do. repolished	4·042	...	...
Q750° C., T300° C.	Series 1 polish + etch	...	4·072	...
	,, 2 etch	4·049	4·072	Fig. 3
	,, 3α flash etch	...	4·072	Fig. 4
	,, 3β deep etch	4·049	4·072	...
	,, 3γ very deep etch	...	4·075	...
Q750° C., T500° C.	Series 1 polish + etch	4·064	...	...
	,, 3α flash etch	...	4·075	Fig. 4
	,, 3β deep etch	4·064	...	Fig. 3
Q750° C., T750° C.	Series 1 polish + etch	4·061	...	...
	,, 2 etch	4·061	...	Fig. 3
Q800° C., T800° C.	do. + polishing	4·061	...	...
	,, 4α flash etch	4·064	...	...

It is natural to inquire why specimen (4α)Q should not have given this result. The authors can only suggest that either the salt bath had a deleterious effect, or else that the outer skin did not quench efficiently. As regards the (3α) series, it is believed that these did not yield proper results because the polishing after quenching caused the outer layer, on reheating, to accelerate its precipitation. When this skin was dissolved away as in specimen (3β)T300, the correct result was obtained, but very deep etching caused the high-silver ring as shown in specimen (3γ)T300. Incidentally, Norbury's work shows that the strained alloy recrystallizes at 250°–300° C., so that the polished layer will not go through the same process in treatments Q and T200 (see Table I) as in the others.

PLATE XL

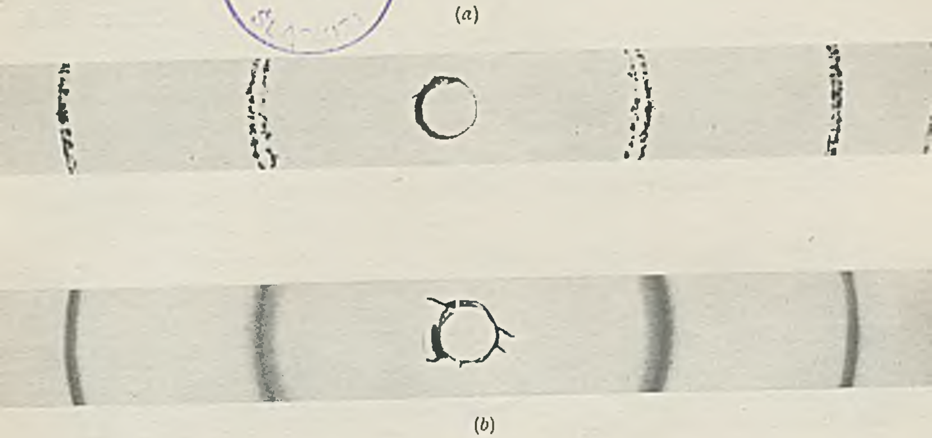

FIG. 2.

(*a*) Precision Spectrogram of Annealed Silver. (*b*) The same after Polishing on "000" Emery Pa

(A different camera-radius was used for Figs. 3 and 4.)

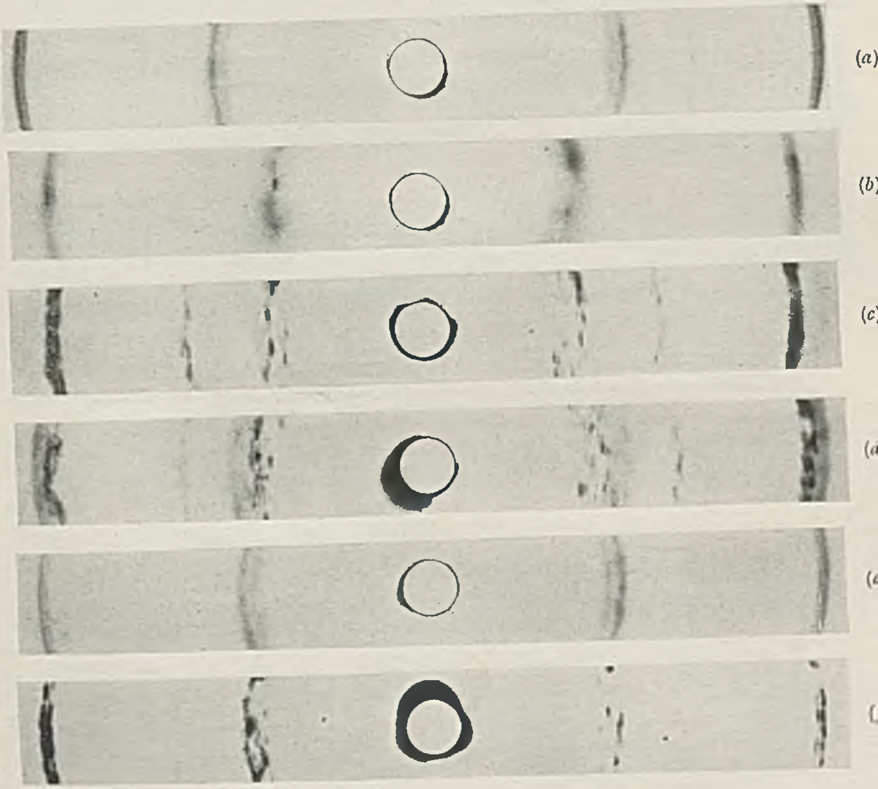

FIG. 3.

(*a*) As Received.
(*b*) Q750° C. or 800° C.
(*c*) Q750°, T200° C.
(*d*) Q750°, T300° C.
(*e*) Q750°, T500° C.
(*f*) Q750°, T750° C.

PLATE X

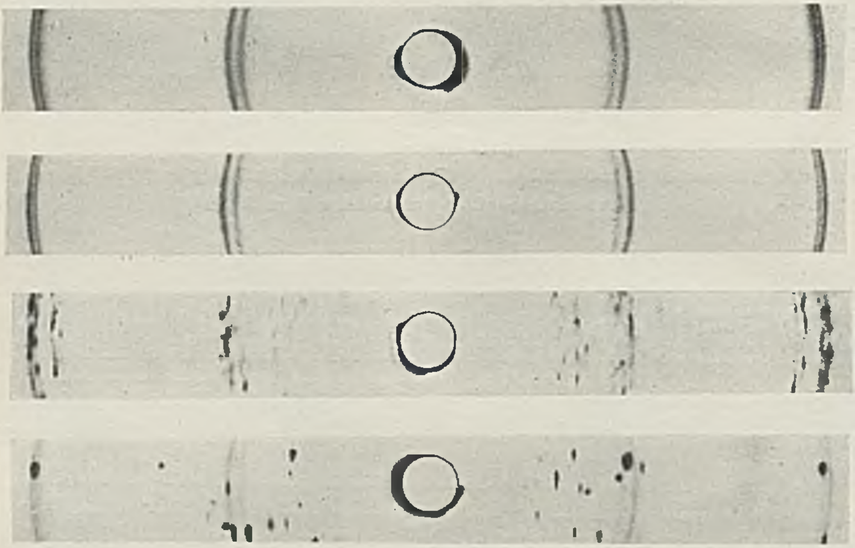

FIG. 4.

(*a*) T300° C.—3α (Flash Etch).
(*b*) T500° C.—3α (Flash Etch).
(*c*) T200° C.—3β (Deep Etch).
(*d*) Q800° C.—4γ (Very Deep Etch).

It is evident from Table III that the deeply-etched specimens when X-rayed tended to give a ring corresponding with $a = 4{\cdot}075$ A. This strongly suggested that the reagents used dissolved away most of the copper atoms in preference to the silver (Ag = 4·077 A.) or else precipitated the copper. Avoiding these etch results, it appears that the specimens examined gave evidence of a surface layer differing from the remainder to the following extent:

Specimen.	Q.	T200.	T300.	T500.	T750.
Surface (A)	4·056–·064	4·061	4·072	4·075	4·064
Remainder (core) (A)	4·038	4·042	4·049	4·064	4·061

It is believed that the parameters given above for the "core" of the specimens are those which must be considered in relation to the hardness results.

The "As Received" Specimen.

The alloy in the original, rolled condition was examined for heterogeneity by taking an X-ray spectrogram from the unetched surface after cleaning with "000" emery paper. The specimen was then etched away until it was very thin, and again X-rayed. This brought up the 4·075 A. ring, and so the metal was slightly polished to remove the etching effect. The subsequent spectrogram showed two parameters, the 4·075 A. having disappeared, as was expected. The values obtained may be summarized as follows:

Surface, cleaned on "000" emery paper	4·077 A.
Core (after very deep etching) . .	4·061–4·075–3·63 A. (faint).
Core after repolishing . . .	4·061 ... 3·63 A. (faint).

The very indistinct line at 3·63 A. must be due to the precipitate of copper-rich solid solution, for copper has a spacing of 3·6078 A. The as received specimen therefore appears to be heterogeneous, with $a = 4{\cdot}077$ A. at the surface, and $a = 4{\cdot}061$ A. in the interior. There is a difference of opinion as to the solubility of copper in silver at room temperatures, but Stockdale[3] suggests that it is greater than 0·8 per cent. at 200° C., and this appears to give a spacing of about 4·071 A.[2]

TESTS ON VACUUM-QUENCHED SPECIMENS.

It is obvious that any possible effect due to salt bath attack could be avoided by quenching the alloy *in vacuo*. Cleaned pieces of metal were therefore heated and quenched in a Rosenhain furnace. The vacuum obtained was not sufficiently perfect to prevent a slight tarnishing of the specimens, and it was unfortunately considered necessary to clean the metal by very gentle treatment on "000" emery paper. The results obtained from this series were as follows:

Vacuum quenched 750° C.	4·038 A.
V.Q.750°, T200° C. in oil	4·042 A.
do. T300° C. in oil	4·072 A.
do. T500° C. *in vacuo*	4·061 A.

Repeated attempts were made in this way to secure a specimen reheated at 300° C. which would give the 4·049 A. spacing recorded in Table III. The slight polishing treatment apparently upsets the equilibrium condition in such a way that the worked layer jumps over to the precipitated state. This effect was confirmed by taking the specimen from series 2 which showed the 4·049 A., and a faint 4·072 A., spacing. After polishing it by hand on "000" emery paper, only the 4·072 A. rings could be obtained, the remaining solid solution having apparently become precipitated by the energy applied during polishing.

A further experiment, though in itself not entirely critical, gave results consistent with this conclusion. Pieces of alloy after reheating at 200° and 300° C. were cold-rolled to 92 per cent. reduction in thickness. Whatever the surface preparation of the unrolled specimens may have been, the original "changed layer" after this amount of reduction can have only a practically infinitely small thickness, consequently an X-ray spectrogram will be representative of the body of the metal. The spacings obtained after rolling were 4·042 A. and 4·072 A. respectively, indicating that deformation had fully precipitated the specimen T300 but not the T200.

DENSITY RESULTS.

From the parameter values obtained by the authors for the "core" of the specimens, it is possible to calculate their densities and to obtain comparisons with actual determinations made by Norbury[1] for a similar alloy quenched from 770° C. For this purpose it is necessary to know the equilibrium amount of dissolved copper corresponding with the lattice parameters of the variously heat-treated specimens, and the difference between this and the total copper must be treated as precipitated "copper constituent." The latter is practically pure

TABLE IV.

Specimen.	Lattice Parameter, A.	Amount by Weight of Dissolved Copper Corresponding to this Parameter (from Ageew and Sachs), Per Cent.	Average Density (Calculated).	Density Determined by Norbury for a Similar Alloy.
Q	4·038	6·65	10·32	10·322
T200	4·042	5·85	10·33$_5$	10·330
T300	4·049	4·56	10·35	10·342
T500	4·064	2·10	10·36	10·353
T750	4·061	2·75	10·34	10·345

copper and can be assigned a cube edge of 3·61 A. An average density for the two phases is then calculated in the ordinary way. Equilibrium solubility values have been interpolated from the graphs of Ageew and Sachs [2] and are recorded with the other data in Table IV.

Norbury's values, reported in Table IV, are interpolated from his published curves, and the agreement between them and our calculated values may be considered satisfactory.

REFERENCE TO OTHER WORK.

When the authors' experiments were concluded, the results of Ageew, Hansen, and Sachs [4] were examined for any evidence of the trouble which had been encountered in this investigation. The alloy which they describe most nearly corresponding with that of the present authors contained only 6·3 per cent. copper, but the general type of the results should be the same. Only one of their treatment temperatures actually corresponded with those of the present investigation, and the particulars of this are given in Table V, which has been compiled from their curves and spectrograms. (Figs. 17 and 9, respectively, in their paper.)

TABLE V.—*Silver* + 6·3 *per cent. Copper* (*after Ageew, Hansen, and Sachs*).

	Quenched at 770° C. *in vacuo.*	Quenched at 770° C.; Tempered at 300° C. for		
		10 minutes.	20 minutes.	360 minutes.
Approximate Brinell No.	48	55	70	95
X-ray spectrum	supersaturated lattice	stable precipitation lattice + trace of supersaturated lattice	stable precipitation lattice only (4·075 A. approx.)	

Their X-ray evidence obtained with Cu-radiation indicates that precipitation of the quenched alloy to the final stable form is to all intents and purposes complete after 20 minutes' heating at 300° C. This condition might be expected to give a microstructure of the troostitic or sorbitic type, yet such a structure is not found as a result of the treatment. Furthermore, complete precipitation in this alloy would suggest that the Brinell number would by then have reached its maximum value or would be declining. Actually, however, the maximum in the Brinell hardness appeared only after much longer heating than the 20-minute treatment. The authors are therefore inclined to wonder whether the large "precipitation lattice" shown for the reheating at 300° C. for 20 minutes is not due to an unrepresentative surface layer, such as might be caused by rubbing the specimen with emery prior to reheating.

Then again, Ageew, Hansen, and Sachs found that the behaviour of a quenched single crystal of their alloy differed remarkably from that of a single aluminium crystal containing 5 per cent. dissolved copper. The latter preserves essentially its mono-crystalline character during precipitation at 250°–300° C., whereas the former "appears to decompose into a disarranged complex."[5] The authors would point out that this latter result may be obtained if the silver alloy is distorted by polishing during the course of its preparation.

SUMMARY.

(1) The reheating of a supersaturated solid solution (quenched "Standard silver") to bring about progressive precipitation gives a hardness (P_u) curve passing through a maximum which corresponds with a minimum in the Meyer n value curve. The coarsening of the precipitated micro-constituent is accompanied by a fall in hardness (P_u) and a slight rise of n.

(2) The lattice parameter of quenched "Standard silver" (7·25 per cent. copper) after reheating for 30 minutes at 200° C., 300° C., and 500° C., has been measured by a method taking precision X-ray spectrograms from relatively thick plates or discs of metal. The results indicate a normal progressive precipitation of the copper constituent with increase of reheating temperature.

(3) When X-radiation from copper is employed for this work, great care must be taken with the surface preparation of the specimens. Polishing and etching after quenching should be avoided, and heat-treatment in a high vacuum is to be recommended.

(4) The quenched alloy after reheating to 300° C. seems in particular to be in a very sensitive condition. There is evidence in this case that plastic deformation after reheating brings about a further degree of precipitation than is induced by the reheating alone.

ACKNOWLEDGMENTS.

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REFERENCES.

[1] A. L. Norbury, *J. Inst. Metals*, 1928, **39**, 145.
[2] N. Ageew and G. Sachs, *Z. Physik*, 1930, **63**, 293.
[3] D. Stockdale, *J. Inst. Metals*, 1931, **45**, 154.
[4] N. Ageew, M. Hansen, and G. Sachs, *Z. Physik*, 1930, **66**, 350.
[5] G. Sachs, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1931, 39.

MAGNESIUM ALLOY PROTECTION BY SELENIUM AND OTHER COATING PROCESSES. PART II.*

By G. D. BENGOUGH,† M.A., D.Sc., MEMBER, and L. WHITBY,† M.Sc., MEMBER.

SYNOPSIS.

Small losses of weight of Elektron alloy AZM (sheet) resulting from corrosion by immersion in, or spraying with, sea-water have been found to be associated with serious losses of elongation. Visual inspection did not suggest the extent of the damage, which occurred even when the alloy was protected by chemical coatings and paint.

THE methods of comparison used were loss of weight, visual inspection, and change in tensile properties. Some tensile results, obtained by Dr. L. Aitchison, are given in Table I, and refer to Elektron AZM, in sheet form, sprayed three times daily with, or immersed in, natural sea-water for 21 days. The test-bars were only 1·6 mm. thick × 1·5 cm. wide and it is clear that a great deterioration of properties of the

TABLE I.—*Effect of Corrosion by Sea-Water on Bare and Selenium-Coated Elektron AZM Specimens.*

Corrosion Treatment.	Proof Stress, Tons/in.².	Ultimate Stress, Tons/in.².	Elongation, Per Cent. on 2 in.	Loss in Weight, Grm.
		Uncoated Specimens.		
Nil	7·65	18·9	10	...
21 days' spray	6·3	10·1	1	1·61
"	5·8	10·8	2	1·58
21 days' immersion	2·5	3·0	nil	2·37
"	1·5	2·9	"	2·25
		Selenium Coated.		
Nil	7·6	19·3	13·5	...
21 days' spray	8·0	12·9	2·5	0·56
"	7·7	13·7	2·5	0·42
21 days' immersion	7·7	12·2	2·5	0·34
"	7·8	14·4	3·5	0·25

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bare alloy has been brought about by both types of test; also, that a selenium coat preserves, to some extent, the proof and maximum stress figures, but does not prevent an almost complete loss of elongation. Moreover, this loss is much greater than would be expected from the losses of weight and visual inspection. Figs. 1 and 2 (Plate XLII) are photographs of uncoated and coated specimens after corrosion, and although the latter shows much less attack, the ductility of both has almost vanished.

TABLE II.—*Effect of Chemical Coats and Paints on Subsequent Corrosion of Elektron AZM Sheet.*

Treatment.	Ultimate Stress, Tons/in.^{2}.	Elongation, Per Cent. on		Loss in Weight, Grm.
		2 in.	1 in.	
(1) Selenium only	18·4, 17·7	14·0, 11·0	14·0, 10·0	...
(2) Selenium and paint after storing for 4 months	18·6, 18·3	14·0, 13·0	15·0, 12·0	...
(3) As (2), but after 4 months' sea-water spray	16·7, 16·8	6·0, 6·0	7·0, 6·0	(Fig. 5) 0·03, 0·03
(4) As (3), but scratched . . .	15·3, 15·7	4·5, 4·5	5·0, 5·0	(Fig. 6) 0·05, 0·04
(5) Alum-dichromate treatment only	18·9, 18·9	15·5, 16·5	14·0, 19·0	...
(6) As (5), but painted and stored for 4 months	19·1, 19·0	13·5, 15·0	14·0, 16·0	...
(7) As (6), but sprayed for 4 months .	12·8, 13·0	2·5, 2·0	2·0, 2·0	(Fig. 4) 0·75, 0·42
(8) I.G. treatment only . . .	18·6, 18·4	15·0, 11·0	17·0, 10·0	...
(9) As (8), but painted and stored for 4 months	18·8, 19·0	15·0, 15·0	15·0, 16·0	...
(10) As (9), but sprayed for 4 months .	16·1, 15·9	5·0, 4·5	4·0, 4·0	0·05, 0·09
(11) Panalumin treatment only . .	19·0, 18·7	17·0, 16·0	16·0, 15·0	...
(12) As (11), but painted and stored for 4 months	18·6, 18·5	12·5, 11·5	12·0, 11·0	...
(13) As (12), but sprayed for 4 months	13·8, 15·9	2·0, 4·0	2·0, 4·0	0·33, 0·12
(14) Blanks (no treatment) . .	19·3, 19·1	18·0, 17·5	16·0, 16·0	...
(15) As (14), but painted and stored for 4 months	18·7, 18·7	12·0, 12·0	12·0, 12·0	...
(16) As (15), but sprayed for 4 months	11·8, 11·6	1·5, 2·0	1·0, 2·0	(Fig. 3) 1·25, 1·19

It is clear that the selenium coat alone has not given adequate protection, and its value must depend on its behaviour as a paint base.

Table II relates to specimens with paint under-coats of zinc chromate in sulphur-treated oil and top coats of zinc oxide in thermoprene resin superposed on bare metal or on metal coated with a selenium film,* an alum-dichromate film,† or other chemically produced paint base; uncorroded (control) specimens were used for each protection scheme. The test-pieces were strips 15·6 cm. long × 1·5 cm. wide between test marks, × 1·6 mm., and were sprayed with sea-water thrice daily for 4 months.

Table II shows notable variations between duplicates, which may be partly due to variations in the alloy itself, so that interpre-

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* *J. Inst. Metals*, 1932, 48, 151. (The selenious acid bath was used.)

† Sutton and Le Brocq, *J. Inst. Metals*, 1931, 46, 53.

tations must be made cautiously. All the coating processes seem to have lowered the elongation of the specimens by amounts up to 6 per cent. before any corrosion has occurred. Table I, however, based on another batch of material, shows that the selenium process has not decreased it. In both Tables losses of weight greater than about 0·1 grm. almost eliminate ductility.

The paints used, when applied to bare metal or over a Panalumin coat, seem to have lowered the elongation by 4 or 5 per cent. before spray treatment, but have had no important effect when applied over the selenium, alum-dichromate, or I.G. process coatings.

None of the sprayed specimens retained its initial elongation; the selenium-coated specimens behaved best, and retained more than one-third of the original amount, or 6–7 per cent. in all; the I.G. process specimens were next best, with about 4 per cent.; the others resembled the uncoated metal. Figs. 3–6 (Plate XLIII) show some of the test-specimens after spraying. A scratch, sufficiently deep and wide to expose the alloy itself through coats of selenium and paint, caused a drop of elongation from about 6 to 4–5 per cent.

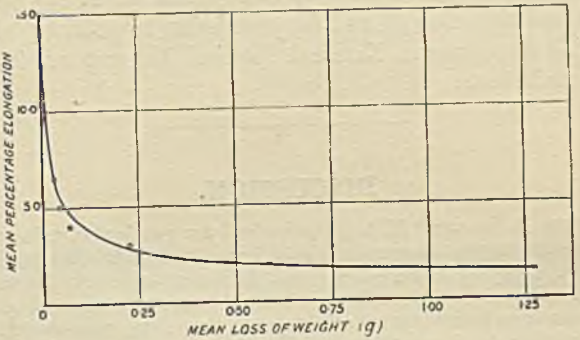

Fig. 7.

These results are serious, because visual inspection and loss of weight measurements again failed to give any idea of the real damage to the mechanical properties; for instance, the painted selenium specimens lost only 0·03 grm. in 4 months, and appeared to be almost unattacked (see Fig. 5), yet serious fall of elongation had occurred. Fig. 7 illustrates the relation between loss of weight and elongation; the curve rather resembles a rectangular hyperbola, a form that would indicate that elongation was inversely proportional to loss of weight; close agreement with this relation would not be expected, since some of the shallower corroded areas would not affect the tensile results. Since elongation is not a definite property of a metal, but varies with the conditions of test, the curve-form cannot be regarded as typical of the alloy tested, but only of the alloy in the special conditions of test.

The paint scheme used for the tests of Table II was not as good as at least one other tried by us, as judged by loss of weight tests. This included a top coat of cellulose medium pigmented with aluminium over selenized metal and the under-coat of Table II. Tensile tests will be made on this and other promising combinations.

ACKNOWLEDGMENTS.

This research is being carried out for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, and the thanks of the authors are due to the Chairman, Sir Harold Carpenter, F.R.S., and to Professor G. T. Morgan, F.R.S., for many facilities afforded and for permission to publish; also to the Engineering Department, National Physical Laboratory, for carrying out the tensile tests.

DISCUSSION.

DR. ULICK R. EVANS,* M.A. (Member): I am particularly glad to express accord with this paper, because I shall be forced shortly to express dissent with some of Dr. Bengough's recent statements about differential aeration. On that subject, I would ask that final judgment be suspended until both sides of the case have been heard, and would suggest that those who share Dr. Rosenhain's misgivings on the matter should refer to a paper published by T. P. Hoar and myself,† in which the velocity of corrosion, calculated from purely electrical data by the help of the differential aeration principle, has been compared with the values obtained by direct experiment. The excellent accord gives an assurance that the differential aeration principle has not yet outlived its value.

The authors' first paper on the present subject was most promising; the present paper is pitched, perhaps, in a minor key, and, whilst we all regret the need for that, the authors have clearly been wise in stating quite openly the imperfections of the protection process in its present form.

A paper by Herzog and Chaudron,‡ tabulates, for several metals and corrosive conditions, a certain index number, obtained by dividing the percentage loss of strength by the percentage loss of weight. If the corrosion has taken off a uniform slice of material, that index number should clearly be unity, and as a matter of fact for many cases of approximately uniform corrosion the index does fall between 1·0 and 1·2. In the case of localized or intergranular attack, the index is much higher; in one case, the figure 8·6 is quoted. I believe that if Mr. Whitby cared to calculate the Herzog–Chaudron index for

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* Cambridge.

† U. R. Evans and T. P. Hoar, *Proc. Roy. Soc.*, 1932, [A], 137, 364.

‡ E. Herzog and G. Chaudron, 8^{me} Congrès de Chimie Industrielle (*Chim. et Ind.*, **1929**, Special Number (Feb.), 335).

FIG. 1.—Untreated Elektron AZM Alloy Test-Bar after Immersion in Sea-water. Corrosion Product Removed.

FIG. 2.—Selenized Elektron AZM Alloy Test-Bar after Immersion in Sea-water. Corrosion Product Removed. Several of the dark marks are due to selenium not removed by cleaning bath.

(All test-bars shown full size; corrosion products *in situ* in Figs. 3–6.)

[*To face p.* 88.

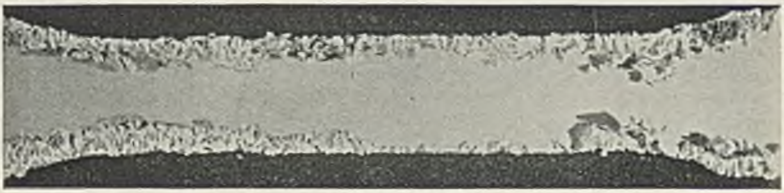

FIG. 3.—AZM Alloy Test-Bar Painted and Sprayed for 4 Months.

FIG. 4.—As Fig. 3, but with Alum-Dichromate Film as Paint Base.

FIG. 5.—As Fig. 3, but with Selenium Film as Paint Base.

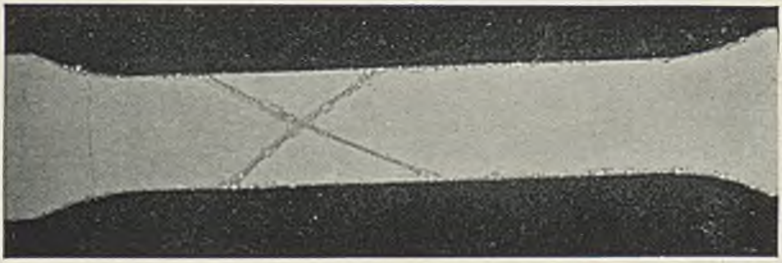

FIG. 6.—As Fig. 5, but Scratched.

(All test-bars shown full size; corrosion products *in situ* in Figs. 3–6.)

his own results, they would show still higher numbers. The necessary data are not published in the paper, but they are doubtless available in his notebook.

Now, why does corrosion produce abnormal weakening in certain cases and not in others? Speaking quite generally, one would expect to obtain weakening where the pitting ends in a sharp V-point, and this will become serious unless the pit becomes saucer-shaped as it develops. On theoretical principles,* which, however, may not quite apply to magnesium, a V-shaped pit would be expected to turn into a saucer-shaped pit, unless stresses are present, in which case it is likely to continue as a knife-shaped crack. Whether the theoretical treatment is applicable or not, one does tend frequently to obtain a saucer shape when no stresses are present, and (as is very well shown in Dr. Gough's work †) a knife-edge type where there are stresses continually present. That may mean that under service conditions, where stresses arise, the results may be even worse than are shown in the present paper. This is not said to criticize the work, but it is necessary to consider all the facts before a possible line of improvement is suggested.

How can the corrosion be expected to go in such a way as to avoid this weakness? The best hope of avoiding undue weakening appears to rest on a combination of coating and alloy which will produce a maximal rate of penetration *parallel* to the surface and not *at right angles* to it; this will cause local stripping of the coat, but that would be preferable to the alarming loss of strength actually obtained. Is it hopeless to expect this parallel penetration? I believe that it is not, because it does occur in many other cases. The familiar weathering-off of scale from steel plates exposed to the weather is simply due to the fact that corrosion starts at a break in the scale and, instead of progressing downwards, proceeds sideways, loosening the scale, which after a few months peels off. If it penetrated downwards as quickly as it proceeded sideways, the exposure would be very dangerous. Another example is the transfer to glass or cellophane of the oxide films responsible for the interference tints on heated metal, notably nickel, which has been heated in air. The edge of the specimen is simply trimmed, exposed to anodic treatment, and the corrosion penetrates just under the skin, hardly touching the rest of the nickel. Other examples could be given of preferential velocity at an interface between oxide and metal or between some other foreign body and metal.

It appears, therefore, that a combination of film and metal is needed, which would give the maximum velocity horizontally instead of downwards. This may mean modifying the metal and perhaps avoiding some constituent which is causing maximum velocity along the edge of crystals. Here the view of Akimow ‡ may prove helpful. It may also mean modifying the film covering the metal. Theoretically the matter has been treated elsewhere on the basis of adhesional work,§ but the theory is possibly rather speculative, and the authors may be wise to approach the problem empirically. One hopes that in due course a satisfactory combination may be obtained which will fulfil all practical purposes and yet give a Herzog–Chaudron index not greatly exceeding unity.

Mr. H. Sutton,‖ M.Sc. (Member): The form of corrosion test employed by the authors appears to me a suitable one to provide information on the behaviour of the treated materials under marine conditions. The results,

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* U. R. Evans, *J. Inst. Metals*, 1932, 49, 116.

† H. Gough, *ibid.*, 1932, 49, 71.

‡ G. Akimow, *Korrosion u. Metallschutz*, 1932, 8, 197.

§ U. R. Evans, *J. Iron Steel Inst.*, 1933, 127, 440.

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

therefore, should be of practical value to all who are interested in this aspect of the subject.

The coating on selenized magnesium alloys seems to be more satisfactory with paints of the sulphur-treated oil type than with others. With enamels and varnishes of the more usual types the film appears to roughen, and very small bubbles or blisters can be seen when the films of paint or enamel are examined closely. I should be interested to know whether the authors associate the formation of these blisters or bubbles with oxidation of selenium.

The authors have referred to a chromate treatment developed at Farnborough. Since Mr. Le Brocq and I presented to the Institute our paper * on this subject, there has been some improvement in the chromate treatment of magnesium alloys, particularly with regard to the protection afforded by chromate treatment supplemented by enamels. There appears to be no harmful effect of chromate treatment films on enamels and paints of the usual types, so that from the practical point of view the chromate treatment processes have an advantage there.

In the case of the alloy of magnesium with 1·5–2·5 per cent. of manganese, chromate treatment followed by enamels has so far given results at least as good as, and generally better than, selenium treatment supplemented by the same enamels. The manganese alloy is preferred for parts exposed to marine conditions, on account of its higher intrinsic resistance to corrosion, and for many purposes the manganese alloy is preferred because it can be welded in a simple way.

The loss of ductility is a very interesting feature of the authors' tests, and its cause provides considerable scope for the imagination. It is early, perhaps, to ask the authors for their views on this point. In some samples of wrought aluminium alloys examined recently intercrystalline corrosion was first detected at a magnification of 1000 diam., and then clearly seen. In some cases it is extremely fine, and particularly so in thin-gauge sheets.

I was much interested in Dr. Evans's lucid exposition of possibilities in relation to new methods of protection of magnesium, and as regards the extension of the deep crack or fissure and the propagation of weakening in that way. He has made a suggestion which seems a very probable one with reference to the way in which the corrosion-resistance of the manganese type of alloy is achieved, and perhaps it would be fitting to refer to that again. Dr. Evans suggested in the discussion of Mr. Le Brocq's and my paper,† that the anodic parts received a deposit of an insoluble corrosion product, in the form of manganese oxide or some such compound of manganese, and that indeed seems to be the case. It is possible to detect traces of films on the manganese alloys, and there seems little doubt that other methods may be employed of protecting those parts which become anodic through ordinary corrosion reactions, by providing something in the alloy which, with the corroding agent, will form a solution depositing an insoluble product on the anodic parts.

Mr. WHITBY (*in reply*) : Dr. Evans made some very interesting suggestions as to the possible mechanism of the loss of elongation. We are very glad indeed to have these suggestions, since we must confess we had none of our own at all ! The question was quite open. No cracks could be seen from the corrosion pits, but that was under a magnification of only 300 diam. and Mr. Sutton has suggested that under much higher magnification we might have been able to see some type of intergranular action.

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* *J. Inst. Metals*, 1931, 46, 53–72.

† *Ibid.*, 1931, 46, 75, 76.

Dr. Evans has also been extremely optimistic about the possibilities of overcoming this trouble, and has suggested a possible means, but unfortunately has not gone far enough and told us exactly what type of film to use.

We are very glad to have Mr. Sutton's confirmation of the advisability of using this type of test for all kinds of marine corrosion. He asks if blisters on certain types of paint over selenium may be due to oxidation of selenium. I do not think that would be the case. Selenium is extremely stable, far more so even than sulphur, and it would not, I imagine, oxidize in air. It is possible that there is an intermediate coating between the selenium and magnesium of magnesium selenide, which is easily hydrolyzed by water vapour, so that blisters may be due to the evolution of traces of hydrogen selenide.

I am glad to hear that Mr. Sutton and Mr. Le Brocq have improved their chromate process, and I can only hope that they will be able to publish the method in due course.

With regard to the A.M.503 alloy, to which I think Mr. Sutton referred, it is interesting to know that certain other methods of treatment have given satisfactory results. We found A.M.503 alloy exceedingly difficult to deal with at times; one never seems to be able to get two successive batches of the metal the same so far as its subsequent corrosion rate is concerned. Sometimes the material resists attack extremely well for some months, while a second batch may corrode badly and disintegrate entirely in a few days. Whether this is due to local segregations of a manganese-rich phase of some sort we do not know, but on the whole the alloy, while very easy to protect when it is good, is on occasions exceedingly difficult to protect, so that its reliability is rather an open question at the moment.

CORRESPONDENCE.

Dr. Bengough (*in reply*): Dr. Wormwell and I have dealt fully with Dr. Evans's experiments elsewhere,* and see no reason for further discussion until further experiments are forthcoming.

The Authors (*in reply*): We see no advantage in the use of the proposed Herzog–Chaudron index. The introduction of a new term such as this is justified only if it indicates something more than the experimental results themselves or gives a better or wider comparison. The proposed index does not do this; its value would not depend solely on the material, but would vary with the shape of the test-bar—just as the experimental results do, so why not use them directly instead of a derived index?

We have not found the roughening or blistering mentioned by Mr. Sutton, except with very porous paints which would be unsuitable for use over any of the well-known types of protective film on magnesium. In addition to sulphur-treated oil, we have obtained satisfactory results with tung oil, linseed oil, glyptal resins, and varnishes; on AZM alloy all these paints gave better results on selenium films than on any other.

* *Proc. Roy. Soc.*, 1933, [A], 140, 401 *et seq.*

NOTE ON THE GREEN PATINA ON COPPER: EXAMPLES FROM ELAN VALLEY (WALES) AND DUNDALK (IRELAND).*

By W. H. J. VERNON,† D.Sc., Ph.D., Member.

Synopsis.

The patina from a copper structure in mid-Wales contained 20·75 per cent. basic copper chloride, as compared with 8·15 per cent. in the patina from a copper spire at Dundalk, on the east coast of Ireland (approximate ratio 2·5 : 1); this result is attributed to the influence of prevailing winds. Basic copper sulphate constituted the bulk of the deposit in each case, relationship of formula with period of exposure confirming the conclusions of previous work.

Examples of green patina on copper previously studied ‡ have represented a fairly wide range of open-air conditions; nevertheless, a further example has been sought that would illustrate the characteristic green coating under conditions as remote as possible from the town, yet not too near the sea. Such conditions appeared to be realized in a specimen recently obtained, through the kindness of Mr. J. W. Wilkinson, M.Inst.C.E., Chief Engineer of the Department, from the territory of the Birmingham Water Department, in the Elan Valley, mid-Wales. Recently, also, through the courtesy of the Rev. T. F. Campbell and of Mr. H. G. Tempest, plates dismantled from the old green copper spire of St. Nicholas Church, Dundalk, Co. Louth, Ireland, have been secured, from which the patina has been removed in the Laboratory. Analyses of both products have yielded results of some intrinsic interest, which are therefore now recorded.

Source of Materials.

Elan Valley: There are three valve towers in the Elan Valley (two on the masonry dams and one on the Foel Tunnel Inlet in Caban Reservoir), each of which is covered by a copper dome, 15–30 ft. in

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

‡ Vernon and Whitby, *J. Inst. Metals*, 1929, 42, 181; 1930, 44, 389. Vernon, *ibid.*, 1932, 49, 153.

diameter. Patina is displayed both by the domes and also by the lightning-conductor strips which lead from them, and from which, in fact, the sample of patina used in the analysis was obtained. The age of the structures is approximately 30 years. No products of combustion are liberated in the vicinity; the village of Rhayader is about 4 miles to the east, *i.e.*, away from the prevailing wind; at this point also the local branch railway line is nearest. To the west the country is wild and hilly, the whole gathering ground of nearly 45,600 acres having a population of less than 200, distributed over scattered farmsteads. The long average annual rainfall over this area reaches the high value of 67·2 in. The sea is about 30 miles distant, Aberystwyth (lying due west) being approximately the nearest point on the coast.

Dundalk: The copper spire of St. Nicholas Church, erected in 1787, had long displayed a fine green patina, and was known locally as "the old green spire"; for many years "crooked," due to the twisting of the underlying timbers, lightning finally led to its demolition in 1932. (It has since been replaced by another copper spire, laid this time on a steel frame.) Its height was 50 ft. above a supporting stone tower, which itself rises 60 ft. from the ground, or 75 ft. from sea level. Dundalk is a sea-port town, the population of which has grown from about 5,000 to a little over 14,000 during the "life-time" of the old spire. The church is about ¼ mile from the tidal estuary of the river and 2½ miles from the open sea.

DISCUSSION OF RESULTS.

Ultimate analyses of the products (Table I) and proximate analyses (Table II) generally confirm the conclusions of the earlier work. In particular, the proportion of basic copper sulphate in the Dundalk sample is the highest yet encountered. Whilst the combined amount of basic sulphate and basic chloride is approximately the same in each,

TABLE I.

	Elan Valley. Per Cent.	Dundalk. Per Cent.
Cu	52·11	54·53
SO_4''	19·92	18·16
Cl'	4·47	1·36
CO_3''	0·82	0·75
S''	0·12	Very small trace
Fe_2O_3	2·20	1·54
Al_2O_3	nil	1·92
Organic matter	0·33	0·35
Siliceous matter	0·26	0·05

it is remarkable that basic chloride is considerably higher in the Elan Valley than in the Dundalk sample, notwithstanding that the sea (to the influence of which the presence of basic chloride must be entirely due) is at a very much greater distance. The explanation is believed to lie mainly in the influence of prevailing winds (from west or south-west). This would be expected to favour the formation of chloride in the Elan Valley, since the sea lies to the west and south-west, the large English industrial districts lying to the east and north-east. On the other hand, at Dundalk, where the prevailing winds blow towards the sea and from the land (including both the town immediately behind and the greater part of the rest of Ireland), the formation of basic sulphate should be favoured at the expense of basic chloride.

TABLE II. *Proximate Analyses of Products.*

	Elan Valley.	Dundalk.
Basic copper sulphate	73·5% ($CuSO_4.2Cu(OH)_2$)	85·25% ($CuSO_4.3Cu(OH)_2$)
Basic copper chloride	20·75% ($CuCl_2.2Cu(OH)_2$)	8·15% ($CuCl_2.3Cu(OH)_2$)
Basic copper carbonate	2·6% ($CuCO_3.0{\cdot}7Cu(OH)_2$)	2·75% ($CuCO_3.Cu(OH)_2$)
Copper sulphide	0·35% (CuS)	...
Wind-borne material :	2·8%	3·85%
Ferric oxide	2·21	1·54
Alumina	nil	1·91
Organic matter	0·33	0·35
Siliceous matter	0·26	0·05

A noteworthy feature is presented by the formulæ of the basic sulphates and basic chlorides in relation to the period of exposure. In the Dundalk sample, taken from a structure after 150 years' exposure, the formulæ conform exactly to the requirements of the co-ordination theory, *i.e.*, $CuSO_4.3Cu(OH)_2$ (brochantite), $CuCl_2.3Cu(OH)_2$ (atacamite). On the other hand, in the Elan Valley sample (30 years' exposure) maximum basicity has not yet been reached, and basic sulphate, for example, has the formula $CuSO_4.2Cu(OH)_2$.

Basic copper carbonate is low in each case, confirming previous results. The actual values approximate very closely to each other (2·60 and 2·75 per cent.) and also to values obtained in other comparable examples (*e.g.*, the copper spire of North Mimms Church, Herts., 2·7 per cent.; weathercock of Moulton Church, Northants., 2·2 per cent.). Higher values of basic carbonate appear to be characteristic of more urban conditions of exposure.

Extraneous (wind-borne) material is also particularly low, as would be expected from the rural environment of the Elan Valley domes and the comparatively high altitude of the Dundalk steeple.

From the foregoing results it is clear that conditions in this country are such as to favour the formation of basic sulphate even in the most rural districts.

Acknowledgment is due to Mr. E. G. Stroud, by whom the analyses have been carried out. The work has formed part of a larger investigation under the Corrosion Research Committee of the Department of Scientific and Industrial Research; and for permission to publish this note the author is indebted to the Chairman, Professor Sir Harold Carpenter, F.R.S., and to Professor G. T. Morgan, O.B.E., F.R.S., Director of Chemical Research.

DISCUSSION.

Dr. J. A. **Newton Friend** * (Member): The paper is of interest to me from two points of view. First, there is the fact that it does deal with problems of corrosion, and secondly there is the fact that it is of very great interest mineralogically. Dr. Vernon has given analyses of the different patinas, and there are one or two remarkable points about them. It will be noticed, first of all, that the composition corresponds to five quite well known minerals. Omitting the copper sulphide, there are four. There is the malachite, $CuCO_3.Cu(OH)_2$, which occurs in the Dundalk specimen, and there is a somewhat smaller percentage of basic copper carbonate in the Elan Valley specimen; Dr. Vernon's analysis there corresponds very closely indeed to azurite. All his analyses indicate less basicity in the Elan Valley, which seems to suggest that an early product of carbonation would be more or less basic copper carbonate, which would gradually lose carbon dioxide and take up water, giving azurite; this would gradually lose more carbon dioxide and take up more water to give malachite. Of course, it is quite well known that malachite is frequently formed from azurite. I have a specimen here of azurite, the outer surface of which has been converted in places by aerial oxidation to malachite. There is also an interesting specimen of copper pyrites which, since it was dug up, has undergone a certain amount of oxidation, and has given a surface layer of brochantite, the material which Dr. Vernon found predominantly in the patinas of both the Dundalk and the Elan Valley specimens.

I should like to ask Dr. Vernon whether the figures which he gives on p. 95 are round figures, or if he has definitely ascertained that the analysis is so close that the basic sulphate, for example, may be definitely represented by $CuSO_4.3Cu(OH)_2$. That brings me to the second point. I take it that the patina is limited in quantity; indeed, from the specimen here it can be seen that there could not have been very much to analyse. I should like to ask Dr. Vernon what weight of patina he was able to analyse, what was the sensitiveness of his balance and what the percentage error would be.

I do not know if Dr. Vernon has seen the copper top to the Lickey Tower. I have been told that the Black Country side of the copper dome appears to have corroded differently from the other side. I certainly think that is worth looking at, and I am going to make a journey there as soon as I can.

Dr. J. C. **Hudson** † (Member): I am happy to be able to give immediate

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* Head, Chemistry Department, Central Technical College, Birmingham.

† Investigator, Corrosion Committee, Iron and Steel Institute and National Federation of Iron and Steel Manufacturers, Birmingham.

confirmation to the correctness of Dr. Vernon's explanation of the abnormally high content of basic copper chloride in the sample of patina from the Elan Valley in Central Wales. It so happens that one of the main corrosion stations of the Corrosion Committee of the Iron and Steel Institute and the National Federation of Iron and Steel Manufacturers is situated at Llanwrtyd Wells, about 20 miles from the Elan Valley; routine determinations of the atmospheric pollution are made here by collecting the rain water in a suitable gauge and analysing it for the total deposits of insoluble matter, soluble matter, chlorides, and sulphates. The results for the last period of 12 months are given below. Parallel results obtained at Woolwich, which has a mild industrial atmosphere, are added for purposes of contrast.

	Rainfall,* Inches.	Pollution (grm./Dm.²/year).			
		Insoluble Matter.	Soluble Matter.	Sulphates.	Chlorides.
Llanwrtyd Wells .	79	960	2,960	350	880
Woolwich . .	20	6,410	6,580	2,260	450

* Owing to evaporation from the gauge, the rainfall figures are necessarily only approximate.

The results for Llanwrtyd Wells probably apply fairly well to the Elan Valley. The low figure for the insoluble matter agrees with the fact that Dr. Vernon found very little wind-borne material in his patina sample. The most significant fact, however, is that not only is the total pollution at Llanwrtyd Wells much lower than that at Woolwich, 3920 and 12,990 grm./Dm.²/year, respectively, but there is also a marked inversion of the sulphate : chloride ratio. Thus, at Llanwrtyd Wells this ratio is 0·4, as against 5·0 at Woolwich. Chlorides preponderate at Llanwrtyd Wells, no doubt, as Dr. Vernon states, as a result of the heavy rainfall which carries inland a certain amount of sea-salt, and the character of the atmospheric pollution thus explains the high chloride content of his sample from the Elan Valley. On the other hand, at Woolwich and probably at most inland places in this country the deposit of sulphates is greater than that of chlorides.

Apart from the bearing of these figures on Dr. Vernon's observations, they are of interest in illustrating the variation in the character of the atmospheric pollution to be expected in this country, which is of practical importance as regards atmospheric corrosion. It seems to me that the sulphate : chloride ratio in the pollution at any particular locality is a very good indication of the general character of the atmosphere, because, in general, most of the sulphates come from the combustion of coal. I might add that for some time I have advocated that instead of using solutions of sodium chloride for laboratory spray tests on corrosion, as has been customary hitherto, a mixed solution should be used containing both sulphates and chlorides in which the sulphate radical predominates, because this approximates more nearly to practical conditions. A solution containing 16 grm. of ammonium sulphate and 4 grm. of sodium chloride per litre would represent the character of the observed rain water deposit in industrial atmospheres more closely than a 3·5 per cent. solution of sodium chloride.

Dr. C. H. M. Jenkins † (Member): The rather high chloride values of the

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† Senior Assistant, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

samples exposed in the Elan Valley are of interest, and suggest to me that the effect of spray on the corrosion product might be worth consideration. An examination of the dam usually shows that considerable quantities of spray arise from the water, and I should therefore like to hear the author's views on the influence of this factor.

The AUTHOR (*in reply*) : The examples described by Dr. Friend of changes taking place at the surface of minerals bear most cognately on the subject of the paper, because in the early stages of patina formation there is a transitional period during which the metal has a characteristic black appearance, and during this period there are sulphides and oxides present. As Dr. Friend has shown, atmospheric exposure of the corresponding minerals results in the formation of basic sulphate, or brochantite, at the surface. Clearly, such parallel mineralogical changes must be taken into account in considering the mechanism of patina formation. The development of malachite by way of azurite, as illustrated by Dr. Friend's minerals, is also of much interest; and I quite agree that the evidence supports the view that a similar transition results in the malachite found in the patina.

With regard to the accuracy of the analyses, we have been greatly helped by a method of weighing, due originally to Professor Conrady, that is capable of weighing to the nearest thousandth of a milligram on ordinary loads. Such precision is obviously not necessary when the final accuracy is dictated in other ways, and I do not suggest that it has been consistently attained in the present work, but our methods have been chosen as far as possible so as to restrict other sources of error, and the system of weighing has permitted, at all events, precipitates as small as 2 mg. in weight to be dealt with satisfactorily. It is difficult to quote a definite percentage error, because this depends on the particular radical under estimation and the amount of material available for analysis. To permit each constituent to be estimated in a separate operation, a minimum quantity of 0·25 grm. of patina is desirable. In the case of the Dundalk patina we had a generous supply of the material, and the percentage error must be very low. This is shown by the fact that the composition of basic copper sulphate in the deposit is in theoretical agreement with the brochantite formula; *e.g.*, the experimental " basicity figure " of 3 in the formula $CuSO_4.3Cu(OH)_2$ is not merely a " round number," but *accurately* 3·0. Incidentally it is perhaps a little unfortunate that the corresponding value for the Elan Valley sample happens to be very nearly 2; in this case, of course, the round number is purely a coincidence.

I am sorry that I have not seen the Lickey dome, but I hope to do so, particularly in order to examine the directional effect to which Dr. Friend refers.

Apart from their intrinsic interest, the data contributed by Dr. Hudson are most welcome as confirming, by a different method of approach, the conclusions of the present paper. A useful purpose would seem to have been served by both groups of results in demonstrating the importance of prevailing winds as a factor in atmospheric corrosion. I am in full agreement with Dr. Hudson as to the undue reliance that has been placed in the past on the salt-spray test; clearly it is illogical as a test for atmospheric corrosion in which the major part is played by the sulphate radical. Dr. Hudson's suggestion to use a spray in which sulphates and chlorides are jointly present is very pertinent, and is certainly in greater accord with observations in the field.

The point raised by Dr. Jenkins is an interesting one. It seems unlikely, however, that contact with spray from the reservoir could contribute, in virtue of the chloride content of the water, to the high content of chloride in the corrosion product. Possibly it may indirectly favour the accumulation of basic chloride as distinct from basic sulphate. On the whole, however, it seems more reasonable to regard the effects observed as being due simply to the high proportion of chlorides in the wind blowing from the Atlantic, and this view is supported by Dr. Hudson's figures, which show, in the *rain-water* collected in that district, an abnormally high chloride–sulphate ratio.

CORRESPONDENCE.

THE AUTHOR (*in further reply to the discussion at the meeting*): Regarding Dr. Jenkins' suggestion, whilst the evidence as a whole offers no support for the idea that contact with water spray may account for the high proportion of basic chloride in the corrosion product, there is nevertheless one direction in which some influence may be credited to this factor. From information supplied by the Chief Engineer of the Birmingham Water Department it would seem that patina made its appearance on the domes in an abnormally short period of time—(" colour appeared after about four to five years' exposure "). Very probably, therefore, the fact that the domes are kept wet for long periods encourages the formation of basic salts and reduces the duration of the transitional " black stage," without, however, affecting appreciably the relative proportions of chlorides and sulphates, which would still be dictated essentially by purely air-borne agencies.

Mr. A. N. CATHCART * (Member): I am glad that Dr. Vernon has continued his investigation of the green patina on copper with further notes on Elan Valley and Dundalk.

The appearance of the green patina at Elan Valley in the comparatively short time of 30 years is rather surprising in such a remote locality, as I have recently heard of an example of similar age, the copper spire at Kea Church in Cornwall, where conditions are apparently more favourable, but where there is no appreciable change. Kea Church is about 3 miles south-west of Truro, where there is a good example of patina on one of the spires of the Cathedral (completed about 1885). The prevailing wind here would come from the sea over a sparsely populated country with no towns, and consequently no products of combustion, while the Cathedral is in the centre of a small town. Kea is, I believe, rather low, whilst the Cathedral is, of course, a high building, and there seems to be no doubt that altitude plays a great part in the early production of the green patina.

The central dome of the Imperial Institute, South Kensington, now a conspicuous feature of that part of London, was green long before the lower domes and copper ornaments. This same downward progress can be seen at the present time at the Imperial Hotel, Russell Square. The central spire was completed about 2 years later than the lower spire (about 1903). The lower part has only partly changed, but the upper portion of the higher spire is quite a delicate green. The lower central dome of the adjacent Russell Hotel, although several years older than the Imperial Hotel, is much less pronounced in colour.

The AUTHOR (*in reply*): I am indebted to Mr. Cathcart for the further interesting examples he has quoted. The longer time taken for the appearance of green patina at Kea as compared with Elan Valley is no doubt due in part to the fact that prevailing winds in the one case bring practically only chlorides from the sea, whereas in the other they also carry sulphur dioxide from the industrial districts of South Wales. Very possibly, however, the factor

* Ewart and Son, Ltd., London.

suggested by Dr. Jenkins may also play a part, since at Elan Valley the metal surface must remain wet for longer periods than at Kea.

Comparing Kea with Truro, the difference in age of the structures is probably quite sufficient to account for the observed difference in appearance; but here again prevailing winds would favour Truro more than Kea. In addition, there is the influence of altitude which, within limits, is undoubtedly favourable to patina formation. It is interesting to learn that the topmost dome of the Imperial Institute was green " long before the lower domes "; even when all domes had been green for some years the upper ones appeared to rather greater advantage than those lower down.* I am glad that Mr. Cathcart has referred to other and at present better examples in London in which the influence of altitude may be observed.

* Vernon and Whitby, *J. Inst. Metals*, 1929, **42**, 193.

WEAR IN THE POLISHING OF PLATED AND OTHER SURFACES. *

By O. F. HUDSON,† A.R.C.S., D.Sc., Member.

Synopsis.

A series of tests was made in the laboratory of the British Non-Ferrous Metals Research Association to determine the comparative rates of wear of plated and other metal specimens under conditions of polishing as distinct from abrasion. The apparatus used is described, and the results obtained with the following materials are given, using magnesia on wet parchment as the polishing medium: pure platinum, pure palladium, platinum plating on brass, palladium plating ("soft," "hard," and burnished) on brass, nickel plating ("soft" and "hard") on brass, silver plating on brass (60 : 40).

Considered as loss of thickness, the rate of wear of the palladium-plated specimens was found to be greater than that of the platinum-plated specimens, but considered as loss of weight the wear of the palladium coatings was slightly less than that of the platinum coatings; whilst the precious metal coatings generally were more resistant than the same metals in massive form. Of the three types of palladium plating, that in the "soft" condition showed the greatest wear, but the differences were not great; there was little difference in the rates of wear of the two kinds of nickel plating. No definite or consistent relationship between hardness and rate of wear in polishing was revealed in these tests.

In some recent work carried out in the research laboratory of the British Non-Ferrous Metals Research Association, a series of tests on plated and other metal specimens was made to determine the comparative rates of wear under conditions of polishing as distinct from abrasion. A brief description of the apparatus used and the method of making the tests, together with examples of the results obtained, may be of interest.

I.—The Apparatus Used.

One of the chief requirements of an apparatus for tests such as these is that it shall give uniform wear over one surface of a specimen approximately 1 in. in diameter and about $\frac{1}{16}$ in. thick, a condition by no means easy to fulfil. After a number of preliminary trials, a fitting for attachment to one of the polishing machines used for metallographic work was designed, and is illustrated in Fig. 1. This fitting

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

consisted of a brass frame, *A*, carrying two spindles, *B*, which were rotated through gearing, *C* and *H*, from the central spindle, *F*, fitted to the rotating disc of the polishing machine. The spindles *B* were free to move up and down vertically, and were supported by springs, *D*. The top of each of these spindles was provided with a small platform on which weights could be placed, and the bottom ends carried detachable holders, *E*, in which the specimens were fixed. The holders were recessed, as seen in the spare holder shown at the base of the machine, to receive the specimen discs, allowing the surface to be polished to project slightly beyond the rim of the holder.

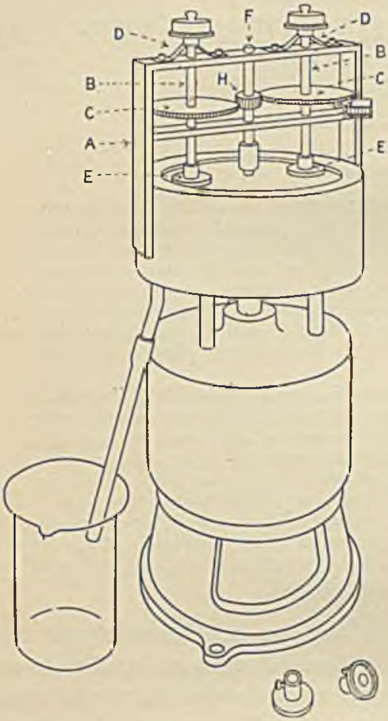

Fig. 1.

The mean diameter of the path of the specimens on the polishing disc was 4 in., and the length of run in each test was controlled by a counter to within 40 ft. The speed of test averaged 10 ft. per second. The counter used was an ordinary "cyclometer" fixed to the frame as shown and operated by one of the gear wheels (*C*). This simple device was considered sufficiently accurate for the purpose of these experiments, enabling the length of run in each test to be determined to within 1 per cent. The majority of tests consisted of a total run of 40,000 ft., although some were only 10,000 ft.

II.—Method of Carrying Out the Tests.

1. *Adjusting the Specimens in the Holders.* The specimen discs were secured in the holders by a small quantity of "Sira" wax, just sufficient to allow of a small adjustment of level under heavy pressure. The holders were then placed on the lower ends of the spindles, with the test surfaces bearing evenly on the polishing disc, but not tightened until the vertical position of the spindle had been adjusted to a gauge. When the holders had been firmly secured to the spindles by means of

set screws, the specimens were pressed down on the polishing disc, using a second gauge $\frac{1}{100}$ in. smaller than the first in order to obtain in all tests as far as possible uniform light loading of the specimen against the springs holding up the spindles. Tests made under these conditions are referred to as tests under " light loading." Other tests, referred to as tests under " heavy loading," were made with a weight (100 grm.) placed on the top of the spindles.

2. *Polishing Medium.* In these tests the polishing conditions were kept as constant as possible, magnesia on wet parchment being used throughout. In starting each test, magnesia was worked into the wet parchment along the path of travel of the specimens, and fresh magnesia, in the form of a thin cream with water, was fed on to the polishing disc at frequent intervals with a camel-hair brush.

3. *Procedure of Tests.* In all tests two specimens were used, one on each spindle, to allow of direct comparison of different materials. The standard complete test run of 40,000 ft. was run in four stages each of 10,000 ft., the specimens being cleaned, weighed, and changed over from one spindle to the other after each stage.

III.—MATERIALS TESTED.

1. Pure platinum, annealed, diamond hardness No. 53 increasing to 110 at the extreme surface layer.
2. Pure palladium, annealed, diamond hardness No. 49 increasing to 134 at the extreme surface layer.
3. Platinum plated on brass; thickness of coating 0·0001 in., diamond hardness No. 600 (approx.).
4. Palladium plated (" soft ") on brass; thickness of coating 0·0001 in.; diamond hardness No. 200 (approx.).
5. Palladium plated (" hard ") on brass; thickness of coating 0·0001 in.; diamond hardness No. 400 (approx.).
6. Palladium plated (" burnished ") on brass; thickness of coating 0·00015 in.
7. Nickel plated (" soft ") on brass; thickness of coating 0·002 in.; Brinell hardness No. 150 (approx.).
8. Nickel plated (" hard ") on brass; thickness of coating 0·002 in.; Brinell hardness No. 300 (approx.).
9. Silver plated on brass.
10. Brass (60 : 40); diamond hardness No. 130 (approx.).

The platinum and palladium specimens and the platinum- and palladium-plated specimens were supplied by the Refinery and Research Laboratory (Acton) of the Mond Nickel Co., Ltd., who also kindly provided the information regarding the hardness. Before the brass discs were plated they were polished on one face (the test surface) with the apparatus used for the tests.

For the tests on nickel-plating, silver-plating, and brass, discs were cut from a 1-in. diameter 60 : 40 brass rod. The nickel-plated specimens were prepared at the Research Department, Woolwich, by the kindness of Mr. D. J. Macnaughtan and Mr. W. A. Hothersall. The nickel-plated specimens were plated under conditions to give a coating with an approximate Brinell hardness number of 150 for the "soft" coatings and 300 for the "hard" coatings. The silver-plated specimens were plated by the usual commercial method.

IV.—RESULTS OF THE TESTS.

The results of the tests are summarized in Tables I and II, of which Table I gives the average figures for the rate of wear (loss of weight and loss of thickness), generally in three or more tests under conditions of "light loading" and "heavy loading," and Table II gives the ratios of the rates of wear (loss of thickness) of the materials when tested in the same test run.

TABLE I.—*Rate of Wear.*

Material.	"Light Loading."			"Heavy Loading."		
	No. of Tests.	Loss of Weight, Mg./cm.^{2}/1000 ft.	Loss of Thickness, Mm./1000 ft.	No. of Tests.	Loss of Weight, Mg./cm.^{2}/1000 ft.	Loss of Thickness, Mm./1000 ft.
Pure platinum . .	3	0·053	0·000025	3	0·098	0·000045
Platinum-plated . .	5	0·030	0·000014	2	0·080	0·000037
Pure palladium . .	3	0·065	0·000058	3	0·117	0·000103
Palladium-plated (soft)	3	0·038	0·000034	3	0·069	0·000059
Palladium-plated (hard)	4	0·031	0·000027	1	0·060	0·000053
Palladium-plated (burnished) . . .	2	0·028	0·000025	1	0·049	0·000043
Nickel-plated (soft) .	3	0·018	0·000020	3	0·033	0·000037
Nickel-plated (hard) .	3	0·025	0·000027	3	0·028	0·000031
Silver-plated . .	5	0·077	0·000073	3	0·094	0·000089
Brass 60 : 40 . .	7	0·039	0·000046	5	0·066	0·000078

The figure obtained for loss of thickness represents the average loss over the whole area of the disc. Actually it was not found possible in these tests to ensure perfectly even wear, and the platinum and palladium coatings were partly stripped in all tests, generally, although not always, near the edges. The tests were not, however, continued after about 10 per cent. of the area of the disc showed brass, and in most cases were stopped well before this stage was reached. The thicker coatings of the nickel-plated and silver-plated discs showed no sign of being worn through in any of the tests.

Table II.—*Ratios of Depth of Wear for Same Length of Test.*

Platinum-Plated.	Palladium-Plated.			Nickel-Plated.		Silver-Plated.	Brass 60 : 40.
	Soft.	Hard.	Burnished.	Soft.	Hard.		
"Light" Loading.							
1	2·3	2·4	...	...	...	4·9	...
	1	0·99	...	...	0·65	1·7	1·7
		1	1·04	...	...	...	1·8
			1	...	...	...	2·3
				1	1·13	3·7	2·4
					1	3·0	2·0
						1	0·7
"Heavy" Loading.							
1	3·3	...	...	...	1·9	...	...
	1	1·1	...	...	...	...	1·9
			1	...	...	...	1·7
				1	0·78	4·7	...
					1	4·5	3·8

The tests were carried out during a period of several months, and, although considerable differences in the rate of wear were obtained in separate tests of the same material made at different times, owing to difficulty in reproducing exactly the conditions of test, particularly the condition of the polishing pad and pressure of the specimen on it, the average figures obtained, and especially the ratios obtained for tests made at the same time, are believed to be reasonably representative of the comparative rates of wear of the different materials when polished with magnesia paste on wet parchment.

V.—Conclusions.

The results obtained in this investigation have shown that:

1. The rate of wear of "pure" palladium, considered as loss of thickness, was about twice as great as that of "pure" platinum in these tests under both conditions of loading. Considered, however, as loss of weight, the wear of palladium was only slightly greater than that of platinum.

2. The rates of wear of platinum-plated and palladium-plated specimens were less than the rates of these metals in massive form, the palladium-plated specimens having a greater rate of wear, considered as loss of thickness, than the platinum-plated specimens. Considered

as loss of weight, the wear of the palladium coatings was slightly less than that of the platinum coatings.

3. The differences in the rate of wear of the three types of palladium plating were not great, although the " soft " coating showed definitely the greatest rate under both conditions of loading.

4. On the whole, the rate of wear (loss of thickness) of the precious metal coatings was roughly of the same order as that of nickel plating.

5. There was little difference in the rates of wear of the two kinds of nickel plating.

6. Silver plating was definitely the least resistant to wear by polishing, of all the coatings tested.

VI.—Relation between Hardness and Rate of Wear by Polishing.

The results of these tests have shown generally very little relationship between the rate of wear and the Brinell or diamond hardness numbers; thus, the two kinds of nickel plating, of which the " hard " had approximately double the hardness of the " soft," gave about the same rate of wear. The " hard " and " soft " kinds of palladium plating showed a small difference in the rate of wear in favour of the " hard " plating, but the difference was nothing like so great as the difference in hardness. Except in the very broadest sense that the hardest surface (platinum-plated) had the greatest resistance to wear (loss of thickness) and the softest (silver-plated) had the least, the hardness number of the materials tested cannot be taken as a guide to the wearing properties, under conditions of polishing. Where there is abrasion, the hardness number may have greater significance.

Acknowledgments.

The author is indebted to the Council of the British Non-Ferrous Metals Research Association for permission to publish this note. His thanks are also due to Mr. F. G. Morris for the construction of the apparatus, and to Mr. L. Reeves for assistance in carrying out the tests.

DISCUSSION.

DR. W. ROSENHAIN,* F.Inst.Met., F.R.S. (Past-President): I am particularly interested in this paper because of the polishing material which Dr. Hudson has selected. I think that I am right in saying that the use of magnesia as a polishing agent for metallographic purposes was introduced by myself about 1904 and has since been very widely adopted. I was at that time very anxious to obtain polished surfaces of specimens consisting of two metals, namely iron and copper, in juxtaposition, and the difficulty was that the ordinary polishing reagents used, such as rouge and chromium oxide, dragged the one metal over the other to such an extent that the boundary line between the two became difficult to trace. I found that magnesia did less of that dragging than any other agent. It did not entirely abolish it, but it made it very much less. That was the reason why I used it extensively, and why afterwards it acquired a great deal of popularity.

The explanation which was always present in my mind for this behaviour of magnesia was that it was not a true polishing agent, but rather a very fine-grained abrasive. To discuss the theory of polishing now would take much too long a time; it is connected with the solubility of the polishing agent in the metal being polished, and I can imagine that magnesia has very little of that property, and that therefore its action is very largely abrasive and not wholly polishing. That can be verified by a high-power examination of a surface of steel, for instance, which has been polished by magnesia, on which can always be seen at any rate an appearance which suggests the presence of very minute scratches, whereas if a surface polished with rouge or chromium oxide is examined that is not the case. Whether it is merely a question of the degree of scratching I do not know, but it is an important matter, and I suggest to Dr. Hudson that possibly the rate of wear which he gets would be rather different if he used rouge instead of magnesia. No doubt he has realized that.

The other point to which I wish to refer is that it has been shown in recent years that abrasion, and I am speaking now definitely of abrasion, in spite of the fact that the author does not take abrasion as coming into his purview, is partly a chemical action, and oxidation plays a very considerable part, and therefore when metals like platinum on the one hand and nickel and even silver on the other, are compared, they are not compared under identical conditions unless the action of oxygen is excluded. The failure to discriminate between hard nickel and soft nickel is due very possibly to the fact that they are chemically attacked at very much the same rate. It is true that the experiments to which I refer have been carried out definitely with abrasion, but I suggest that abrasion cannot be eliminated from such experiments as these on polishing, and in fact if there is no abrasion I cannot see how there could be any loss of weight, although there might be a loss of thickness.

The AUTHOR (*in reply*): This paper was put forward as a record of certain experiments which had been carried out with one particular polishing material. If the opportunity occurs for us or for others to carry out further tests with different polishing materials—rouge, for example—I feel sure that some very interesting results would be obtained.

Dr. Rosenhain has said that in polishing operations such as this there is really abrasion, and probably it is quite correct that abrasion of a sort does take place. When I refer to the distinction between polishing and abrasion I mean the distinction between an operation such as the final polishing of metallographic specimens as compared with the grinding by abrasive such as emery before the final polishing stage.

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* London.

CORRESPONDENCE.

Capt. R. H. Atkinson,[*] (Member): It has occurred to me that particulars about the plating conditions of the palladium- and platinum-plated discs would add to the interest of Dr. Hudson's paper.

The soft palladium was deposited from an ammoniacal solution of tetramino-palladous chloride used as the catholyte in a diaphragm cell. The hard palladium was deposited by the so-called soluble anode process, in which a palladium anode was used and an electrolyte containing sodium palladonitrite and sodium chloride. The full description of these two processes is contained in a paper by A. R. Raper and myself.[†]

Mr. A. B. Coussmaker, of Messrs. Johnson, Matthey & Co., Ltd., who did the platinum plating, has contributed the following remarks:

The platinum plating bath used contained 10 grm./litre of platinum in the form of sodium hexahydroxyplatinate ($Na_2Pt(OH)_6$) dissolved in 5 grm. of caustic soda. To this solution 30 grm. of anhydrous sodium sulphate and 5 grm. of sodium oxalate were added. The method of preparing the plating bath is fully described in Patent Specification No. 391,119.

The deposits on the test-pieces were obtained by plating for 20 minutes at 65° C. at a current density of 0·05 amp./in.^{2}, the voltage across the plating vat being approximately 1·2 v.

It may be of interest to point out that the rate of wear of a platinum-plated specimen is to some extent influenced by the metal on which the platinum is deposited, that is, the metal of the specimen, or of any undercoat which may be applied, such as silver, copper, &c.

It is found, for example, that a deposit of silver on to nickel-silver or brass improves both the wearing and tarnish-resisting properties of a subsequent platinum plate. In practice, such an undercoat is usually applied, and platinum is found under these conditions to provide a highly satisfactory commercial plate, in spite of its extreme thinness.

Mr. H. N. Bassett[‡] (Corresponding Member to the Council for Egypt): Dr. Hudson's paper is very interesting indeed, but the fact that impresses one is that what he has measured actually is the rate of abrasion using a material which has only slight abrasive properties, and under conditions not precluding the formation of a surface film.

Dr. Rosenhain referred at the Meeting to chemical action as responsible sometimes for the formation of films under conditions similar to those under which Dr. Hudson's work was done. In the work carried out by French [§] on the wear testing of metals, in which bearing bronzes were tested in the Amsler machine, it was found that films of two general types were formed. In the case of lead-free bronzes these films were apparently copper oxide, but with leaded bronzes the film (also black) was either lead or a lead compound. Tests which included X-ray analysis failed to establish the precise composition. Such films had considerable effect on the bearing properties of the bronzes, and on the rate of wear. A noticeable fall in torque frequently accompanied the formation of the film, this fall being wiped out, and the torque increased when the film broke down with prolonged wear. It appeared that the films were most often formed in alloys containing from 15 to 25 per cent. of lead cast in sand moulds. Films were formed also on steel ring and plug gauges tested dry, the film causing seizing. The films were apparently iron oxide,

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[†] *Electrodepositors' Tech. Soc. Advance copy*, **1933**, April.

[‡] Chief Chemist, Egyptian State Railways, Cairo, Egypt.

[§] *Proc. Amer. Soc. Test. Mat.*, 1927, **27**, (II), 212.

and their formation was ascribed to the fact that the small metallic particles torn from the contact surfaces were pyrophoric, being of such small mass in proportion to the energy required to tear them from the body of metal that they burned, or at least oxidized, and when forced against the metal formed a coating or film. The films were not formed so easily when the testing was carried out in the presence of water.

Beilby showed many years ago that polishing of a metal, when properly carried out, caused a flow of the surface layer of molecules, so that an impervious layer free from discontinuities resulted. It would be interesting to know to what extent the surfaces prepared by Dr. Hudson are possessed of this "Beilby film," and whether in the case of the oxidizable specimens the surfaces were free from oxide or contaminated with it.

The formation of a metallic film under pressure was observed also some years ago in connection with the "Keenok" gear, using a lubricant containing zinc oxide. It was found that with a grease containing zinc oxide in excess of 50 per cent. the corrosion formerly experienced in the gear was overcome completely. The film which formed was of mirror-like appearance, and was of a thickness below the limit of microscopic visibility. From chemical analysis it was estimated that its thickness was of the order of 0·0004 mm. The building up of this film was due, no doubt, to electric stress caused by rapid variation of local contact pressure, and the conditions were therefore somewhat different from those in the experiments made by Dr. Hudson. It would be interesting to know, however, whether any of the polished surfaces contained traces of magnesium.

The AUTHOR (*in reply*): I thank Capt. Atkinson and Mr. Coussmaker for supplying particulars of the palladium- and platinum-plating processes. It is evident from this contribution that further tests on platinum and palladium plating in relation to the undercoat would probably give interesting results.

I also thank Mr. Bassett for his comments. There is much still to be learned regarding what actually occurs in various polishing processes. In the experiments described in the paper no visible oxide films were noted in any of the specimens after polishing. Dr. Rosenhain pointed out in the verbal discussion that magnesia caused far less "dragging" than other polishing materials, and I am of the opinion that there was very little of what Mr. Bassett referred to as the "Beilby film" present on the polished surfaces of the specimens. No attempt was made in these experiments to determine whether any magnesia was present in the polished surfaces.

THE CONSTITUTION OF THE ALUMINIUM-RICH ALUMINIUM-COPPER ALLOYS ABOVE 400° C.*

By D. STOCKDALE,† M.A., Ph.D., MEMBER.

SYNOPSIS.

A part of the work of Dix and Richardson on the solubility of copper in aluminium has been repeated and their results have been closely confirmed. Alloys near the composition $CuAl_2$ have been examined in detail by the micrographic method. A considerable range of solid solutions has been found, but no evidence for the existence of the compound $CuAl_2$ has been obtained.

THE aluminium used in these experiments was given by Messrs. The Aluminum Company of America, and contained not more than 0·03 per cent. of impurities other than copper: these impurities were chiefly iron and silicon in about equal proportions by weight. The copper, which contained not more than 0·004 per cent. of impurities other than oxygen, was supplied by Messrs. Thomas Bolton and Sons, Ltd. The author wishes to thank both these Companies.

THE ALUMINIUM SOLID SOLUTION.

A hardener containing 53 per cent. of copper was made by adding aluminium to molten copper in an Alundum crucible under hydrogen. A suitable set of alloys was prepared by melting together some 25 grm. of aluminium and different quantities of this hardener in Alundum crucibles under air. The metal was cast in a very hot, 1 cm., iron mould. By this means it was sometimes possible to cast unsegregated bars. The author's usual method for obtaining a uniform alloy by casting on to a cold, polished, steel block and at once covering the metal with iced water here quite failed; indeed, some plates cast by this method, after suitable heat-treatment to develop traces of a second phase, were excellent examples of inverse segregation. They showed layers rich in copper at both the top and the bottom.

The alloys were then annealed at 550° C. (just above the tem-

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† King's College, Cambridge.

perature of the eutectic—548° C.), until they were uniform solid solutions, and quenched. A triple furnace [1] was used in finding the solidus. The tubes were so arranged that the temperature difference between the alloys would be 3° C. Specimens of any one alloy were then put into the tubes in such a way that their temperature increased quickly to that at which the solid solution is stable. The temperature was then allowed to creep slowly up to that at which the specimens were to be annealed. This temperature was maintained for some 18 hrs. The electro-thermostatic control was so efficient that accidental variations in temperature during this short period were almost undetectable. The specimens were then quenched and examined under the microscope, the etching reagent being 0·5 per cent. aqueous hydrofluoric acid. The solidus is determined in every case probably correct to 3° C.; in the case of the 5·3 per cent. copper alloy all experiments were duplicated and the accuracy here may be somewhat greater.

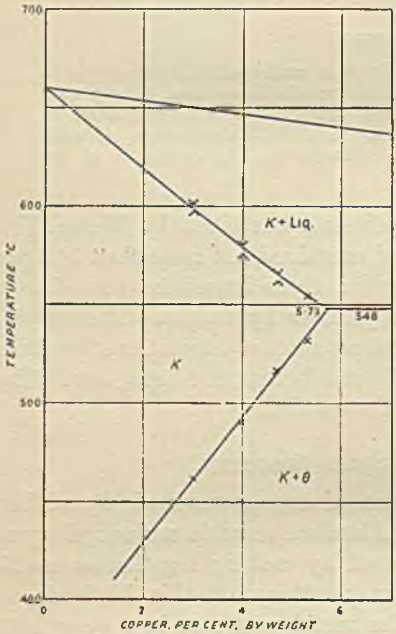

Fig. 1.

The results are shown in Fig. 1. The solidus line is very slightly convex to the aluminium-rich solid solution, this convexity being more apparent if the results are expressed in atomic percentages, but for practical purposes it may be taken to be a straight line. It passes through the point (3Cu, 599° C.) and cuts the eutectic line at 5·7(2) per cent. copper. Dix and Richardson [2] found the solidus to be a straight line intersecting the eutectic horizontal at 5·65 per cent. copper.

Similar methods were employed to determine the solid solution boundary. Uniform solid solutions were prepared and quenched. Specimens were heated rapidly to some temperature above the boundary and cooled slowly to the annealing temperature. The annealing time was at least 42 hrs., and the tube difference was 5° C. As many experiments were carried out in duplicate, and as it is possible to estimate the critical temperature from the amounts of second phase in alloys

FIG. 3.—52·68% Copper. Quenched from 570° C. × 150. θ + traces of liquid.

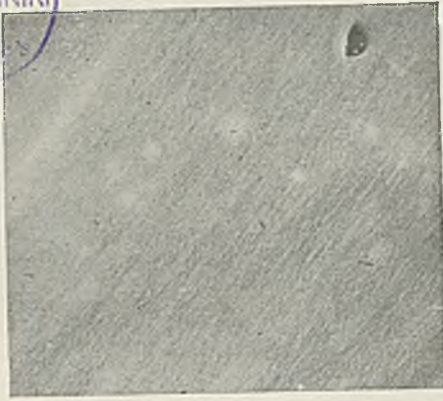

FIG. 4.—52·68% Copper. Quenched from 511° C. × 150. θ + minute traces of κ.

FIG. 5.—52·68% Copper. Quenched from 403° C. × 150. $\theta + \kappa$ (black).

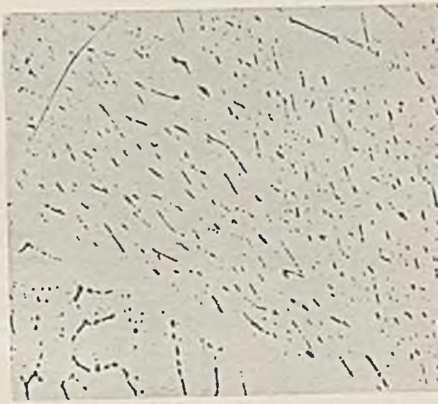

FIG. 6.—51·52% Copper. Quenched fro 500° C. × 75. $\theta + \kappa$.

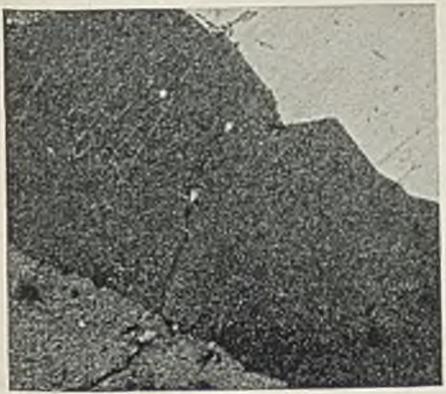

FIG. 7.—53·69% Copper. Quenched from 551° C. × 150. θ + minute traces of η (white).

FIG. 8.—Same alloy as Fig. 7. Quenched fro 588° C. × 150. $\theta + \eta$.

quenched at known temperatures below the phase boundary, it may be that each point was obtained with greater accuracy than 5° C. The boundary at these temperatures is a straight line leaving the eutectic horizontal at 5·7(4) per cent. copper and passing through the point (3Cu, 462° C.) (see Fig. 1). None of the experimental points falls farther than 2° C. from this line. This boundary is almost coincident with that of Dix and Richardson, who obtained their results by annealing alloys of different compositions at a constant temperature in contrast to the method adopted here.

The alloy nominally containing 5·3 per cent. copper was analyzed. It was found to contain 5·32 per cent. This close agreement and the manner in which the various points fell about straight lines rendered further analyses unnecessary.

The structures seen were almost identical with those illustrated by Dix and Richardson in their paper.[2] They are therefore not reproduced here. A point of interest is that the "rosettes and crescent-shaped particles" sometimes seen by Dix and Richardson in low copper alloys at high temperatures were never observed in this work, but it must be pointed out that here the lowest percentage copper alloy used contained as much as 3 per cent. copper.

THE θ-ALLOYS.

The letter θ was given by the author in an earlier paper[3] to denote the compound $CuAl_2$. As this new work throws doubt on the existence of such a compound, it is convenient now to refer to the range of solid solutions near 66 atomic per cent. aluminium by this letter and not by the customary formula. The lettering of the earlier paper is retained throughout.

The work here described is a repetition of the former work, undertaken because recent X-ray analysis[4] has pointed to a definite range of solid solutions, and because the author's somewhat tentative theory of alloys showed that his former results could not be correct.

The apparatus and methods were similar to those used in the determination of the aluminium-rich phase boundary. A copper-rich stock alloy was made and analyzed as before. A suitable set of alloys was prepared by adding aluminium–copper eutectic to the molten stock alloy under air, the melting being carried out in an electric furnace. The bars were chill-cast in a 1-cm. mould. No segregation was detected in these alloys. In fixing the solidus line (*BE*, Fig. 2) the specimens were given that heat-treatment which converted them into uniform solid solutions. The temperature was then increased to the quenching temperature and maintained there for at least 42 hrs. A similar plan was adopted for fixing *EF* except that the temperature was lowered and the annealing time was longer. The point *F* at 400° C. was obtained by cooling a set of alloys of slightly different composition to that temperature and annealing for 4 weeks. The points on *BG* were obtained by this last method, but the alloys were heated to the quenching temperature. The point *G* at 400° C. was also obtained after 4 weeks.*

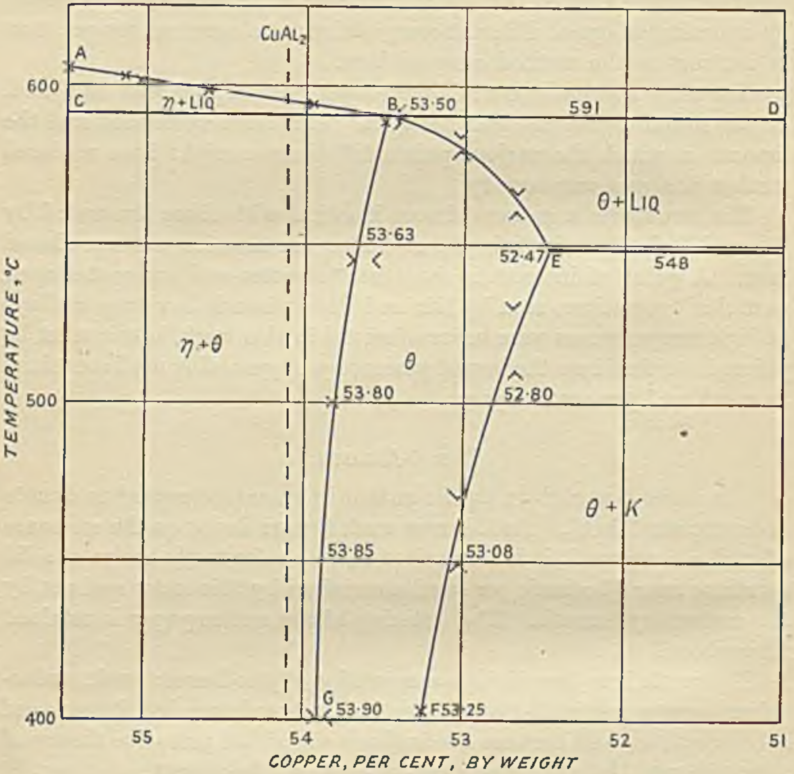

Fig. 2.

The alloys in this group are extremely brittle, and it is almost impossible to prepare for examination sections free from cracks and holes. Attempts to find an etching reagent which would leave the liquid and κ white, thus rendering easy the identification of traces of these phases, failed. These alloys are best etched with a 5 per cent. aqueous solution of hydrofluoric acid, and the characteristic triangular shape of patches of liquid and the rod-like form of the κ crystals must

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* The Table from which Fig. 2 was constructed is available for consultation in the archives of the Institute.

be relied on for their recognition (Figs. 3–6, Plate XLIV). Traces of η are left white by the following reagent: 20 c.c. concentrated nitric acid, 1 c.c. concentrated hydrochloric acid, and a few drops of an aqueous solution of copper sulphate, diluted to 100 c.c. By the use of this reagent, a thin film of copper is deposited on the θ, but not on the η (Figs. 7 and 8, Plate XLIV). It was thought that the recognition of the small traces of phases was faulty. A miscellaneous collection of sections was therefore prepared, all recognition marks were hidden, and a senior student was asked to arrange the specimens. Not only did his placing of the alloys in the various phase-fields agree with that of the author, but also in every important case his judgment on the relative quantity of second phase in the sections was the same.

The evidence given above shows that it is doubtful whether the compound $CuAl_2$ (Fig. 2) exists. As this is an important conclusion, attempts were made to confirm it.

In the first place, the analysis of the alloys is obviously of great importance, as low copper analyses move the θ-field to the right, away from $CuAl_2$. In the case of one alloy, four results were obtained by the possible combinations of solution in nitric acid and bromine, solution in *aqua regia*, deposition of copper (rotating anode) from nitric acid solution, deposition from nitric–sulphuric solution. The four results were 53·68, 53·67, 53·64, 53·66 per cent. copper. In another alloy, solution in *aqua regia* and deposition from nitric–sulphuric solution gave a mean of 52·68; the cuprous thiocyanate method gave a mean of 52·64 per cent. To obtain a further check, one of the alloys was sent to a recognized analyst, who returned a figure of 52·95 per cent. against the author's 53·28 per cent. copper. This at least indicates that the author's results are not too low.

In the second place, in order to make quite certain of the slope of the $\theta - (\eta + \theta)$ boundary, two alloys of similar composition were annealed for 44 hrs. at 551° C. After this treatment the first alloy (Fig. 7, Plate XLIV) showed minute traces of η and the second was a uniform solid solution, although when chill-cast both had contained considerable quantities of the second phase. The specimens were then divided, and a piece of each alloy was annealed for 44 hrs. at 588° C. Each showed a considerable quantity of η (Fig. 8, Plate XLIV).

In the third place, an attempt was made to determine the liquidus *AB* accurately. A sensitive apparatus and method were used,[5] but the quantity of η separating between *AB* and *CB* was so small that conclusive results were difficult to obtain. It is, however, almost certain that the liquidus line touches *CD* at some point poorer in copper than 54·1 per cent. ($CuAl_2$). The given diagram (Fig. 2) is probably the best expression of the experimental results. *CB* was found to be at 591° C. (Sb 630° C.; Cu–Al eutectic[6] 548° C.) and the liquidus given in the earlier paper[3] is substantially correct.

It is believed that this is the first time that a metallographer has doubted the existence of the compound $CuAl_2$ and has found such a range of solid solutions, except that Carpenter and Edwards[7] show the θ — (θ + liq.) boundary much as it is now shown. They do not appear to have made a detailed examination of the solid alloys. The idea of the compound is firmly rooted. $CuAl_2$ must have been carefully prepared and examined scores of times. Traces of η in the alloy of that formula have been found (for example, see Dix and Richardson).[2] It was therefore quite natural to conclude that $CuAl_2$ was incapable of forming solid solutions. It is also possible that the iron and silicon introduced through the use of impure aluminium cause other constituents to appear, and that they, together with the cracks and holes almost unavoidably present in sections, have hitherto made accurate work difficult. For one of these reasons, the author's 1924 diagram[3] fails to give a satisfactory account of these alloys and must now be revised.

CONCLUSIONS.

1. The solubility of copper in aluminium has been measured, and the results are in close agreement with those of Dix and Richardson.[2]

2. An alloy of the composition $CuAl_2$ always contains two phases above 400° C., although it is possible that it might become uniform at low temperatures.

3. A narrow range of solid solutions exists near the composition $CuAl_2$. An alloy containing 53·50 per cent. of copper exists as a uniform solid solution over a large temperature range, and probably melts at constant temperature. No simple formula can be given to such an alloy.

4. The triple point (θ, θ + liq., $\theta + \kappa$) is at 52·47 per cent. copper.

THE GOLDSMITHS' LABORATORY,
THE UNIVERSITY OF CAMBRIDGE.
May, 1933.

REFERENCES.

[1] Stockdale, *J. Inst. Metals*, 1932, **49**, 276.
[2] Dix and Richardson, *Trans. Amer. Inst. Min. Met. Eng.*, 1926, **73**, 560.
[3] Stockdale, *J. Inst. Metals*, 1924, **31**, 275.
[4] See Bradley and Jones, *J. Inst. Metals*, 1933, **51**, 131.
[5] Stockdale, *J. Inst. Metals*, 1930, **43**, 193.
[6] Archer and Jeffries, *Trans. Amer. Inst. Min. Met. Eng.*, 1925, **71**, 828.
[7] Carpenter and Edwards, "Eighth Report to the Alloys Research Committee of the Institution of Mechanical Engineers," *Proc. Inst. Mech. Eng.*, **1907**, 57.

CORRESPONDENCE.

Dr. A. J. Bradley,* (Member): I have read Dr. Stockdale's paper with great interest, especially with regard to the θ-phase. Some time ago we made up an alloy of the exact composition $CuAl_2$ in the hope of obtaining a specimen of the pure θ-phase. Much to our surprise, X-ray photographs of a slowly-cooled powder showed the existence of a considerable quantity of the η-phase. The purity of the metals being suspected, the experiment was repeated using other samples of aluminium from another source, but with the same result.

The X-ray analysis by Bradley and Jones † was made with an alloy containing considerably more than the theoretical amount of aluminium. It was found that the atomic arrangement was of the type AX_2, in which there are exactly twice as many X as A positions. The intensities of the X-ray spectra show that the A positions are occupied by much heavier atoms than the X positions. The latter are evidently filled by aluminium atoms, but since there are too few copper atoms to fill all the A positions, it is clear that a certain number of these must be occupied by aluminium atoms.

Because the structure of the θ-phase is of the type AX_2, it is convenient to describe the phase as $CuAl_2$, in spite of the fact that it is not a definite compound like CaF_2. There is a real difference between atoms in A positions and atoms in X positions, and the surplus aluminium atoms in A positions have not the same interatomic distances as those in X positions.

Mr. G. Phragmén ‡: Dr. Stockdale's observations on the composition range of the θ-phase are very interesting. He has found that the composition corresponding with the formula $CuAl_2$ is outside this range; *i.e.*, the θ-phase never contains more than 53·9 per cent. copper, whereas the compound $CuAl_2$ should contain 54·1 per cent. copper. The difference is not large, but must be accepted as experimentally proved. On account of this, Dr. Stockdale doubts the existence of the compound $CuAl_2$.

The crystal structure of the θ-phase has been investigated by X-ray methods.§ The elementary parallelepiped contains 12 atoms, and all the observations can be explained on the assumption that 8 atoms are aluminium and 4 copper. The fact that the composition does not exactly correspond with $CuAl_2$ is easily explained by the assumption that in a few of the elementary cells an aluminium atom is substituted for one of the 4 copper atoms. The formula $CuAl_2$ is thus of real importance for the description of the θ-phase, in spite of the fact that the composition of this phase never exactly corresponds with the formula.

There are some analogous cases. In the iron–silicon alloys there is a phase nearly corresponding with $FeSi_2$; the elementary cell contains only 3 atoms.‖ The formula corresponds with 50·2 per cent. silicon. However, an alloy with 52·5 per cent. silicon contains traces of a phase with lower silicon content; that is, the $FeSi_2$-phase is stable only if some of the iron atoms are replaced by silicon atoms or if some iron atoms are absent, leaving their places in the

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* The University, Manchester.

† *J. Inst. Metals*, 1933, **51**, 131.

‡ Metallografiska Institutet, Stockholm, Sweden.

§ E. R. Jette, G. Phragmén, and A. Westgren, *J. Inst. Metals*, 1924, **31**, 193; J. B. Friauf, *J. Amer. Chem. Soc.*, 1927, **49**, 3107; A. J. Bradley and P. Jones, *J. Inst. Metals*, 1933, **51**, 131.

‖ G. Phragmén, *J. Iron Steel Inst.*, 1926, **114**, 397; J. L. Haughton and M. L. Becker, *ibid.*, 1930, **121**, 315.

crystal lattice empty. The low number of atoms in the elementary cell excludes every formula other than $FeSi_2$.

The phases corresponding with the formulæ FeO, FeS, and FeSe also deviate in composition from that exactly corresponding with the formula. In these cases it has been found that the formulæ are the bases of the crystal lattice. The deviation in composition is caused by the fact that some of the "iron points" of the lattice are empty.*

In my opinion, it is appropriate to describe a phase of this kind as a derivative (by solid solution) of that chemical compound which is indicated by the crystal structure.

The AUTHOR (*in reply*): Dr. Bradley and Mr. Phragmén differ from me in that they wish to retain the formula $CuAl_2$. This formula, in the normal chemical sense, indicates a molecule containing one copper atom and two aluminium atoms in some kind of intimate association. In this special case the symbol "Cu" does not represent an atom of copper, but a position on the crystal lattice. Similarly "Al" represents a position. It so happens that the first set of positions are filled mostly by atoms of copper, and the second exclusively by atoms of aluminium, and that there are twice as many "Al" positions as there are "Cu." Here it is therefore convenient to use a chemical formula with a well-defined conventional meaning to describe a crystal lattice, but there is a danger that such use will lead to confusion.

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* G. Hägg, *Nature*, 1933, 131, 167; E. R. Jette and F. Foote, *J. Chem. Physics*, 1933, 1, 29.

THE CONSTITUTION OF THE SILVER-RICH ALUMINIUM-SILVER ALLOYS.*

By N. AGEEW,† Met.Eng., MEMBER, and D. SHOYKET,‡ Chem.Eng., MEMBER.

SYNOPSIS.

The constitutional diagram of the silver-rich aluminium-silver alloys has been determined by micrographic examination, X-ray analysis, and hardness measurements. The β'-phase (Ag_3Al) is converted on heating above 400° C. into a mixture of α and γ. The α- and γ-phase boundaries at high temperature have been determined by precision measurements of the lattice parameter and by micrographic examination of the quenched alloys. The β-phase is stable only at high temperatures, and below 600° C. is converted into the $\alpha + \gamma$ eutectoid.

INTRODUCTION.

THE intermediate phases in the silver–aluminium system are of great interest from the theoretical point of view. Although both metals have face-centred cubic lattices with almost the same parameter, $a = 4{\cdot}077_7$ A. for silver and $a = 4{\cdot}040_6$ A. for aluminium, the intermediate phases in the system have lattices with radically different symmetry.

The equilibrium diagram of the silver–aluminium system was first constructed by G. I. Petrenko [1] by thermal analysis and micrographic examination, and his work has been substantially confirmed by the X-ray investigations of A. F. Westgren and A. J. Bradley,[2] who also determined the lattice constants of the intermediate phases. Hardness and electrical conductivity measurements by G. Le Grix and W. Broniewski [3] indicated the existence of the compounds Ag_3Al and Ag_2Al_3, whereas E. Crepaz [4] from thermal analysis and micrographic examination postulated the existence of the compounds Ag_3Al, Ag_2Al, and Ag_3Al_2.

The equilibria in silver-rich alloys above 600° C. have been determined with great accuracy by T. P. Hoar and R. K. Rowntree [5] using thermal and microscopic methods, and R. T. Phelps and W. P. Davey [6] have investigated the α-solid solution by X-ray analysis.

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The main object of the work described in this paper was to determine the constitution of alloys containing up to 10 per cent. aluminium (about 30 atomic per cent.) at temperatures below 600° C. In constructing the diagram at this end of the system, the data of Hoar and Rowntree[5] have been used for the liquidus line. Fig. 1 shows the diagram constructed from the results recorded in this work.

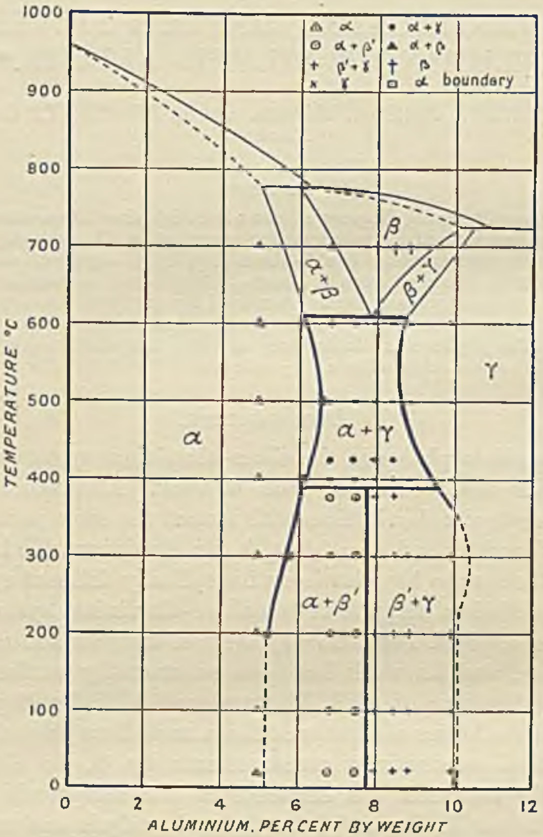

Fig. 1.—Constitution Diagram of Silver-rich Aluminium–Silver Alloys.

Preparation of the Alloys and Details of Experimental Procedure.

The aluminium used contained 0·08 per cent. iron, 0·15 per cent. silicon, and 0·16 per cent. copper; the silver was chemically pure. The alloys were prepared under a layer of potassium chloride in a

PLATE XLV.

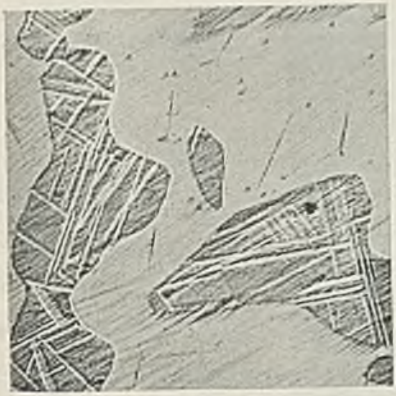

FIG. 2.—6·77 per cent. Aluminium. Slowly Cooled. β' (white) and α (grey) with the Needles of the β'-phase. × 50.

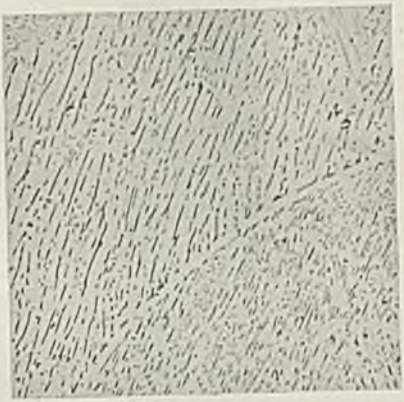

FIG. 3.—7·96 per cent. Aluminium. Slowly Cooled. β' (white) and γ (dark). × 200.

FIG. 4.—9·95 per cent. Aluminium. Slowly Cooled. γ (dark) and β' (white) at the Boundary. × 50.

FIG. 5.—7·48 per cent. Aluminium. Quenched at 600° C. α (grey) and γ (dark). × 50.

PLATE XLVI.

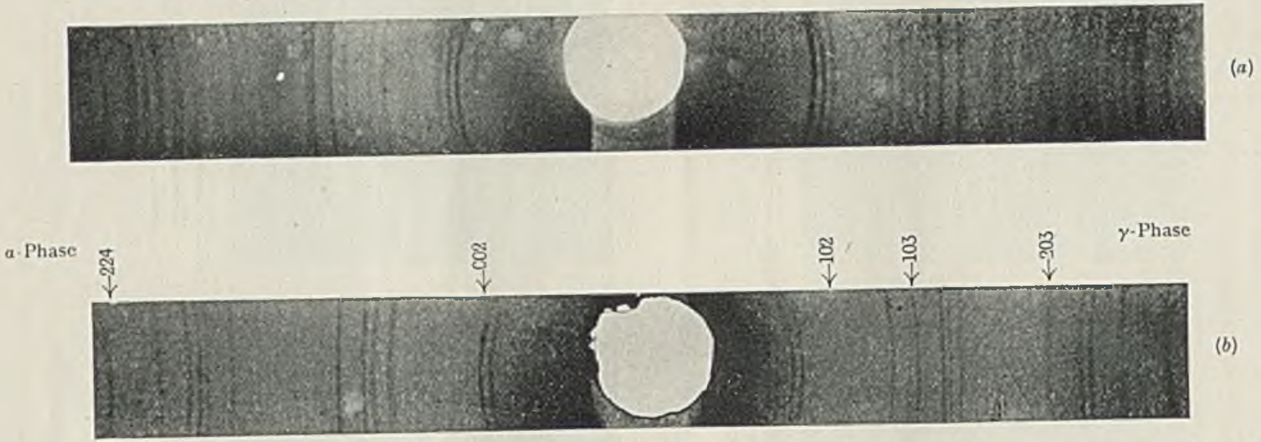

Fig. 6.

(a) 7·96 per cent. Aluminium. Slowly Cooled. β' + Traces of γ.
(b) ,, ,, ,, Quenched at 500° C. $\gamma + \alpha$.

graphite crucible in a carbon resistance furnace; the silver was melted first, the aluminium added, the mixture well stirred, and the alloy cast into a steel mould.

All the alloys were annealed for several days at 650°–700° C. to remove coring, and then cooled slowly over a period of 15–20 days. All further heat-treatments were made with this material as the starting point.

Eight alloys containing 2·91–9·95 per cent. (10·71–30·65 atomic per cent.) aluminium were used in the work, and their composition was checked by analysis, the silver being determined gravimetrically as chloride. Sections were prepared of all the alloys in the slowly cooled state, and after quenching in ice water from various temperatures at which they had been annealed for a sufficient time to reach equilibrium; the etching reagent used was the ordinary chromic acid–sulphuric acid mixture diluted with several times its volume of water. The lattice structures of the annealed and quenched alloys were determined by the powder method, and the boundary of the α-phase was ascertained by an X-ray method[8] using copper radiation ($K_{\alpha_1} = 1{\cdot}5373$ A., $K_{\alpha_2} = 1{\cdot}5410$ A., $K_\beta = 1{\cdot}3893$ A.); quenching of the powder for this work was carried out in alcohol at 0° C.

Hardness measurements were made in the Brinell machine using a 2·5-mm. ball under a load of 62·5 kg. maintained for 30 seconds.

THE α-PHASE.

This phase is a solid solution of aluminium in silver. The lattice parameters were calculated from photograms obtained in a camera of Preston's type[7] calibrated against pure silver, the lattice parameter of which was taken as $4{\cdot}077_7$ A.[8] To determine the change in parameter with increasing aluminium content, measurements were made on alloys with 2·91, 4·91, 6·77, and 7·48 per cent. aluminium after quenching from 500° C. and on alloys with 6·77 and 7·48 per cent. aluminium after

TABLE I.—*Boundary of the α-Phase.*

Aluminium, Weight Per Cent.	Parameter of the α-Phase in A.			
	500° C.	400° C.	300° C.	200° C.
0	4·0777	...	...	...
2·91	4·0654	...	...	...
4·91	4·0595	...	...	...
6·77	4·0537	4·0555	4·0567	4·0587
7·48	4·0543	4·0558	4·0567	...
Aluminium, Weight Per Cent. in saturated α-phase	6·52	6·08	5·77	5·10

quenching from 400°, 300°, and 200° C. Table I shows the results obtained and the composition of the saturated α-phase at the various temperatures. Fig. 1 shows the boundary of the α-phase constructed from these data.

The present authors' results for the parameters of the α-phase differ considerably from those of Phelps and Davey,[6] but are in close agreement with those of Westgren and Bradley.[2]

THE β′-PHASE (Ag_3Al).

According to Petrenko[1] and Westgren and Bradley[2] this phase contains exactly 25 atomic per cent. aluminium, and has a crystal structure similar to that of β-manganese.

Microscopic examination and X-ray analysis of slowly cooled alloys containing 0–10 per cent. aluminium show the presence of three phases. The structure of the α-solid solution has already been illustrated by Hoar and Rowntree[5]; Fig. 2 (Plate XLV) shows the typical (α + β′)-structure obtained by slow cooling, the β′-needles having separated on cooling from the homogeneous α-phase. Fig. 3 illustrates the structure of an alloy very near to the homogeneous β′-region with a small amount of γ regularly distributed throughout the β′-grains. With increasing aluminium content the proportion of γ increases at the expense of β′ until the structure shown in Fig. 4 is obtained in the alloy with 9·95 per cent. aluminium; here the β′ appears as small particles along the edges of the γ-grains indicating that the boundary of the homogeneous γ-field is very close to 10 per cent. aluminium at room temperature. This conclusion is confirmed by X-ray analysis.

The structure observed in alloys containing the β′-phase is not affected by prolonged annealing at 100°–375° C. followed by quenching, but the amount of β′-needles is increased by this treatment in alloys containing 8·83 and 9·95 per cent. aluminium. The duplex field β′ + γ is enlarged on the γ side with rise in temperature up to about 300° C.

When alloys containing 6–9·5 per cent. of aluminium are annealed at 400° C., and quenched, however, both the microstructures and the X-ray patterns show that the β′-phase has been entirely converted into α + γ. Figs. 6*a* and 6*b* (Plate XLVI) show the changes in the X-ray pattern of the alloy with 7·96 per cent. of aluminium after this treatment and Fig. 5 shows the characteristic α + γ structure obtained by quenching from above 400° C. The change from β′ to α + γ is also shown by hardness measurements (Fig. 7); whereas the β′-phase has a Brinell hardness of about 230, the hardness of the corresponding α + γ mixture is only 70.

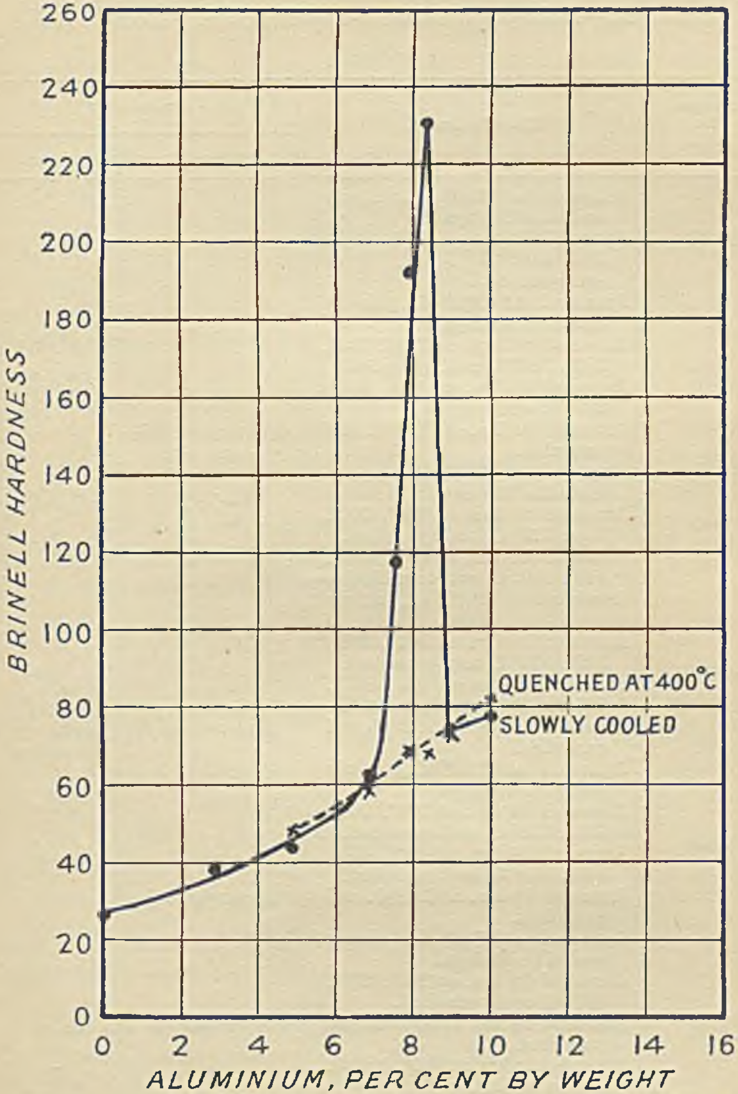

FIG. 7.—The Hardness of the Aluminium–Silver Alloys Slowly Cooled and Quenched at 400° C.

THE γ-PHASE.

The approximate boundary of this phase below 400° C. has been determined by micrographic examination, but at about 400° C. and above this method is uncertain, as the mixture of $\alpha + \gamma$ etches similarly

TABLE II.—*Micrographic and X-Ray Structure of Heat-Treated Alloys.*

Aluminium, Weight Per Cent.	Heat-Treatment.	Structure by	
		Micrography.	X-Ray.
4·91	Annealed at 700° C., slowly cooled in 10 days. Annealed 14 hrs. at 100°, 200°, 300°, 400°, 500°, 600°, 700° C. and quenched.	a	a
6·77	Annealed at 700° C., slowly cooled in 10 days. Annealed 14 hrs. at 100°, 200°, 300°, 375° C. and quenched.	$a+\beta'$	β', a
	Annealed 14 hrs. at 400°, 500°, 600° C. and quenched	$\gamma+a$	a, γ (weak)
	Annealed 14 hrs. at 700° C. and quenched.	decomposed $\beta+$ traces of a	
7·48	Annealed at 700° C., slowly cooled in 10 days. Annealed 14 hrs. at 100°, 200°, 300°, 375° C. and quenched.	$\beta'+a$	β', a (weak)
	Annealed 14 hrs. at 400°, 425°, 500°, 600° C. and quenched.	$\gamma+a$	
7·96	Annealed at 700° C., slowly cooled in 10 days. Annealed 14 hrs. at 100°, 200°, 300°, 375° C. and quenched.	$\beta'+\gamma$	β'
	Annealed 14 hrs. at 400°, 425°, 500°, 600° C. and quenched.	$a+\gamma$	a, γ
	Annealed 14 hrs. at 700° C. and quenched.	decomposed β	similar to γ lattice
8·43	Annealed at 700° C., slowly cooled in 10 days. Annealed 14 hrs. at 100°, 200°, 300°, 375° C. and quenched.	$\beta'+\gamma$	β', γ
	Annealed 14 hrs. at 400°, 425°, 500°, 600° C. and quenched.	$\gamma+a$	γ, a
	Annealed 14 hrs. at 700° C. and quenched.	decomposed β	
8·83	Annealed at 700° C., slowly cooled in 10 days. Annealed 14 hrs. at 100°, 200°, 300° C. and quenched.	$\gamma+\beta'$	γ, β' (weak)
	Annealed 14 hrs. at 400° C. and quenched.	$\gamma+a$	γ, a
	Annealed 14 hrs. at 500°, 600° C. and quenched.	γ	γ
	Annealed 14 hrs. at 700° C. and quenched.	decomposed β	
9·95	Annealed at 700° C., slowly cooled in 10 days. Annealed 14 hrs. at 100°, 200°, 300° C. and quenched.	$\gamma+\beta'$	γ
	Annealed 14 hrs. at 400°, 500°, 600° C. and quenched.	γ	γ

to the homogeneous γ-phase. Hence the authors have determined the boundary in this region with the aid of X-rays. Although many of the lines in the diffraction patterns of the α- and γ-phases overlap, the lines due to the planes (002) and (224) are characteristic of α, and those due to the planes (102), (103), and (203) are characteristic of γ.

The evidence afforded by the micrographic and X-ray work leads to the conclusion that at about 400° C. there exists a two-phase field of $\alpha + \gamma$. Quenching experiments have shown that alloys containing 6·77–8·43 per cent. aluminium when quenched from 400°, 425°, 500°, and 600° C., and the alloy with 8·83 per cent. aluminium when quenched from 400° C., all consist of a mixture of α and γ. Fig. 5 (Plate XLV) shows the structure of the 7·48 per cent. aluminium alloy after quenching from 600° C.; the two phases are quite distinct. X-ray photographs of these alloys also show distinctly lines due to the face-centred cubic lattice of α and to the hexagonal close-packed lattice of γ. The alloy with 8·83 per cent. aluminium quenched from 500° and 600° C., and the alloy with 9·95 per cent. aluminium quenched from 400°, 500°, and 600° C. show only the interference lines due to γ. The above data provide the basis on which is drawn the boundary of the γ-field shown in Fig. 1; they are summarized in Table II.

THE β-PHASE.

This phase is stable only above 600° C., and undergoes transformation below this temperature into a mixture of α and γ. The actual boundaries of the β-field have been determined by Hoar and Rowntree,[5] and the present authors have not repeated their work. Westgren and Bradley[2] have pointed out that it is impossible to retain the β-phase at room temperature by quenching, and we have confirmed this statement by micrographic examination of alloys quenched from 700° C.; in all cases the polygonal grains of β were completely decomposed and X-ray examination showed a lattice structure corresponding with that of γ.

CONCLUSION.

From the results of this work it is possible to point out analogies in the shape of the constitutional diagrams of the alloys of copper, silver, and gold with aluminium.[9] The α-solid solution phase extends to 9·5 per cent. aluminium in the copper alloys, to 5·4 per cent. aluminium in the silver alloys, and to 2·5 per cent. aluminium in the gold alloys. In all three systems the β-phase is stable only at high temperatures, and on cooling decomposes into a eutectoidal mixture; in the copper system this is stable at room temperature, but in the silver system it is converted into a new β′-phase (Ag_3Al) at 400° C. According to Heycock and Neville,[9] the gold system shows a similar behaviour to the silver system.

SUMMARY.

1. The constitutional diagram of the aluminium–silver system has been studied up to 10 per cent. aluminium by micrographic examination, X-ray analysis, and hardness measurements.

2. The β'-phase decomposes on heating at 400° C. into a mixture of α and γ.

3. The boundary of the α-field has been determined by precision measurements of the lattice parameter of quenched alloys.

4. The boundary of the γ-field has been determined by micrographic examination and X-ray analysis.

5. A two-phase region ($\alpha + \gamma$) has been found separating the β' and β-phases between 400° and 600° C.

REFERENCES.

[1] *Z. anorg. Chem.*, 1905, **46**, 49.
[2] *Phil. Mag.*, 1928, **6**, 280.
[3] *Rev. Mét.*, 1913, **10**, 1055.
[4] *Atti III Congr. naz. Chim. pura appl. Firenze e Toscana*, 1929, 371. (Abstract *J. Inst. Metals*, 1931, **47**, 378.)
[5] *J. Inst. Metals*, 1931, **45**, 119.
[6] *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, (Inst. Metals Div.), 234.
[7] *J. Inst. Metals*, 1929, **41**, 191.
[8] N. Ageew and G. Sachs, *Z. Physik*, 1930, **63**, 293.
[9] *Proc. Roy. Soc.*, 1914, [A], **90**, 560: cf. also Stockdale, *J. Inst. Metals*, 1922, **28**, 273.

CORRESPONDENCE.

THE AUTHORS: This year has proved to be very fruitful in regard to the investigation of the aluminium–silver alloys. Subsequent to the presentation of our paper to the Institute of Metals, there have been published the results of some investigations which in general agree well with our own.

We would direct attention, in particular, to the paper by C. Barrett,* who determined the change of the parameter of the α-solid solution and has shown, as a result of a comparison of the calculated and observed densities, that this solid solution is of the simple substitution type. These results were confirmed by E. Jette and F. Foote.† The data obtained by Barrett are in close agreement with our own and this coincidence in observations made simultaneously in two different parts of the world greatly enhances the value of the results. The results of Phelps and Davey differ from those of Barrett and of ourselves and may be in error.

Further, F. Tiskenko ‡ has recently investigated the compounds of the system aluminium–silver and constructed a constitution diagram as the result of microscopic and thermal analyses. The experimental results of this work

* *Metals and Alloys*, 1933, **4**, 63.
† *Ibid.*, 1933, **4**, 78.
‡ *Journal of General Chemistry*, 1933, **3**, 549.

coincide with our own, but there is a great difference in the explanation of the experimental data. We cannot agree with many of those advanced by Tiskenko, as these are not confirmed by our experiments.

Dr. T. P. Hoar,* M.A., B.Sc. (Member): The authors have successfully bridged the gap in the aluminium–silver equilibrium diagram between the high-temperature results obtained by Rowntree and myself by micrographic methods and the low-temperature results of the X-ray work of Westgren and Bradley. It is very satisfactory to note that all three investigations are in substantial agreement.

The difficulty found by the authors in distinguishing $\alpha + \gamma$ from pure γ micrographically was also encountered by Rowntree and myself, and the success of the X-ray technique in this matter is yet another illustration of the usefulness of the method.

Do the authors consider that the composition of the β-phase, where it first makes its appearance just above 600° C., has any theoretical significance, as it seems to coincide so precisely with Ag_3Al?

The authors state that it is not possible to preserve the β-phase unchanged by quenching, but that $\alpha + \gamma$ is largely produced. In view of the fact that specimens quenched from the β region frequently, but not always, show acicular structure very similar to the β' needles shown in Fig 2, do they think it likely that, with rather inefficient quenching, β' may also be formed?

I find it a little difficult to accept the authors' interpretation of the hardness measurements. These seem at first sight to afford conclusive evidence for the correctness of the authors' representation of the $\alpha + \gamma/\beta'$ transformation, β' being always pure Ag_3Al. I note, however, that the maximum Brinell value (Fig. 7) is obtained at about 8·4 per cent. aluminium content, whereas Ag_3Al contains 7·69 per cent. aluminium; the alloy containing 8·4 per cent. aluminium would appear to be well in the $\beta' + \gamma$ region, and only at 8·8 per cent. aluminium does the Brinell value fall to that which I take it the authors consider typical of $\beta' + \gamma$. If it is the hardness of the β' phase which gives rise to the maximum in the Brinell values, I should have expected the maximum hardness to correspond with single-phase β'. It may be that there is in fact sufficient solid solubility of aluminium in Ag_3Al to make the very hard 8·4 per cent. aluminium alloy a single-phase β' system. I would like to know whether the authors have considered this possibility, or whether, if the particular specimen giving the Brinell value of 230 was found micrographically or by X-rays to be $\beta' + \gamma$, they have some other explanation of the matter.

I think that it would be desirable to carry out experiments in which specimens of composition 7·0–9·0 per cent. aluminium were annealed for several weeks at temperatures just below 400° C., to see whether there is any solid solubility whatever of aluminium or silver in Ag_3Al. The authors, on the basis of their 14-hr. annealings, conclude with Westgren and Bradley that there is not, but it would be of interest, in view of the hardness values discussed above, and also of theoretical considerations, to make quite certain of this point by much more prolonged annealing.

Dr. W. Hume-Rothery,† M.A. (Member): At Oxford we have been investigating in the last two years the solubility limits of the silver–aluminium α-solid solution, and the results of this work are to be published shortly. We have obtained a diagram somewhat similar to that of the authors, but it seems to me that they have interpreted their X-ray data incorrectly.

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* Research Electrochemist, International Tin Research and Development Council, Cambridge.

† Oxford.

At 500° C. the only alloys which are in the homogeneous region are those containing 2·91 and 4·91 per cent. of aluminium by weight, since the alloy containing 6·77 per cent. of aluminium is just outside the homogeneous area. In Fig. A I have plotted the authors' values for the lattice constants against the composition. It will be seen that the points for 0, 2·91, and 4·91 per cent. of aluminium are by no means on a straight line, and if these points are taken by themselves, we can only say that the limiting solid solubility at 500° is between 5·5 and 6·52 per cent. aluminium. The authors seem to have preferred the point for the 4·91 per cent. alloy, but there appears to be little justification for this.

We may, however, obtain a more probable estimation of the solubility limit in the following way. The authors calibrate their camera against the lattice parameter of pure silver, which is taken as 4·077$_7$ A., and is thus uncertain in the fourth decimal place, and their own measurements are uncertain to at least the same amount, since the lattice constants of the 6·77 and 7·48 per cent. alloy, which should be identical, are given as 4·0537 A. and 4·0543 A., respectively, and thus differ by 0·0006 A. Each of their experimental points should be represented therefore by a circle of radius approximately 0·0005 A., as is shown by the dotted lines in Fig. A. The most probable straight line is then approximately as drawn, and gives the limiting α-solid solubility as 6·1 per cent. Al ± 0·1 to ± 0·2. This value is in almost complete agreement with the results of our annealing experiments, and as these were carried out with alloys of which the compositions varied in very small steps, the results are probably correct to within 0·1 per cent. by weight.

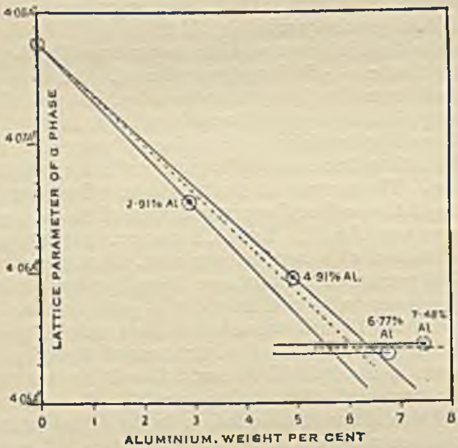

FIG. A.

It seems probable, therefore, that all the authors' values for the α-solid solubility limit require reducing by a corresponding factor, but until the points for the alloys within the α-solid solution area have been obtained to a higher degree of accuracy, the authors' X-ray measurements do not seem to enable the α-solubility limit to be determined conclusively, and the values given to two decimal places in Table I appear unjustified. To a rough approximation 1 per cent. by weight of aluminium corresponds to a change of 0·004 A., so that 0·01 per cent. by weight is equivalent to 0·00004 A., and this, of course, is quite beyond the accuracy with which the lattice constants have been measured.

It is very satisfactory to note that both the authors' and our own results are in agreement as regards the double bend in the α-solubility curve, and their explanation in terms of the decomposition of the β-phase is most interesting.

The AUTHORS (*in reply*): We thank the contributors to the discussion for the many interesting points raised, which lead us to conclude that this system will well repay further study.

Dr. Hoar's question about the coincidence of the eutectoid point at 600° C. with the composition of the compound Ag_3Al cannot be answered without investigating the properties of the β-phase stable at high temperature and the displacement of the eutectoid point with change of equilibrium conditions. We do not believe that the coincidence of eutectic and eutectoid compositions with simple atomic ratios has any theoretical significance. The β′-phase (Ag_3Al) as shown by our experiments is formed only by slow cooling below 400° C., and hence cannot be produced by quenching. The acicular structure of quenched alloys is most probably formed by a process similar to that which yields martensite on quenching steel. The β′-phase exists only in alloys containing between 7·48 and 7·96 per cent. aluminium, and both these alloys are already non-homogeneous (see Table II); the alloy with 8·43 per cent. aluminium has also a duplex structure. The range of homogeneous β′ cannot exceed 0·48 per cent., hence the hardness maximum cannot be due to pure β′. The sole possible explanation is that the small quantity of γ in the hardest alloys is dispersely distributed throughout the β′-phase. The investigation of the narrow homogeneous region of the β′-phase by prolonged annealing experiments at 400° C. for determining solid solubility is very interesting and is engaging our attention.

We cannot agree with the majority of Dr. Hume-Rothery's remarks, as they appear to be based on a series of misapprehensions arising from a too cursory perusal of our paper.

The slight uncertainty in the parameter of silver has no influence on the accuracy of the determination of the α-phase boundary, which is determined not by absolute X-ray measurements of parameters, but by relative measurements of the change in parameter of solid solutions saturated at different temperatures.

Our experimental work, of course, has a definite degree of uncertainty, but, if Dr. Hume-Rothery had more carefully examined the paper, he would not have overlooked the fact that at the high quenching temperature the difference in the parameters of the alloys with 6·77 and 7·48 per cent. aluminium has increased; this shows that the difference in the parameters can be ascribed to difficulties connected with the high-temperature quenching. In any case, this difference can only relate to the α-phase boundary at 500° C.

If the uncertainty in the measurements is taken as 0·0006 A., as Dr. Hume-Rothery suggests, it is impossible to agree with his interpretation of our results. The dotted line in Fig. A passes by the points represented by the circle of radius 0·0005 A. Dr. Hume-Rothery's view that the change of parameter of the α-solid solution must be a straight line is erroneous, and he attempts to adapt the experimental results to this faulty opinion. The change of parameter in the α-solid solution is not a straight line, and must pass through the experimental points. Although we are pleased to hear that our results are in agreement with those of Dr. Hume-Rothery, we cannot accept his interpretation of our work. Taking into account all the possible uncertainties in our results, we believe that they give the α-solid solubility limit with an accuracy of 0·1 per cent. aluminium. Therefore, as is usual in such cases, we have given the results to two decimal places, and we are sorry that Dr. Hume-Rothery has been led astray by the second place not being printed in smaller type.

A GRAPHICAL METHOD FOR CONVERTING THE WEIGHT PERCENTAGE COMPOSITIONS OF TERNARY SYSTEMS INTO ATOMIC OR MOLECULAR PERCENTAGES.*

By WILLIAM HUME-ROTHERY,† M.A., Ph.D., MEMBER.

SYNOPSIS.

A graphical method is described for the conversion of the weight percentage compositions in ternary systems into atomic or molecular percentages, which is suitable for use where 60° ruled triangular paper is available. The method permits the direct transference of a triangular diagram drawn on the weight percentage scale to one in atomic percentages, and the accuracy obtained is of the order 0·1–0·5 per cent., according to the precision of the instruments and of the ruled paper.

IN connection with the study of the theory of ternary alloys, it is frequently necessary to convert the weight percentage compositions of the alloys into atomic percentages. The calculations involved are simple divisions and additions, but they are very laborious when many alloys are being dealt with, and are of a nature in which it is extremely difficult to detect arithmetical errors. In the case of binary alloys, the calculations may be checked by plotting the given weight percentages against the calculated atomic percentages, when a mistake in the calculation is shown by the deviation of the point from a smooth curve. In ternary alloys there appears to be no simple method of detecting a mistake in this way, and the following graphical method has therefore been developed. Where the accuracy required is of the order 0·5 atomic per cent. the method may be used for direct calculation without any difficulty, whilst with suitable drawing instruments this degree of accuracy could be considerably improved.

To illustrate the method, we may consider the calculations involved in converting the composition of an alloy containing a, b, and c per cent. of three elements of atomic weights w_a, w_b, and w_c, into the corre-

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† Royal Society Warren Research Fellow, Oxford.

sponding atomic percentages. The relative numbers of atoms of the three elements are clearly

$$\frac{a}{w_a} : \frac{b}{w_b} : \frac{c}{w_c} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The calculation of these involves three operations on the slide rule, or the looking up of three antilogarithms and six logarithms, three of the latter being the same for a whole series of alloys. One of these divisions may, however, be omitted, since the ratios in equation (1) are clearly the same as :

$$\frac{a}{w_a} \times w_a : \frac{b}{w_b} \times w_a : \frac{c}{w_c} \times w_a \quad . \quad . \quad . \quad (2)$$

or as

$$a \times 1 : b \times \frac{w_a}{w_b} = B : c \times \frac{w_a}{w_c} = C \quad . \quad . \quad (3)$$

In this way once the logarithms or values of $\frac{w_a}{w_b}$ and $\frac{w_a}{w_c}$ have been obtained they are constant for a given series of alloys. It is then necessary to add together $a + B + C$, when the atomic percentages of the three elements are clearly $\frac{100a}{a + B + C}$, $\frac{100B}{a + B + C}$, and $\frac{100C}{a + B + C}$ respectively. This involves three operations on the slide rule, or the looking up of two new logarithms and three antilogarithms, since the logarithms of B and C are already known. If these results add up to 100, there is a check on the accuracy of the work after equation (3) has been reached, but not on the earlier part of the calculation.

The following method is suggested for use when 60° triangular ruled paper is available. According to the usual convention, the weight composition of the alloy which is being considered is represented by a point P (Fig. 1) inside the equilateral triangle ABC of height 100 units, so that the weight percentages of A, B, and C are given by $PX = a$ units, $PY = b$ units, and $PZ = c$ units, where the property of the triangle is such that $PX + PY + PZ = 100$.

In accordance with relation (3) the points y in PY, and z in PZ are then marked off so that $Py = PY \times \frac{w_a}{w_b}$ and $Pz = PZ \times \frac{w_a}{w_c}$, where these values are obtained either by means of a slide rule, or graphically by ruling lines of slope $\frac{w_a}{w_b}$ and $\frac{w_a}{w_c}$ on ordinary squared paper. Alternatively, if two pairs of accurate proportional compasses are available, these may be set to give the required fractions $\frac{w_a}{w_b}$ and $\frac{w_a}{w_c}$, and may be used to reduce a whole series of lengths by the same fraction. As in equation (3), $a = PX$ is left at its original value.

Through y and z lines are now drawn parallel to AC and AB, respectively, so as to form the equilateral triangle $\alpha\beta\gamma$. In this triangle the point P is situated at a position equivalent to its atomic composition, since PX, Py, and Pz are in the ratio given by equation (3). The treatment so far consists of course in nothing but the translation of the calculations of equations (1), (2), and (3) into graphical form.

It is possible, however, to avoid the necessity of measuring Pz and Py, and adding these to PX, and then carrying out three division sums, provided that a simple geometrical construction can be found which will enable the transfer of the point P to a new point p, such that p occupies in the triangle ABC, a position geometrically similar to that occupied by P in the triangle $\alpha\beta\gamma$. To do this it is only necessary to draw through B and C lines parallel to βP and γP respectively. If these meet at p, then, since the angles pBA and pCA are equal to the angles $P\beta\alpha$ and $P\gamma\alpha$, respectively, the points p and P are in positions which are geometrically similar in the triangles ABC and $\alpha\beta\gamma$, and hence the atomic composition is given by the position of the point p relative to the ruled lines of the original triangle ABC.

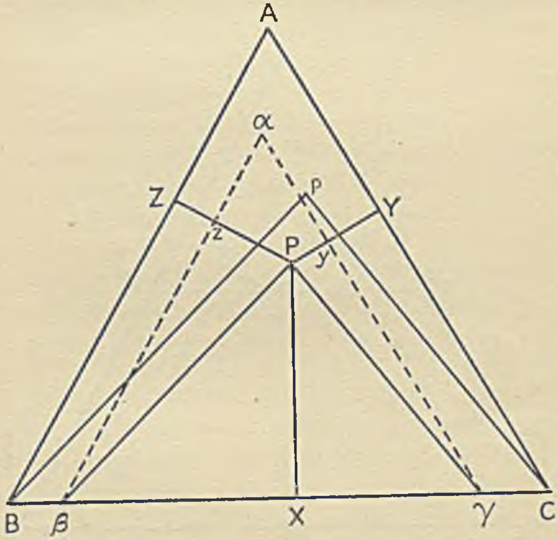

Fig. 1.

The drawing of the two perpendiculars PY and PZ (PX need not be drawn), and the marking off of the points y and z should not take more than one minute, whether a slide rule or graphical method is used for determining the lengths Py and Pz. The remaining operations involve nothing but the drawing of four lines * with parallel rulers, and are so simple that there is little likelihood of an error being made, whilst if the 60° lines on the ruled paper are sufficiently close together, the positions of the points β and γ can be marked off by eye from those of z and y, and only two lines need be drawn with the parallel rulers.

It will be seen that the above method can really be divided into two stages, of which the first is the establishment of the points β and γ. Where a slide rule or graphical method is used for the fractional calculations, the drawing of the two perpendiculars PY and PZ is probably the shortest method, since the values of b and c are the given quantities used in marking the point P. If proportional compasses are used, however, the construction may be still further simplified, for, as can be seen from Fig. 2, instead of drawing the two perpendiculars PY and PZ, the single line MPN may be drawn parallel to BC. If this cuts the sides of the triangle $\alpha\beta\gamma$ at y' and z', it can be seen from the properties of similar triangles that $\frac{Py'}{PN}=\frac{Py}{PY}$, and $\frac{Pz'}{PM}=\frac{Pz}{PZ}$, and consequently the points y' and z' may be used, instead of y and z, in order to establish the position of the points β and γ. In this case when the point P has been marked, the construction consists only of drawing the one line MPN parallel to BC, followed by the marking of the points y' and

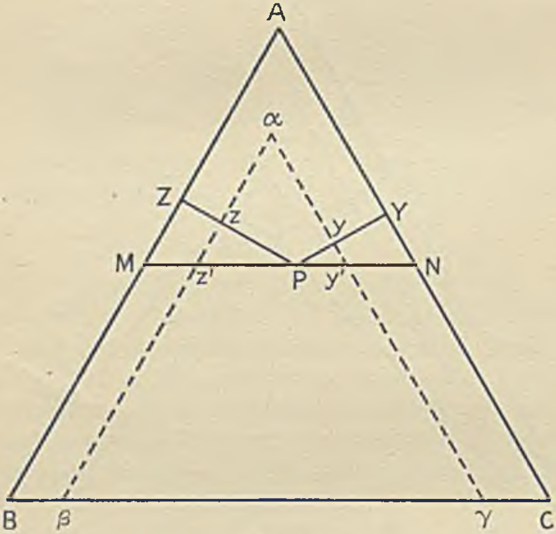

Fig. 2.

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* There is of course no need actually to draw the lines βP and γP, since the lines Bp and Cp can be drawn parallel to βP and γP without actually drawing the latter.

z' by the two pairs of proportional compasses. From these, the points β and γ may be obtained by eye if the 60° ruled lines are close together, or by drawing $y'\gamma$ and $z'\beta$ parallel to AC and AB, respectively. The point p is then obtained, as before, by drawing Bp and Cp parallel to βP and γP, respectively. The general method is the same whether the fractions $\frac{w_b}{w_a}$ and $\frac{w_c}{w_a}$ are greater or less than unity, but it is usually more simple to arrange the three constituents so that the fractions are less than unity, since all the lines then remain inside the triangle.

If the drawing is carried out in pencil, and the final point marked in ink, the construction lines can readily be rubbed out, and the method used for the direct transference of a diagram drawn on the weight per cent. scale to one in atomic percentages. It will be appreciated that where one or two calculations only are concerned, the method has little advantage over a direct calculation by logarithms checked by repetition, or by calculation on a slide rule, but, where a large number of alloys of the same ternary system is being dealt with, it is hoped that the simple graphical construction may be of value not only as a check on calculations, but for the direct conversion of weight percentages into atomic percentages where the highest accuracy is not required.

Professor C. H. Desch, F.R.S., has kindly directed the attention of the author to an alternative method described by Redlich.* In this a " nomograph " is constructed containing five scales situated at distances which are calculated from the atomic weights. Once this nomograph has been drawn, each conversion of weight percentages into atomic percentages involves the drawing of four straight lines. The intersections of three of these lines with three of the scale lines then give the differences between the weight percentages and the atomic percentages of the constituents, so that if the weight percentage of one constituent is, say, 50·0, and the scale reading − 17·3, the atomic percentage is 32·7. The two methods appear to be equally accurate, but, apart from being more simple in principle, the present method has the advantage of giving the actual atomic percentages instead of the difference terms, and can also be used for the direct transference of the triangular diagram from one form to the other.

ACKNOWLEDGMENTS.

The author must express his gratitude to Professor F. Soddy, F.R.S., for most kindly providing laboratory accommodation, and to the Council of the Royal Society for election to a Warren Research Fellowship.

THE OLD CHEMISTRY DEPARTMENT,
THE UNIVERSITY MUSEUM,
OXFORD.

May, 1933.

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* Redlich, *Z. anorg. Chem.*, 1928, 174, 285.

CORRESPONDENCE.

Mr. W. Schischokin[*] (Member): If the quantities $Py = PY \times \frac{w_a}{w_b}$, and $Pz = PZ \times \frac{w_a}{w_c}$ are calculated, then the ternary diagram can be much more simply constructed than in the way indicated by the author. Indeed, if we represent by x', y', and z', respectively, the atomic percentages of the components A, B, and C, then it can easily be shown that the following relationships exist: $\frac{x'}{y'} = \frac{a}{Py}$ and $\frac{x'}{z'} = \frac{a}{Pz}$, following directly from expression (1) (presumably $\frac{a}{w_a} : \frac{b}{w_b} : \frac{c}{w_c}$ on p. 132 of Hume-Rothery's paper.—*Translator's note*).

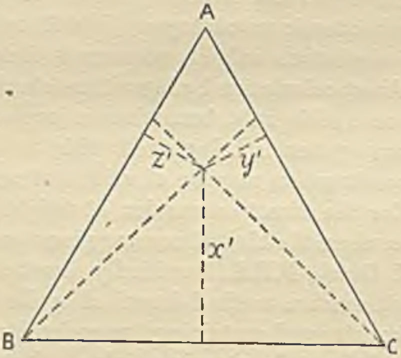

Fig. A.

It is then sufficient to draw two straight lines in the ternary diagram (see Fig. A)—one dividing the triangle in the proportion $\frac{x'}{y'}$ and the other in the proportion $\frac{x'}{z'}$, the point of intersection of these straight lines giving the values x', y', and z'. Since all points on the line from C correspond to a constant ratio of x' to y', and all points on the line from B correspond to a constant ratio of x' to z', the intersection of the lines takes place at the point corresponding to the ratio $x' : y' : z'$.

A similar simple geometrical construction can be made for transition from atomic to weight percentages (which is not possible with the method suggested by the author). For this purpose, actually, the following expressions hold good:

$$\frac{a}{b} = \frac{x'}{y'} \cdot \frac{w_a}{w_b} \text{ and } \frac{a}{c} = \frac{x'}{z'} \cdot \frac{w_a}{w_c},$$

which also follow from expression (1).

The right-hand side of these expressions can be calculated graphically or from a log. slide-rule. Then, in the ternary diagram, the lines of the relations $\frac{a}{b}$ and $\frac{a}{c}$ are drawn, their point of intersection giving the values of a, b, and c.

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[*] Metallurgical Institute, Leningrad, U.S.S.R.

The method that I have just described is given in my paper: "A Graphico-Analytical Method of Transition from Weight to Atomic Percentages, and Vice-Versa, in Ternary Systems," published in *Metallurg* (*The Metallurgist*). In the paper "The Use of Nomograms in Metallographical Calculations" (*Metallurg*, **1933**, No. 1) is given a graphical method of passing from weight to atomic percentages, and *vice versa*, in any ternary system, in which arithmetical calculations are completely avoided.

The AUTHOR (*in reply*): I thank Mr. Schischokin for his interesting contribution, but I do not think that it results in any real advantage. Both methods begin by determining the quantities Py and Pz graphically, by calculation, or by the use of proportional compasses. The method which I have given then proceeds by purely graphical methods, whilst the variation suggested by Mr. Schischokin involves first the calculation of the quantities $\frac{x'}{y'}$ and $\frac{x'}{z'}$ followed by a simple construction. Any advantage gained by simplicity of construction is more than counterbalanced by the additional calculations or measurements involved.

Mr. Schischokin is, however, incorrect in stating that the method which I have given cannot be used for the opposite transition from atomic to weight percentages. If x', y', and z' are the atomic percentages of three elements of atomic weights w_a, w_b, w_c, then the relative proportions by weight of the three elements are

$$x' \times w_a : y' \times w_b : z' \times w_c.$$

If these are divided through by one of the atomic weights, say w_a, the same ratios become

$$x' \times \frac{w_a}{w_a} : y' \times \frac{w_b}{w_a} : z' \times \frac{w_c}{w_a}$$

or as

$$x' \times 1 : y' \times \frac{w_b}{w_a} : z' \times \frac{w_c}{w_a}.$$

In this way, since $\frac{w_b}{w_a}$ and $\frac{w_c}{w_a}$ are constant for any one system, exactly the same construction can be used as that given in my paper for the reverse operation. Here w_a would preferably be chosen as the largest of the three atomic weights so as to keep the construction within the triangle.

I am interested to hear of Mr. Schischokin's paper on this subject, and hope that he will arrange to have it published in English, French, or German.

PRECIPITATION-HARDENING NICKEL–COPPER ALLOYS CONTAINING ALUMINIUM.*

By D. G. JONES, M.Sc., Member,† L. B. PFEIL,‡ D.Sc., A.R.S.M., Member, and W. T. GRIFFITHS,§ M.Sc., Member.

Synopsis.

The properties of nickel–copper–aluminium alloys with nickel contents from 10 to 45 per cent. and aluminium contents up to 4 per cent. have been investigated.

The relationships between composition and capacity for hardening by heat-treatment have been studied by means of hardness tests on the heat-treated specimens. A study has also been made of the most suitable heat-treatments to produce the soft condition and the stability at elevated temperatures of a selection of the alloys in the precipitation-hardened condition. Finally, the mechanical properties have been determined of a group of alloys selected and prepared in accordance with the results of the preliminary experiments.

In certain cases the properties of the 20 per cent. nickel alloys were studied in greater detail than those at other nickel levels, but sufficient work has been carried out on alloys containing 10, 30, and 45 per cent. nickel to enable the properties of alloys at these levels and over a range of aluminium contents and in various conditions of heat-treatment to be deduced.

Introduction.

The research was confined to nickel–copper–aluminium alloys with nickel contents in the range 10–45 per cent. and with aluminium contents for the most part less than 4 per cent. The investigation should therefore be regarded as a study of the effect of small aluminium additions to nickel–copper alloys, rather than the effect of nickel additions to "aluminium–bronze." The previous work bearing directly on the present investigation is not very extensive, and reference ¶ need be made only to the researches of Andrews,[1] Guillet,[2] Read and Greaves,[3] and Iitaka.[4]

The present investigation was undertaken in order to find compositions in which specially useful combinations of workability, mechanical properties, and corrosion-resistance could be developed in nickel–copper alloys containing less than 50 per cent. nickel and rendered susceptible

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¶ At the request of the Institute, details of the earlier work have been omitted, in order to shorten the paper.

to heat-treatment by aluminium additions. In many respects the work undertaken was similar to that dealt with in a paper recently presented to the Institute by the authors,[5] in which were given the properties of a series of precipitation-hardening nickel–copper–silicon alloys.

The procedure adopted for the present work was first to find, by means of hardness determinations carried out on heat-treated specimens, the relationship between composition and capacity for hardening by heat-treatment. This was followed by studies of the most suitable heat-treatments to produce the soft condition, and of the stability at elevated temperatures of a selection of the alloys in the precipitation-hardened condition, and finally the mechanical properties were determined of a group of alloys selected and prepared in accordance with the results of the preliminary experiments.

In certain cases the properties of 20 per cent. nickel alloys were studied in greater detail than those at other nickel levels, but sufficient work was carried out on alloys containing 10, 30, and 45 per cent. nickel to enable the properties of alloys at these levels and over a range of aluminium contents and in various conditions to be deduced.

THE EFFECT OF ALUMINIUM CONTENT ON PRECIPITATION-HARDENING CAPACITY.

The present investigation was initiated by determinations of the ranges of composition in which precipitation-hardening could most usefully be developed. Ingots weighing about 2·5 lb. and of the dimensions 6 × 2 × 0·75 in. were prepared over a range of aluminium contents at nickel levels of 10, 20, 30, and 45 per cent. The ingots were soaked for 1 hr. at 900° C. and quenched in cold water. They were then cold-rolled to a thickness of 0·25 in. and again heated for 1 hr. at 900° C. and quenched. Small pieces cut from the strips were then reheated for 1 hr. at temperatures in the range 500°–700° C. Brinell hardness determinations were made on the quenched and reheated specimens. All the alloys were not analyzed, but the determinations which were made showed that the compositions obtained approximated very closely to those desired. The Brinell hardness results obtained are given in Tables I to IV for 10, 20, 30, and 45 per cent. nickel levels respectively, and in the right-hand column of these tables figures are given for the maximum Brinell hardness increment obtained.

From these figures it may be noted that the aluminium content just sufficient to result in precipitation-hardening is greater when the nickel content is greater, and that with increasing aluminium content the precipitation-hardening effect increases to a maximum and then decreases. The smaller hardness increment obtained at the higher aluminium levels is due mainly to an increased hardness in the quenched condition, resulting, no doubt, from the quenching treatment not being sufficiently drastic to retain the whole of the hardening phase in solid solution. It may be noted also from the figures in Tables I to IV that

Table I.—*Hardness of Heat-Treated* 90 : 10 *Copper–Nickel Alloys Containing Aluminium.*

Mark.	Aluminium, Per Cent.	Brinell Hardness.						Maximum Hardness Increment.
		Quenched at 900° C.	Reheated for 1 Hr. at					
			500° C.	550° C.	600° C.	650° C.	700° C.	
SU	0·2	63	69	66	66	...	65	...
SV	0·3	65	66	68	65	...	68	...
SW	0·4	65	72	68	68	...	66	...
TK	0·45	68	...	123	97	...	68	55
TL	0·5	70	...	129	101	...	72	59
TM	0·6	76	...	140	136	...	72	64
RE	0·75	71	...	154	150	...	96	83
TN	0·8	73	...	157	154	...	83	84
RF	1·0	69	...	161	160	...	118	92
SE	1·25	75	150	174	174	158	114	99
SF	1·5	80	178	179	196	177	165	116
SG	2·0	81	200	218	229	207	166	148
SH	2·5	87	207	222	229	206	174	142
SI	3·0	87	191	218	218	220	185	133
SX	4·0	87	159	194	211	211	203	107

Table II.—*Hardness of Heat-Treated* 80 : 20 *Copper–Nickel Alloys Containing Aluminium.*

Mark.	Aluminium, Per Cent.	Brinell Hardness.							Maximum Hardness Increment.
		Quenched at 900° C.	Reheated for 1 Hr. at					2 Hrs. at 550° C.	
			500° C.	550° C.	600° C.	650° C.	700° C.		
RR	0·4	84	84	83	...	82	...	84	...
RS	0·6	80	98	112	...	85	...	134	54
RT	0·8	85	104	123	...	126	...	151	66
RU	1·0	84	110	125	...	144	...	154	70
RV	1·25	90	116	140	...	167	...	178	88
RW	1·5	86	115	146	...	187	...	173	101
RX	1·75	88	150	152	...	196	...	204	116
RY	2·0	102	168	188	...	246	...	230	144
SJ	3·0	116	211	197	255	265	244	251	149
SK	3·5	136	195	237	260	275	251	214	149

Note.—Alloys containing 4, 5, 6, and 7 per cent. aluminium gave Brinell hardness values of 144, 171, 260, and 204, respectively, in the quenched condition and hardness increments by reheating of 80, 60, 0, and 16, respectively.

TABLE III.—*Hardness of Heat-Treated* 70 : 30 *Copper–Nickel Alloys Containing Aluminium.*

Mark.	Aluminium, Per Cent.	Brinell Hardness.						Maximum Hardness Increment.
		Quenched at 900° C.	Reheated for 1 Hr. at					
			500° C.	550° C.	600° C.	650° C.	700° C.	
QT	0·5	92	...	92	...	...	92	...
QU	0·75	92	...	92	...	...	92	...
TO	0·9	90	...	152	164	...	107	74
QV	1·0	107	...	171	192	...	105	85
TP	1·1	102	...	166	194	...	106	92
TQ	1·3	104	...	166	194	...	104	90
SL	1·5	102	129	157	189	163	112	87
SM	2·0	105	137	161	187	190	169	85
SN	2·5	106	152	180	215	220	216	114
SP	3·0	110	163	222	229	248	237	138

Note.—Alloys containing 4, 5, 6, and 7 per cent. aluminium gave Brinell hardness values of 185, 225, 188, and 246, respectively, in the quenched condition and hardness increments by reheating of 48, 17, 29, and 19, respectively.

TABLE IV.—*Brinell Hardness of Heat-Treated* 55 : 45 *Copper–Nickel Alloys Containing Aluminium.*

Mark.	Aluminium, Per Cent.	Brinell Hardness.						Maximum Hardness Increment.
		Quenched at 900° C.	Reheated for 1 hr. at					
			500° C.	550° C.	600° C.	650° C.	700° C.	
QV	0·5	113	...	113	...	...	110	...
KX	1·0	106	...	110	...	...	111	...
SO	1·5	114	115	112	112	108	104	...
SR	1·75	107	115	112	112	108	111	...
SS	2·0	111	118	119	119	114	112	...
TR	2·25	126	...	197	188	...	126	71
RZ	2·5	125	131	159	214	204	...	89
TS	2·75	118	...	188	218	...	176	100
SA	3·5	124	138	177	223	243	...	110
TT	4·0	121	...	233	251	...	280	159

TABLE V.—*Variation of Aluminium Content with Nickel Content.*

Nickel Content, Per Cent.	Minimum Aluminium Content to Give Precipitation-Hardening, Per Cent.	Aluminium Content Giving Maximum Precipitation-Hardening. Per Cent.
10	0·45	2·0
20	0·60	2·5
30	0·90	3·0
45	2·25	4·0

with increasing aluminium content a higher temperature is necessary to give the best development of precipitation-hardening. For each of the four nickel levels approximate figures are given in Table V for the aluminium contents which are just sufficient to render the alloys susceptible to precipitation-hardening and the aluminium contents which give the maximum precipitation-hardening effect.

THE MINIMUM HEAT-TREATMENT NECESSARY TO PRODUCE THE SOFT CONDITION.

From the alloys dealt with in the preceding section eleven were selected for a study of the heat-treatment necessary to produce the soft condition. Up to this stage all the alloys had been softened by quenching from 900° C., but it was considered likely that at the lower aluminium and nickel levels a lower quenching temperature would suffice. The selected materials were first hardened by furnace cooling, and then one piece of each specimen, 1 in. × ½ in. × ¼ in., was soaked for ¼ hr., ½ hr., and 1 hr. at 650°, 700°, 750°, and 800° C., the heat-treatment being concluded in every case by water-quenching. The Brinell hardness of the specimens was determined, and the compositions of the materials and the results are given in Table VI. No figures are given for the ½-hr. treatments, as these figures differed to no substantial extent from those for the ¼-hr. and 1-hr. treatments.

TABLE VI.—*The Softening Temperature of Precipitation-Hardened Nickel–Copper–Aluminium Alloys.*

Mark.	Composition, Per Cent.		Furnace-Cooled.	650° C.		700° C.		750° C.		800° C.		Precipitation-Hardening Capacity.
	Ni.	Al.		¼ Hr.	1 Hr.	¼ Hr.	1 Hr.	¼ Hr.	1 Hr.	¼ Hr.	1 Hr.	
TK	10	0·45	127	78	71	68	67	66	66	68	68	61
RF	10	1·0	150	108	107	88	93	81	84	74	72	89
SG	10	2·0	168	151	147	121	128	101	95	74	72	156
RS	20	0·6	116	87	92	77	75	77	77	76	78	55
RW	20	1·5	166	143	145	124	128	124	108	83	87	103
RY	20	2·0	193	159	162	149	149	145	148	124	121	144
TO	30	0·9	127	104	99	98	96	97	97	101	99	93
SN	30	2·5	188	174	172	152	154	144	144	108	108	124
SP	30	3·0	240	229	229	204	223	195	192	108	119	152
RZ	45	2·5	209	185	186	127	145	124	117	116	120	86
SA	45	3·5	221	209	205	171	179	162	165	128	134	123

It may be noted from these figures that the soaking time was without substantial effect, whilst the temperature required for softening was not dependent to an important degree on nickel content. The right-hand column of Table VI contains figures for the maximum hardness increment obtainable by reheating after quenching, taken from Tables I to IV, and it may be seen that alloys having mild precipitation-hardening characteristics and giving a maximum hardness increment of about 50–60 units (the 10 per cent. nickel alloy containing 0·45 per cent. aluminium, and the 20 per cent. nickel alloy containing 0·6 per cent. aluminium) were satisfactorily softened by heat-treatment for ¼ hr. at 700° C. On the other hand, alloys capable of a hardness increment exceeding 100 Brinell units required 15 minutes' treatment at 800° C. for softening.

THE EFFECT OF RATE OF COOLING ON HARDNESS.

A precipitation-hardening alloy which can be obtained in the soft condition without employing a quenching operation has the advantage that hot-rolled bars or hot-rolled sheets may be cold-worked without intermediate heat-treatment. A series of experiments was, therefore, carried out on four alloys at the 20 per cent. nickel level and on one alloy at each of the levels 10 and 30 per cent. nickel, in order to find the rate of cooling necessary to give the soft condition.

TABLE VII.—*The Effect of Rate of Cooling on the Hardness of Nickel–Copper–Aluminium Alloys.*

Mark.	Composition, Per Cent.				Water Quenched from 850° C.	Oil Quenched from 850° C.	Air Quenched from 850° C.	Air Cooled from 850° C.
	Cu.	Ni.	Al.	Mn.				
UO	88·03	10·2	1·10	0·75	88	89	88	121
UT	78·65	19·98	0·65	0·73	91	86	90	95
UU	78·27	19·88	1·04	0·82	102	100	137	134
UP	77·83	19·78	1·37	0·75	107	127	191	233
UW	77·73	20·10	1·52	0·79	98	123	194	229
UV	67·06	30·63	1·38	0·89	110	108	107	110

Four pieces, 6 in. × 1 in. diameter, of each composition were heated with the furnace to 850° C., at which temperature they were soaked for ½ hr. One piece of each composition was then quenched in water, one of each quenched in oil, and one of each cooled in a blast of air, whilst the remaining pieces were cooled in still air. Brinell hardness determinations were made on the heat-treated specimens, and the compositions of the alloys and the results are given in Table VII. From these figures it may be noted that those alloys which were capable only of mild precipitation-hardening (nickel 20, aluminium 0·65 per cent.; nickel 30, aluminium 1·38 per cent.) retained the soft condition after all the rates of cooling.

In the alloys capable of pronounced precipitation-hardening (nickel 20, aluminium 1·37 per cent.; nickel 20, aluminium 1·52 per cent.) a quenching operation was necessary in order to retain the soft condition.

THE EFFECT OF RE-HEATING ALLOYS IN THE COLD-ROLLED CONDITION.

In certain applications it is possible to make use of alloys, the properties of which are modified by a combination of work-hardening and precipitation-hardening. For this combination of effects to be developed, it is necessary that the heat-treatment causing precipitation should not result in recrystallization of the cold-worked matrix. In order to study nickel–copper—aluminium alloys in this connection experiments were carried out on eleven alloys, the materials selected being the same as those dealt with in Table VI. Strips in the quenched and soft condition were cold-rolled to reductions in thickness of 10, 25, and 50 per cent. Pieces cut from the cold-rolled strips were then annealed for ½ hr. at 550°, 600°, 650°, 700°, 750°, and 800° C., and at the conclusion of the heat-treatment were quenched in water. The results of Brinell hardness tests made on heat-treated specimens are given in Table VIII.

From these figures it may be noted that, for ½-hr. treatments, maximum hardness was reached after heating at temperatures from 550° to 650° C., the higher temperatures in this range being more suitable the higher the nickel content, the higher the aluminium content, and the less the degree of cold-work. In Table IX figures are given showing the temperatures which, for ½-hr. treatments, gave the maximum hardness by precipitation-hardening alone and by combinations of cold-work and precipitation-hardening.

SOFTENING TEMPERATURES OF ALLOYS IN THE COLD-ROLLED CONDITION.

The figures given in Table VIII are of interest also in connection with the heat-treatment necessary to give the fully-softened condition after cold-working. It may be observed, for example, that the alloys of low-nickel and low-aluminium contents were softened after annealing at temperatures from 650° to 700° C., whilst the alloys of higher nickel and aluminium contents required annealing at 750°–800° C. to give the soft condition. Heat-treatment at 800° C., however, did not result in complete softening of alloys high in both nickel and aluminium contents, and for these heat-treatment at about 900° C. is necessary for softening purposes.

THE EFFECT OF PROLONGED LOW-TEMPERATURE ANNEALING ON HARDNESS.

A series of experiments was carried out in order to find whether the hardening produced in nickel–copper–aluminium alloys by precipitation and by a combination of cold-working and precipitation was removed

TABLE VIII.—*The Effect of Re-Heating on the Hardness of Cold-Worked Nickel–Copper–Aluminium Alloys.*

Mark.	Composition, Per Cent.		As Rolled, Reduction.*			Annealing Temperature, ° C.																	
						550° C. Reduction.*			600° C. Reduction.*			650° C. Reduction.*			700° C. Reduction.*			750° C. Reduction.*			800° C. Reduction.*		
	Ni.	Al.	10.	25.	50.	10.	25.	50.	10.	25.	50.	10.	25.	50.	10.	25.	50.	10.	25.	50.	10.	25.	50.
TK	10	0·45	92	111	132	135	145	165	123	137	158	80	70	71	80	69	72	75	70	72	70	70	...
RF	10	1·0	94	116	136	170	191	184	164	185	177	117	129	148	101	108	117	80	67	72	70	70	...
SG	10	2·0	112	137	157	215	225	245	231	230	240	186	193	197	168	166	166	121	125	120	79	79	81
RS	20	0·6	105	128	151	145	167	184	115	150	178	97	87	82	91	80	78	96	80	86	79	80	...
RW	20	1·5	121	142	164	205	230	254	218	241	260	193	205	211	160	169	182	130	139	166	89	89	88
RY	20	2·0	119	164	193	245	260	276	262	276	280	247	255	257	216	222	231	197	196	194	145	151	156
TO	30	0·9	112	162	188	142	170	197	142	178	196	128	128	106	122	98	102	113	99	95	96	105	99
SN	30	2·5	124	173	207	196	253	283	237	276	297	244	257	272	214	223	246	181	204	213	135	152	140
SP	30	3·0	152	190	211	...	276	270	...	283	...	260	270	277	242	270	257	204	207	231	147	140	122
RZ	45	2·5	160	204	227	230	265	321	244	270	332	227	233	265	173	187	152	149	121	130	122	122	122
SA	45	3·0	163	211	246	225	280	297	272	329	366	280	288	315	243	256	291	219	241	270	169	155	146

* Reduction in thickness per cent. by cold-rolling.

by prolonged heating at moderately high temperatures. Specimens of the same alloys as those dealt with in the preceding section, and in the four conditions set out below, were heated for prolonged periods at 550° C. and at 600° C.

1. Precipitation-hardened by furnace cooling.
2. Softened by quenching at 850° C. and cold-rolled to a reduction in thickness of 10 per cent.
3. Softened by quenching at 850° C. and cold-rolled to a reduction in thickness of 25 per cent.
4. Softened by quenching at 850° C. and cold-rolled to a reduction in thickness of 50 per cent.

The initial hardness and the hardness changes resulting from heat-treatment at 550° C. for 5, 10, and 21 days are shown in Table X. The specimens in the furnace-cooled condition were hard, due to the precipitation which occurred during the slow cooling, and in these annealing at 550° C. had but little effect, although in two cases (10 per cent. nickel and 1 per cent. aluminium, and 20 per cent. nickel with 2 per cent. aluminium) some softening occurred, whilst in four alloys some additional hardening resulted from the 550° C. treatment. In the cold-worked specimens pronounced precipitation-hardening was produced during the first annealing period of 5 days. The hardness figures produced by this heat-treatment were rather higher than those produced by short time heat-treatments at 550° C., as may be seen by a comparison with the figures in the 550° C. column of Table VIII and by the figures

Table IX.—*The Heat-Treatment Giving Maximum Hardness in Cold-Worked Nickel–Copper–Aluminium Alloys.*

Mark.	Composition, Per Cent.		Reheating Temperature to Give Maximum Hardness, ° C.			
			Quenched Alloys.	Alloys Cold-Rolled to Reductions in Thickness Per Cent.		
	Ni.	Al.		10.	25.	50.
TX	10	0·45	550	550	550	550
RF	10	1·0	550	550	550	550
SG	10	2·0	600	600	600	550
RS	20	0·6	550	550	550	550
RW	20	1·5	650	600	600	600
RY	20	2·0	650	600	600	600
TO	30	0·9	600	600	600	600
SN	30	2·5	650	650	600	600
SP	30	3·0	650	...	600	...
RZ	45	2·5	650	600	600	600
SA	45	3·0	650	650	600	600

TABLE X.—*The Effect of Long Time Heat-Treatment at* 550° C. *on the Hardness of Nickel–Copper–Aluminium Alloys.*

Mark.	Composition, Per Cent.		Furnace Cooled. Reheating Period, Days.				Cold-Rolled 10 Per Cent. Reduction. Reheating Period, Days.				Cold-Rolled 25 Per Cent. Reduction. Reheating Period, Days.				Cold-Rolled 50 Per Cent. Reduction. Reheating Period, Days.			
	Ni.	Al.	0.	5.	10.	21.	0.	5.	10.	21.	0.	5.	10.	21.	0.	5.	10.	21.
TX	10	0·45	112	125	117	116	92	135	131	113	111	142	139	131	132	146	147	140
RF	10	1·0	150	134	127	125	94	166	157	135	116	166	162	144	136	184	166	146
SG	10	2·0	168	158	162	160	112	223	215	189	137	214	209	197	157	220	209	190
RS	20	0·6	116	137	143	136	105	147	145	135	128	152	156	154	151	178	173	164
RW	20	1·5	166	159	158	158	121	222	215	196	142	216	220	209	164	237	229	214
RY	20	2·0	193	168	166	162	119	287	260	231	164	262	260	237	193	272	255	239
TO	30	0·9	127	166	166	168	112	190	190	170	162	182	202	192	188	216	205	206
SN	30	2·5	188	196	198	193	124	267	265	242	173	257	270	257	207	285	285	291
SP	30	3·0	229	248	255	255	152	283	275	255	190	291	288	275	211	288	290	279
RZ	45	2·5	209	223	226	229	160	271	270	257	204	283	288	280	227	306	301	297
SA	45	3·0	221	237	233	239	163	298	297	285	211	306	312	306	246	368	334	331

TABLE XI.—*The Effect of Long Time Heat-Treatment at* 600° C. *on the Hardness of Nickel–Copper–Aluminium Alloys.*

Mark.	Composition, Per Cent.		Furnace Cooled. Reheating Period, Days.				10 Per Cent. Reduction. Reheating Period, Days.				25 Per Cent. Reduction. Reheating Period, Days.				50 Per Cent. Reduction. Reheating Period, Days.			
	Ni.	Al.	0.	1.	3.	7.	0.	1.	3.	7.	0.	1.	3.	7.	0.	1.	3.	7.
TK	10	0·45	127	96	88	94	92	127	117	105	111	137	131	117	132	139	143	125
RF	10	1·0	150	114	107	103	94	139	131	124	116	161	140	123	136	177	152	135
SG	10	2·0	168	156	152	155	112	245	193	169	137	223	197	172	157	211	206	170
RS	20	0·60	116	117	109	109	105	156	132	118	128	157	146	135	151	157	163	150
RW	20	1·5	166	152	146	148	121	227	205	179	142	233	213	187	164	227	203	193
RY	20	2·0	193	162	160	156	119	271	233	212	164	265	249	220	193	261	255	212
TO	30	0·9	127	136	129	133	112	181	169	148	162	194	184	165	188	212	212	161
SN	30	2·5	188	193	181	177	124	260	244	223	173	277	260	235	207	288	268	253
SP	30	3·0	240	251	246	244	151	294	288	208	190	294	285	251	211	303	...	...
RZ	45	2·5	209	200	206	207	160	274	248	233	201	285	280	249	227	303	303	272
SA	45	3·0	221	229	222	222	163	294	285	266	211	314	315	283	246	334	327	303

given in Tables I–IV. Continuing the annealing for a further 5 days at 550° C., making a total of 10 days at this temperature, produced a slight softening in some cases and a slight hardening in others, but on the whole the changes were of little significance. Further treatment for 11 days at 550° C., making a total of 21 days at this temperature, produced some softening in every case. The final hardness values were some 5–10 per cent. less than the maximum, the hardness decrease being less pronounced in the higher nickel alloys.

A second series of prolonged annealing tests was carried out at 600° C. on specimens similar to those treated at 550° C. The results of the 600° C. treatment for 1, 3, and 7 days are given in Table XI. Of the furnace-cooled specimens, those containing 10 per cent. nickel suffered appreciable softening, more especially during the first 24 hrs. The 20 per cent. nickel alloys were also softened, but not to an extent so pronounced as the 10 per cent. nickel alloys, whilst the 30 per cent. and the 45 per cent. nickel groups were still less affected. The cold-worked samples were all hardened as a result of the first day's treatment at 600° C., owing, no doubt, to the hardening effect of precipitation exceeding the softening effect of recrystallization, but longer periods of annealing, *viz.* 3 days and 7 days, caused a fall in hardness, especially in the 10 per cent. nickel group.

Although the figures given in Table XI indicate clearly that alloys containing 10 and 20 per cent. nickel soften gradually on prolonged heating at 600° C., both when hardened by precipitation alone and when hardened by cold-work combined with precipitation, the softening was far from complete after 7 days' heat-treatment. Since the results given in Table X showed that heating the 30 and 45 per cent. nickel alloys for as long as 21 days at 550° C. resulted in softening only to the extent of 5 and 10 per cent., the change in the last 10 days being negligible, it is reasonably safe to assume that at 500° C. and lower temperatures these alloys would be, for practical purposes, stable.

THE MECHANICAL PROPERTIES OF NICKEL–COPPER–ALUMINIUM ALLOYS.

For determinations of mechanical properties, 2-in. square ingots weighing about 25 lb. were forged and hot-rolled to 1-in. diameter bars, followed in most cases by cold-drawing to a reduction in cross-sectional area of 25 per cent. Tensile test-pieces with a parallel portion 0·564 in. in diameter and suitable for a 2 in. gauge-length were machined from blanks in various conditions. Where softening treatment was applied, the test-piece blanks were reheated to 850° C. and quenched in water, whilst the precipitation-hardening heat-treatment applied consisted of heating for 1 hr. at 550° C. These heat-treatments were not the most suitable for all the specimens, although the improvement in mechanical properties obtainable by variations on this heat-treatment could not be expected, on the basis of hardness variations, to be very pronounced.

The mechanical properties of 20 per cent. nickel alloys are given in detail, to show the effect of variations in aluminium content and the differences according to heat-treatment. The effect of variations in nickel content at a constant precipitation-hardening level are shown, and from these two groups a satisfactory impression of the properties of alloys over a wide range of compositions may be gained.

The first portion of Table XII shows the mechanical properties of three alloys with varying aluminium content in the quenched and soft condition. There is no special interest in the figures beyond the demonstration of high ductility and the inference which may be drawn that the alloys may be cold-worked without difficulty, an inference well supported by experience.

Table XII.—*The Mechanical Properties of Nickel–Copper–Aluminium Alloys in the Quenched and Re-Heated Conditions.*

Mark.	Composition, Per Cent.		Condition.	Maximum Stress Tons/in.^{2}.	Elastic Limit, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction in Area, Per Cent.
	Ni.	Al.					
WP	20·51	0·45	Soft	23·5	4·4	49	65
QQ	20·05	0·91	,,	23·8	4·0	49	65
WH	19·88	1·20	,,	23·2	4·1	49	71
WP	20·51	0·45	Hard	33·5	12·4	26	44
UT	19·98	0·65	,,	37·8	12·8	23	52
YJ	20·01	0·86	,,	42·4	16·8	33	45
UU	19·88	1·04	,,	43·8	16·8	26	51
WH	19·88	1·20	,,	44·4	17·4	25	36
UP	19·78	1·37	,,	50·6	18·0	21	40
UW	20·10	1·52	,,	57·2	20·4	20	37
PZ	20·08	1·95	,,	58·4	24·8	19	24
UO	10·2	1·10	,,	48·6	18·0	21	43
YL	29·83	1·69	,,	48·8	18·0	32	43

The second portion of Table XII shows the mechanical properties of a group of 20 per cent. nickel alloys in the precipitation-hardened condition. The alloys are arranged in order of increasing aluminium content, and it may be noted that the tensile strength increases uniformly with increasing aluminium content from 33 to 58 tons/in.^{2}. The limit of proportionality increases with increasing aluminium content from 12 to 25 tons/in.^{2}. The elongation and reduction in area figures are somewhat irregular, and, as might be expected, show a ductility decreasing with increasing tensile strength. Nevertheless, even in the alloys with a tensile strength over 50 tons/in.^{2}, there was a pronounced measure of ductility.

The third portion of Table XII deals with two alloys containing 10 and 30 per cent. nickel and having aluminium contents such that a hardness increment of approximately 90 Brinell could be obtained in each alloy by suitable precipitation-hardening heat-treatment. The precipitation-hardening capacity of these two alloys is similar to that of the 20 per cent. nickel alloy mark "UP" already dealt with. The effect of an increased nickel content, apart from increased corrosion resistance, is to develop for a given strength and elastic limit a greater ductility, or for a given ductility a greater strength and higher elastic limit.

It has already been demonstrated that in nickel–copper–aluminium alloys the hardening effects of precipitation can be combined with those due to cold-working, and in Table XIII the mechanical properties are given of a number of alloys which have been cold-drawn to a reduction in cross-sectional area of 25 per cent. and then precipitation-hardened.

TABLE XIII.—*The Mechanical Properties of Nickel–Copper–Aluminium Alloys Cold-drawn to a Reduction in Cross-sectional Area of* 25 *per Cent. and Re-Heated for* 1 *hr. at* 550° C.

Mark.	Composition, Per Cent.		Maximum Stress, Tons/in.^{2}.	Elastic Limit, Tons/in.^{2}.	Elongation on 2 in., Per Cent.	Reduction in Area, Per Cent.
	Ni.	Al.				
UT	19·98	0·65	46·5	25·2	20	50
UU	19·88	1·04	54·2	25·6	15	36
UP	19·78	1·37	61·2	29·6	14	35
UW	20·10	1·52	60·5	29·2	14	25
PZ	20·0	1·95	66·5	41·6	12	24
UO	10·2	1·10	51·3	26·8	18	34
YL	29·83	1·69	58·1	31·2	16	38

Most of the examples given refer to 20 per cent. nickel alloys, one example only being given of alloys at the 10 and 30 per cent. nickel levels. As in the case of alloys hardened by precipitation only, the tensile strength and limit of proportionality increase with increasing aluminium content. The strengths and elastic limits developed in the cold-worked alloys are considerably higher than those developed in the same alloys by precipitation-hardening alone, but the ductility, of course, is reduced. With increasing nickel content, however, it has again consistently been found that the ductility which accompanies a given tensile strength or elastic limit increases, a better combination of mechanical properties being thus obtained. This is particularly the case when the alloys are treated to give high values for maximum stress, say 60 to 70 tons/in.^{2}.

REFERENCES.

[1] G. F. Andrews, "Notes on Aluminium," *J. Amer. Chem. Soc.*, 1894, **16**, 485–486.

[2] L. Guillet, "Alloys of Copper, Nickel, and Aluminium," *Compt. rend.*, 1914, **158**, 704–706.

[3] A. A. Read and R. H. Greaves, "The Influence of Nickel on Some Copper–Aluminium Alloys," *J. Inst. Metals*, 1914, 11, 169–207. "The Properties of Some Nickel–Aluminium–Copper Alloys," *J. Inst. Metals*, 1921, **26**, 57–84.

[4] I. Iitaka, "Some Researches on the Ternary Alloys Copper–Aluminium–Nickel (Especially as Materials Exposed to Moderately High Temperatures, as Turbine Blades, Valves, &c.)," *J. Soc. Mech. Eng. Tokyo*, 1922, **25**, (72), 1–27; and (abstract) *J. Inst. Metals*, 1926, **36**, 439–440.

[5] D. G. Jones, L. B. Pfeil, and W. T. Griffiths, "Nickel–Copper Alloys of High Elastic Limit," *J. Inst. Metals*, 1931, **46**, 423–442.

PROPERTIES OF SOME TEMPER-HARDENING COPPER ALLOYS CONTAINING ADDITIONS OF NICKEL AND ALUMINIUM.*

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SYNOPSIS.

A study has been made of the effect of quenching and tempering on the properties of a number of copper alloys containing nickel and aluminium, and it has been found that when nickel, together with aluminium, are present in certain quantities and ratios, the hardness and other mechanical properties of the alloys are very considerably modified by the thermal treatment to which they are submitted. The alloys are softened by quenching from relatively high temperatures and the quenched alloys both in the soft and cold-worked conditions harden considerably when re-heated or tempered to an intermediate temperature somewhat below the annealing temperature. For a few typical alloys the changes in hardness and mechanical properties that can be brought about by suitable heat-treatment are given in some detail.

INTRODUCTION.

IN the course of an investigation commenced about two and a half years ago into the effect of nickel on aluminium–brasses and of aluminium on cupro–nickel, several difficulties and apparent abnormalities were encountered, particularly with regard to hardness after annealing. For example, it was found that the addition of appreciable amounts of nickel to aluminium–brasses resulted in a marked increase in hardness of slowly-cooled ingots, rendering them unsuitable for cold breaking-down. It was found, however, that the alloys could be softened by quenching from a temperature in the region of 900° C., and that the soft quenched alloys could be hardened considerably by tempering at temperatures of the order of 500°–600° C. It was also found in the case of aluminium–brasses that in the presence of about 2 per cent. of nickel, the temper-hardening effects were only slight, and no appreciable hardening could be produced in alloys containing less than about 0·5 per cent. aluminium. It soon became evident that not only was the

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extent of hardening controlled by the amounts of aluminium and nickel present, but also by the ratio of these two elements, and optimum temper-hardening was obtained when the nickel was present to the extent of at least about four times the aluminium content. The amount of the aluminium addition is limited by the extent to which it is desired to fabricate the alloys, and for cold-working alloys a satisfactory upper limit for this element appears to be about 3 per cent.

Temper-hardening properties can be produced in a very wide range of commercially used copper alloys by adding 1–3 per cent. aluminium, together with nickel to the extent of about four times the aluminium content.

The present investigation has been concerned primarily with determining the properties of the alloys and establishing the conditions of heat-treatment necessary for securing the maximum degree of improvement in properties.

The properties of alpha brasses containing additions of aluminium are quite well known,[1] and their outstanding peculiarity is the high degree of resistance which they offer to certain forms of corrosive attack and oxidation at elevated temperatures. In respect of physical properties they are not very dissimilar from straight brasses of an equivalent composition but containing no aluminium, and they do not exhibit any temper-hardening properties. While this work was in progress a patent was filed in America by W. B. Price [2] for an alloy containing preferably copper 80, aluminium 2, nickel 1 per cent., the remainder being substantially zinc, but no temper-hardening properties were claimed for it. In a booklet [3] published by the Scovill Manufacturing Company, of Waterbury, Connecticut, U.S.A., dealing with similar alloys, Price stated that he would expect that the alloy could be hardened by reheating after quenching from a higher temperature, but that he had not succeeded in producing such hardening.

So far as the authors are aware, it has not been recorded that copper–zinc alloys containing additions of aluminium and nickel exhibit temper-hardening properties. After preliminary work had firmly established the validity of this conclusion, it was decided in the first instance, in view of the complexity of the system, to investigate more fully the temper-hardening characteristics of copper-rich alloys in the copper–nickel–aluminium ternary system. It was found as long ago as 1914 by Read and Greaves,[4] who investigated the effect of nickel on aluminium–bronzes, that certain alloys were softer after quenching from 900° C. than after slow cooling from the same temperature. More recently, Iytaka,[5] Ishikawa,[6] and Saito [7] have described the properties of an alloy containing copper 88, nickel 10, and aluminium

2 per cent., which they have stated to be age-hardenable. The International Nickel Company[8] has taken out patents relating to alloys containing at least 15 per cent. and preferably more than 40 per cent. nickel, 2–17 per cent. aluminium, and the remainder copper, which can be improved by heat-treatment, and since the work described in this paper on the ternary alloys was completed, a patent has been obtained by the Mond Nickel Company, Ltd.,[9] relating to copper–nickel–aluminium alloys containing nickel 2–40, copper 98–60 per cent., and additions of aluminium.

No detailed information, however, is available concerning the properties and temper-hardening characteristics of the copper-rich alloys of the ternary system, and the first part of the paper is therefore devoted to these materials. Subsequent sections deal with more complex alloys containing similar additions of nickel and aluminium, but containing as a base zinc, tin, and manganese, in addition to copper.

COPPER–NICKEL–ALUMINIUM ALLOYS.

A series of copper–nickel–aluminium alloys, containing from 85 per cent. upwards of copper, was prepared containing nickel and aluminium additions in the ratios of 1 : 1, 2 : 1, 3 : 1, 4 : 1, 6 : 1, and 10 : 1, respectively, and various miscellaneous alloys were also made containing nickel and aluminium in different amounts, such as a series of 92 : 8 "aluminium bronzes" containing varying nickel additions, whilst a number of 70 : 30 cupro–nickel alloys were made to which aluminium in amounts varying up to about 3 per cent. was added. For the present purpose small ingots weighing about 8 lb. each were made using high conductivity copper, a 50 : 50 copper–nickel alloy made from high conductivity copper and shot nickel, and aluminium. Alloys containing aluminium in amounts of the order of 2 per cent., together with appreciable quantities of nickel, were too hard in the cast condition for rolling, and therefore before rolling they were softened by quenching from 900° C. The alloys were reduced approximately 50 per cent. in thickness between annealings, and the annealing was carried out at 900° C., from which temperature the strips were quenched.

The temper-hardening characteristics of the whole range of alloys have been determined on specimens of rolled strip 0·125 in. thick which were heated for 1 hr. at the temperature of 900° C. followed by quenching in cold water and subsequently tempering at various temperatures for 2 hrs. In this way direct comparison of the temper-hardening characteristics of the whole series of alloys was determined and subsequent work was carried out on certain selected alloys only, in order to ascertain the influence of time and temperature of tempering and the effect of tempering hard-worked material.

(a) *Influence of Tempering Temperature.*

In this series of experiments the specimens of hard-rolled strip were heated at 900° C. for 1 hr., followed by quenching in water and tempering to temperatures within the range 300°–650° C. for 2 hrs. The results of the various tests are recorded in Table I. Of the alloys studied a 5 per cent. addition of nickel plus aluminium in the proportion 1 : 1 and 2 : 1 did not produce alloys with temper-hardening properties, but similar additions in proportions of 3 : 1 and 4 : 1 resulted in alloys which, with a given heat-treatment, consisting of quenching from 900° C. and tempering for 2 hrs. at 400°–600° C., gave hardness increments of 15 and 59, respectively. A 5 per cent. nickel–aluminium addition in the ratio of 10 : 1 gave a hardness increment of 20.

Approximately 10 per cent. additions of nickel and aluminium in the ratios of 1 : 1, 2 : 1, 3 : 1, 4 : 1, 6 : 1, and 10 : 1 result in the alloys giving hardness increments of 29, 57, 110, 117, 104, and 117, respectively. From these additions it would seem that the optimum proportion of nickel to aluminium is in the range of 4 : 1 up to 10 : 1. The effect of increasing amounts of aluminium with an approximately constant nickel content is shown by comparison of alloys Nos. 27, 30, and 8, which contain nominally 1·5, 2·0, and 3·3 per cent. aluminium, respectively, and approximately 6 per cent. of nickel. The hardness increments on tempering were 112, 119, and 57, indicating that with excess of aluminium alloys actually show less hardening.

The results obtained indicate that the optimum reheating temperature for obtaining maximum hardening effect is 500°–600° C.

(b) *Influence of Duration of Tempering.*

To determine the influence of time of tempering, only a few selected alloys, which were known to show marked temper-hardening properties, were studied. After annealing at 900° C. for 1 hr., followed by quenching, the specimens were reheated at temperatures of 400°, 500°, and 600° C., for periods of up to 20 hrs. The results of these experiments are detailed in Table II.

Some of the alloys which after the 2 hr. tempering treatment show practically no hardening, hardened appreciably after reheating for 20 hrs. These alloys are Nos. 12, 7, and 3, in which increments of 50 69, and 74 were found, as compared with values of 29, 8, and 15 after 2 hrs.' reheating.

While generally the increased time of tempering from 2 to 20 hrs. in the case of alloys showing marked temper-hardening characteristics resulted in still further hardening, the hardness after 20 hrs. was only slightly greater than that recorded after 2 hrs., which again was greater than that recorded after 15 minutes' heating. The time effect is more marked on those alloys which show only very slight temper-hardening, but from a practical point of view it would seem that in those alloys which exhibit hardening characteristics to a marked degree, little is to be gained by prolonging the heat-treatment beyond the 2 hr. period.

There is again evidence both in the specimens tempered for 2 hrs. and for 20 hrs. that the most satisfactory ratio of nickel to aluminium is 4 : 1, for in the series of alloys containing 10 per cent., the hardness increments were 50, 67, 110, 143, 114, and 121 for ratios of nickel to aluminium of 1 : 1, 2 : 1, 3 : 1, 4 : 1, 6 : 1, and 10 : 1, respectively. It would also seem from these values that a departure from its optimum ratio of 4 : 1 in the direction of increasing nickel affects the results adversely to a far less extent than altering the ratio by increasing the proportion of aluminium.

(c) *Influence of Initial Quenching Temperature.*

To determine the effect of initial quenching temperature a few selected alloys were heated to 800° and 1000° C., quenched and subsequently tempered at the same temperatures as materials softened by quenching from 900° C. The results obtained are detailed in Table III. It will be seen from the results that there is little difference in the hardness values of strip which had been quenched from 800°, 900°, and 1000° C., and similar values were obtained on tempering, at given temperatures, materials quenched from any one of the three temperatures enumerated. The only exceptions were alloys Nos. 16 and N21, which were not fully softened by heating at 800° C.

(d) *Tempering of Hard-Rolled Strip.*

In order to ascertain whether it would be possible to effect an increase in the hardness of hard-rolled strip by tempering at low temperatures, a series of samples was annealed for ½-hr. periods at temperatures ranging from 300° to 900° C., and the results obtained are given in Table IV. In no single instance did the hardness increment approach that obtainable on the annealed materials, but this was an expected result, for some degree of softening of the work-hardened material is likely to occur at the temperatures at which the tempering was carried out. The increase in some instances amounted to more than 70 diamond pyramid numbers, the highest hardness being recorded at temperatures just below the point at which softening commences. In some instances this is of the order of 500° C., but several of the alloys did not soften appreciably until a temperature of approximately 600° C. was reached.

Tempering of the hard-rolled alloys for long periods at temperatures of 300°–500° C. in order to ascertain whether higher hardness increments might be obtained has been carried out, and details of the results are given in Table V. It will be observed that, generally, slightly higher increments can be obtained by prolonged tempering. Perhaps the most interesting result is that tempering the alloys which possess the most pronounced hardening tendencies at 500° C. for as long as 20 hrs. results in their being appreciably hardened. Another interesting feature is that the alloys which exhibit less marked hardening tendencies, and which are actually softened as a result of tempering for 30 minutes at 400°–500° C., become, in many cases, appreciably harder after prolonged heating at these same temperatures.

(c) *Mechanical Properties.*

In order to obtain more complete data regarding the properties of the alloys, it was decided to produce a few selected ones in suitable fabricated forms and make a more exhaustive examination of their properties. For this purpose the following alloys were chosen and produced in the form of extruded rod and rolled strip.

Nominal Composition of Alloy.			No. of Sample.	
Copper, Per Cent.	Nickel, Per Cent.	Aluminium, Per Cent.	Extruded Rod.	Rolled Strip.
96·25	3	0·75	L.S.24	...
95·0	4	1	L.S.23	L.S.20
92·5	6	1·5	L.S.7	L.S.10
85	13·5	1·5	L.S.8	L.S.11
70	28·5	1·5	L.S.9	L.S.12

In the preparation of the above nine samples the 1 in. diameter extruded rods were subjected to 10 per cent. reduction by cold-working, and the rolled strips were finished with 50 per cent. reduction, the final thickness being approximately 0·125 in.

The strips were all produced from ingots cast by the Durville process. The ingots measured approximately 15 × 6 × 1·25 in. and weighed about 40 lb. each. Ingot L.S.20 was hot-rolled in four passes to a thickness of 0·25 in., and then cold-rolled to the finished thickness of 0·125 in., without other treatment. The three ingots L.S.10, L.S.11, and L.S.12 were cold-rolled throughout, the final reduction being one of 50 per cent. to the finished thickness of 0·125 in.

The test-pieces used throughout this investigation were either round test-pieces, in the case of the rods, or flat test-pieces, in the case of the strip materials. The former test-pieces had a diameter of 0·564 in. on the parallel portion and a gauge-length of 2 in. The strip test-pieces were 0·5 in. wide at the parallel portion, and the gauge-length was 2 in.; the end portions of these test-pieces were 1 in. wide, and were held in the testing machine by means of wedge grips. For determination of the limit of proportionality a Lamb's roller extensometer was employed and the proof stresses were taken from the stress–strain diagrams.

In the case of alloy L.S.7, a fairly extensive study was made, and it was found that, in general, tempering at different temperatures results in changes in tensile strength and elongation which are comparable with the changes in hardness. The effects on the limit of proportionality were very marked and the improvements were quite exceptional. In Table VI are given the results which were obtained on tensile test-pieces from this rod after tempering at the different temperatures indicated. While the tensile strength is more than doubled, the hardness almost trebled, and elongation reduced to less than one half of its former value as a result of tempering, the limit of proportionality is raised to 17·9 tons/in.^{2}, which is approximately 15 times its former value.

With the remaining samples such an exhaustive study of physical properties has not been made, but the properties have been determined in the following conditions :—

A. As cold-rolled (strip) or drawn (rod).
B. As cold-rolled or drawn, followed by tempering so as to obtain maximum hardness.
C. As softened by quenching from 900° C.
D. As softened, followed by tempering so as to obtain maximum hardness.

The conditions of heat-treatment were those found either by preliminary trials or by the experiments reported in the previous sections of the paper to give the maximum temper-hardening effects.

The results of the tests are given in Tables VII and VIII. Alloys L.S.20, 23, and 24 do not contain sufficient of the temper-hardening constituent to yield very marked improvements on tempering; they may be regarded as mild temper-hardening alloys, and the increase in tensile strength of the quenched material is from approximately 17 tons/in.^{2} to approximately 25–30 tons/in.^{2}. With a larger quantity of nickel and aluminium in the ratio of 4 : 1, *i.e.*, L.S.7 and 10, the improvement in tensile strength is approximately from 20–22 tons/in.^{2} up to 40–44 tons/in.^{2}.

With the other alloys, L.S.8, 9, 11, and 12, the improvements in tensile strength were again of a similar order, being more than doubled by the treatment.

The hard-drawn or rolled materials were also improved by tempering, the tensile strength being appreciably raised, with little loss, and in some instances even a marked improvement, in elongation. In the case of the hard-rolled strips (50 per cent. reduction), the increases in those alloys with more pronounced temper-hardening tendencies, with nickel varying from 6 up to 28·5 per cent. and a constant aluminium content of 1·5 per cent., amounted to 12·4–19 tons/in.^{2} in the different samples, and there were considerable increases in elongation, these being from 5 to 22, from 4 to 15, and from 1 to 7 per cent. In the case of the hard-drawn rods (10 per cent. reduction), the increases in the tensile strengths of the corresponding samples were again most marked; the actual increases were between 20·0 and 26·7 tons/in.^{2} in the three samples, but these changes were accompanied by decreases in elongation. The smallest elongation of such hard-drawn and tempered material was 12 per cent., which is a high value in view of the general range of tensile strengths.

In addition to the properties at ordinary temperatures in the various conditions, some tests were carried out at elevated temperatures and the results are also incorporated in Tables VII and VIII. The tests were carried out at temperatures of 300°, 400°, and 500° C., and the results show that there is a fair retention of tensile strength, but very little elongation. This marked falling off in elongation is a general feature of most copper alloys. 70 : 30 brass, for example, possesses only a very small elongation within a temperature range of about 300°–500° C., and becomes more ductile at higher temperatures. "Aluminium–bronzes" show very similar properties, the elongation falling almost to a zero value at 400° C.

The properties of some of the alloys in the form of wire in various conditions are given in Table IX and in the form of condenser tubes in Table X.

(f) *Microstructure of the Alloys.*

Although a detailed investigation has not been made of the mechanism of the hardening which occurs on tempering, the microstructures of a large number of alloys in different conditions have been examined. In some instances, where the alloy appears to be duplex after quenching, considerable changes occur in the structure on sub-

FIG. 1.—Alloy 27 (Nickel 6%, Aluminium 1·5%). Quenched from 900° C. Diamond Pyramid Hardness 75. × 250.

FIG. 2.—As Fig. 1, but Tempered for 2 at 500° C. Diamond Pyramid Hardn 187. × 250.

FIG. 3.—Alloy 27 (Nickel 6%, Aluminium 1·5%). Hard-Rolled. Tempered at 500° C. for 30 minutes. Diamond Pyramid Hardness 190. × 250.

FIG. 4.—Alloy 26 (Nickel 10%, Aluminiu 2·5%). Quenched from 900° C. Diamo Pyramid Hardness 94. × 250.

FIG. 5.—Alloy 8 (Nickel 6·6%, Aluminium 3·3%). Quenched from 900° C. Diamond Pyramid Hardness 76. × 250.

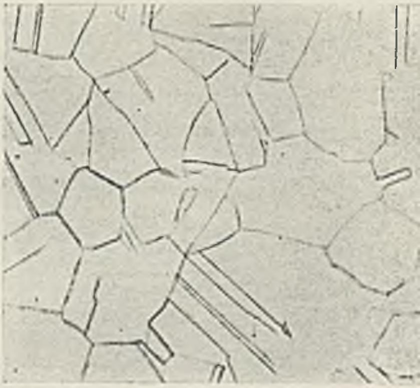

FIG. 6.—Alloy 8 (Nickel 6·6%, Aluminiu 3·3%). Quenched from 900° C. and Te

sequent tempering, and a typical change which takes place in many of these alloys is shown in Figs. 1 and 2 (Plate XLVII), which illustrate respectively the structure of alloy 27 containing nickel 6 and aluminium 1·5 per cent. in the quenched, and quenched and tempered conditions. A typical structure of an alloy in the hard-rolled and tempered condition is shown in Fig. 3 (Plate XLVII). The second constituent occurs at the crystal boundaries, and while in some cases only an apparent double boundary or thickening of the boundary is evident, in others the second constituent occurs in a more massive form, as shown in Fig. 4 (Plate XLVII). Although many of the alloys in which temper-hardening effects have been observed appear to be duplex, temper-hardening has also been noted in alloys which appear microscopically to be structurally homogeneous. An example of an alloy in which little apparent change in structure occurs on tempering is illustrated in Figs. 5 and 6 (Plate XLVII).

COPPER–ZINC–NICKEL–ALUMINIUM ALLOYS.

In studying the temper-hardening characteristics of copper–zinc–nickel–aluminium alloys some 17 alloys of various compositions were examined. In the preliminary work to establish the optimum conditions of tempering and to study the effect of quenching temperature, time and temperature of tempering, small ingots measuring 8 × 3 × 0·75 in. were made and rolled down into strip about 0·125 in. thick, and small samples were subjected to varying tempering treatments, after which diamond pyramid hardness values were determined. As a result of the work described in a previous section, a quenching temperature of 900° C. was adopted as standard, and the specimens were heated to this temperature for 1 hr., quenched, and subsequently tempered at various temperatures for 2 hrs. Some further experiments were undertaken on a few selected alloys to ascertain the influence of time of tempering, and also the influence of quenching temperature prior to tempering. The effect of tempering the alloys in the cold-worked condition was also studied.

(a) *Influence of Tempering Temperature.*

The results of the various tests carried out in this connection are detailed in Table XI, in the last column of which are given the maximum hardness increments for each alloy.

Of the alloys studied, only those with a nickel content in excess of about 2 per cent. showed temper-hardening properties. When nickel and aluminium are present in copper–zinc alloys, similar temper-hardening increments can be obtained as in the case of copper containing corresponding additions of nickel and aluminium. For example, hardness values of alloy No. 40, which contains nickel 4, aluminium 1, and zinc 10 per cent., are 57 and 116 in the quenched condition and after reheating to the ultimate temperature, whilst an alloy of the same nickel and aluminium content, but containing no zinc (alloy No. 33), had corresponding values of 55 and 114. Similarly, in the case of alloy No. 59, containing nickel 8, aluminium 2, and zinc 10 per cent., the hardness values were 72 and 193 in the quenched and tempered conditions, respectively, whereas in an alloy of the same nickel and aluminium content but containing no zinc (No. 34) the values were 69 and 186, respectively.

In the quaternary alloys under consideration there seems to be a tendency for temper-hardening to be produced with smaller amounts of nickel and aluminium. For example, alloy A2, which contains nickel 2·15 and aluminium 1·62 per cent., showed quite appreciable temper-hardening, an actual increment of 48 diamond pyramid numbers being obtained, whereas the ternary alloys containing nickel 2·5 with aluminium 2·5 per cent., nickel 1·32 with aluminium 0·66 per cent., and nickel 3·3 with aluminium 1·65 per cent., showed only a maximum increment of 8 hardness points.

The data given in Table XI indicate that the optimum tempering temperature for obtaining the maximum hardening effect varies from 500° to 600° C., according to the composition of the alloy. The same data show that with the alloys containing approximately zinc 20 and aluminium 2 per cent. the magnitude of the hardening effect obtainable increases progressively with the nickel content, throughout the series, which ends with 10 per cent. of nickel. Of the five gilding metals considered, all of which had a zinc content of 10 per cent., the maximum increment was obtained with the alloy containing nickel 8 and aluminium 2 per cent. Of the three nickel silvers examined, which contained copper 60, nickel 20, and zinc approx. 20 per cent., the temper-hardening effect obtainable was found to increase with increasing aluminium up to the amount considered, *i.e.*, 1 per cent.

(b) *Influence of Time of Tempering.*

Certain of the alloys which showed marked temper-hardening properties were quenched from the temperature of 900° C., and heated at temperatures of 400°, 500°, and 600° C. for periods of 15 minutes, 2 hrs., and 20 hrs. Observations were made upon the diamond pyramid hardness values of the various specimens, the results being recorded in Table XII.

There is a certain amount of evidence indicating that these alloys tend to soften on tempering at lower temperatures than the straight copper–nickel–aluminium alloys, this effect being particularly noticeable when the heating was prolonged. For example, alloy No. 17, which contained nickel 10, aluminium 2, and zinc approx. 20 per cent., lost a considerable amount of its hardness by heating for 20 hrs. at 600° C., as a result of which treatment the actual hardness was 137, as compared with a maximum hardness of 224, which has been noted for this alloy. On the other hand, alloys such as Nos. 34 and 26, which contain nickel 8 with aluminium 2 per cent., and nickel 10 with aluminium 2·5 per cent., were almost at their maximum hardness value as a result of tempering at 600° C. for 20 hrs.

(c) *Influence of Initial Quenching Temperature.*

A series of specimens was quenched from 800° C. and tempered, along with the specimens quenched from 900° C. at 500°, 550°, and 600° C. The results obtained are given in Table XIII, and indicate, generally, that the higher temperature results in a slightly greater hardness effect being obtained on reheating. By quenching from 900° C. the alloy is obtained in a condition definitely softer than it is by quenching from 800° C.

(d) *Tempering of Hard-Rolled Strip.*

In order to ascertain whether it would be possible to effect an increase in the hardness of cold-rolled strip by tempering, a series of samples was annealed for ½-hr. periods at temperatures ranging from 300° to 900° C., and the results are given in Table XIV. The effect of prolonging the time of heating of hard-rolled strip has been studied on a few selected alloys, and the results obtained with annealing periods varying from 30 minutes to 63 hrs. at temperatures up to 500° C. are recorded in Table XV.

These results indicate that the alloys which are amenable to heat-treatment in the softened condition could be hardened somewhat by heating for a 30-minute period at a temperature below that at which softening occurs. The increase in hardness resulting from this heat-treatment of cold-worked material is not, of course, nearly so great as that obtained on heating the alloys in the quenched condition. The maximum increment obtained was 57 with an alloy containing nickel 7·5, aluminium 2·5 with zinc 10 per cent., the hardness of 193 in the rolled condition being raised to 250 by heating for 30 minutes at 500° C. As previously noted with other data, values recorded in Table XIV, when compared with some of those for the copper–nickel–aluminium alloys, show that the presence of zinc causes softening to take place at lower temperatures, this effect increasing with increased zinc content.

The results obtained in experiments dealing with the effect of time of tempering on the hard-rolled material are given in Table XV, and show that the presence of zinc may cause softening to occur on prolonged heating, under conditions which do not produce any softening in a corresponding alloy free from zinc. For instance, alloy 34 of the previous section, which contains nickel 8 and aluminium 2 per cent., acquired hardnesses of 262 and 270 by heating to 500° C. for 3 hrs. and 20 hrs., respectively (in the original hard-rolled condition its hardness was 174), whilst alloy 39 in the present series, which contains similar amounts of nickel and aluminium, together with 10 per cent. of zinc, had an original hardness in the rolled condition of 195, which was increased to 274 by heating for 3 hrs. at 500° C., but decreased to 252 by continued heating at this temperature for a total of 20 hrs. Alloy 17, which had nickel and aluminium contents not far removed from those of alloy 39, but which contained 18 per cent. zinc, had a hardness in the rolled condition of 227, and this could be increased to 290 by heating at 300° C. for 20 hrs., but heat-treatment at higher temperatures actually resulted in softening.

(c) *Mechanical Properties.*

The physical properties of two alloys containing zinc 20 together with aluminium 6 and nickel 1·5 per cent. (alloy 61) and nickel 13·5 and aluminium 1·5 per cent. (alloy 62), were determined in the following conditions:—

A. Cold-rolled (50 per cent. reduction).
B. Cold-rolled, followed by tempering at 500° C. for 2 hrs.
C. Softened by quenching from 900° C.
D. Softened followed by tempering for 2 hrs. at 500° C.

The results obtained are given in Table XVI.

After tempering at 500° C. for 2 hrs. the hard-rolled alloys containing zinc were improved, but the increase in tensile strength was not so marked as in the straight copper–nickel–aluminium alloys. In the quenched condition, the alloys containing zinc were, as would be expected, slightly harder, and showed greater values for elongation than the alloys free from zinc. The increments in hardness values and tensile strength which resulted from tempering of softened samples are much lower in the case of the alloys containing zinc. Whereas with the 92·5 : 6 : 1·5 alloy it was possible to obtain a tensile strength of 40 tons/in.^{2} and for the 85 : 13·5 : 1·5 alloy 48·4 tons/in.^{2} by tempering at 550° and 600° C., respectively, for 2 hrs., alloys containing corresponding quantities of nickel and aluminium together with 20 per cent. of zinc had tensile strength values of 36·6 and 36·7 tons/in.^{2} after tempering.

COPPER–TIN–NICKEL–ALUMINIUM ALLOYS.

The nominal compositions of the alloys investigated are included in Table XVII. Three series were prepared having tin contents of 4, 8, and 12 per cent., and each series consisted of three alloys in which the ratio of nickel to aluminium was 2 : 1, 4 : 1, and 10 : 1, the amount of aluminium being fixed at 1·5 per cent. The alloys containing 4 and 8 per cent. of tin were chill-cast in the form of small ingots (6 × 1·75 × 0·75 in.) suitable for rolling, and those containing 12 per cent. of tin were prepared as sand-cast bars about ⅞ in. diameter by about 8 in. long. The alloys were made from virgin metal, except that the nickel was added as 70 : 30 cupro–nickel. No working of any kind was attempted on the sand-cast alloys; they were simply heat-treated as described later and their temper-hardening properties examined by hardness tests. Hardness values on the cast alloys are given in Table XVII. From observations made on the rolling properties of these alloys it would appear that those with 8 per cent. of tin are not suitable for rolling. The 4 per cent. tin series can be rolled, although rolling difficulties increase with the nickel content.

(a) *Temper-Hardening Characteristics.*

As a result of the previous work carried out, as to the influence of quenching temperature, and of time and temperature of tempering on the hardness increase, the hard-rolled alloys were softened by annealing for 1 hr. at 900° C. and quenching in cold water. The chill-cast alloys which could not be rolled were also softened in this way. The sand-cast alloys, however, were quenched from 850° C., since with a tin content of 12 per cent. there was a danger of partial fusion at 900° C.

The time of tempering the softened material was standardized at 2 hrs., since this had been found suitable for similar alloys; longer times gave only slightly greater hardness values.

In order to establish the optimum tempering temperature for these alloys, samples of alloys 1T and 2T and of the three sand-cast alloys (Nos. 7T, 8T, and 9T) in the soft condition were reheated for 2 hrs. at temperatures within the range 300°–650° C. The values obtained are shown in Table XVIII. With alloy 1T, in which the nickel–aluminium ratio was 2 : 1, only a slight hardening effect was obtained, but with alloy 2T, where the ratio was 4 : 1, very marked hardening resulted. The figures show that the optimum results are obtained by tempering at 500°–550° C., and above 550° C. softening commences.

Alloys 3T, 4T, 5T, and 6T, which had not been successfully rolled, were softened by quenching from 900° C. and hardened by tempering for 2 hrs. at 500° C. Tempering was carried out at the same time on samples of the cold-rolled materials, where these were available; the hardness figures obtained are given in Table XVII.

Considering the three series containing 4, 8, and 12 per cent. of tin, the increases in hardness by heat-treating the softened materials for given nickel–aluminium ratios are :—

Ratio of Nickel–Aluminium.	Maximum Hardness Increase.		
	Tin, 4%.	Tin, 8%.	Tin, 12%.
2 : 1	14	28	57
4 : 1	102	99	96
10 : 1	107	126	114

It will be observed from these figures, in conjunction with the hardness values in Table XVII, that, whilst the hardness of softened alloys containing the same amount of nickel increases progressively with the tin content, the hardening produced by tempering is approximately the same in the three series, except in the alloys having a nickel : aluminium ratio of 2 : 1, where there is an increase in temper-hardening with increasing tin content.

(b) *Mechanical Properties.*

A few tensile tests were carried out on the rolled strip of alloy 2T.

Tensile test-pieces were made (0·5 in. wide over the gauged portion) and treated so as to give material in four conditions :—

(1) Softened by quenching from 900° C.
(2) Softened and tempered at 500° C. for 2 hrs.
(3) Softened and cold-rolled (50 per cent. reduction).
(4) Softened, cold-rolled, and tempered at 500° C. for 2 hrs.

The thickness of strip was 0·1 in. for the first two, and 0·05 in. for the last two, conditions. Besides the tests at room temperature, the material in each condition was tested at 400° C. The results obtained are given in Table XIX. Considering the tests at room temperature, it will be seen that the tensile strength after tempering is almost as high as after a 50 per cent. reduction by rolling (44·0 against 46·2 tons/in.^{2}, respectively), whilst the material is very much more ductile after tempering than after rolling. Moreover, the strength of the cold-rolled material is raised nearly 11 tons/in.^{2} by tempering and the ductility is increased at the same time from 4 to 11 per cent.

When tested at 400° C. the temper-hardened material loses almost three-quarters of its strength and is very brittle. On the other hand, although the cold-rolled and tempered material is also brittle at this temperature, it loses less than half its strength.

The temper-hardening and tensile properties of this alloy may be directly compared with those of alloy L.S.10, containing nickel 6, aluminium 1·5, with copper 92·5 per cent. The increase in hardness obtainable by tempering appears to be about the same in alloy 2T as in L.S.10. In the tensile tests carried out at room temperature alloy 2T is the stronger of the two, by 4–6 tons/in.^{2} when quenched or quenched and tempered, and by 14–15 tons/in.^{2} when cold-rolled or cold-rolled and tempered. The hardness values correspond with those for tensile strength. Alloy 2T loses a greater proportion of its strength at 400° C. than alloy L.S.10, although the actual values are 4–6 tons/in.^{2} higher.

COPPER–MANGANESE–NICKEL–ALUMINIUM ALLOYS.

(a) *Temper-Hardening Characteristics.*

A short study has been made of the effect of nickel and aluminium additions on copper–manganese alloys containing 5 and 10 per cent. of manganese. The temper-hardening characteristics of the 5 per cent. manganese alloy to which 6 : 1·5 and 13·5 : 1·5 per cent. nickel aluminium additions have been made, were examined by carrying out hardness tests on samples of rolled strip quenched from 900° C. and reheated to various temperatures for 2 hrs. The results of these tests are given in Table XX. The maximum hardness increments obtained with the two alloys were 51 and 117, as compared with maximum hardness increments of 112 and 155 for alloys of similar nickel and aluminium contents but containing no manganese, *i.e.*, Nos. 27 and 37 of Table I. These results indicate that manganese exerts a retarding influence on the temper-hardening process, or may possibly reduce the extent to which hardening in an alloy of given nickel and aluminium contents can be effected. Some of the results of tensile tests also indicate that manganese seems to exert a retarding influence on the temper-hardening process.

(b) *Mechanical Properties.*

Both the 5 and 10 per cent. manganese alloys, containing nickel and aluminium, were made in the form of extruded rod and tested in various conditions, the results of these tests being given in Table XXI. Alloy L.S.15 did not harden appreciably when tempered for 2 hrs. at 500° C., as did the corresponding alloy L.S.7 containing no manganese, and it was found necessary to prolong the time of heating to 20 hrs. to obtain substantial improvements in strength and hardness. Alloy L.S.16, which contained the same amount of aluminium but 10 per cent. of manganese, hardened only very slightly under similar conditions of heat-treatment to which alloy L.S.7 was subjected.

With the nickel 13·5, aluminium 1·5 per cent. alloys containing manganese additions the effect of increasing the time of tempering was not studied, and the results were obtained on material reheated for 2 hrs. at 600° C. Although appreciable hardening effects were obtained, it cannot be assumed that the optimum conditions have necessarily been obtained. In fact, it is much more likely that with prolonged heating at this or probably somewhat lower temperatures greater improvements in the properties may result. Neither alloy L.S.17 containing 5 per cent. manganese nor L.S.18 hardened as completely as the corresponding alloy L.S.8 without manganese. While the manganese alloys do not appear to possess at room temperature superior properties to the ternary alloys of copper–nickel–aluminium, the results of tensile tests at 300° C. and 400° C. indicate that the presence of manganese results in a greater proportion of the strength being retained at these temperatures than in the corresponding alloys which do not contain manganese.

COMPOSITION.

Only nominal compositions of the alloys have been indicated, for results obtained on analyzing various samples in the course of the work generally agreed with the synthetic compositions. The compositions of all the alloys made have been checked spectrographically, and since most of the metals used were of the purest quality obtainable commercially, the impurities generally were very small in amount. The alloys containing manganese constituted the only exception, for in the preparation of these the cupro–manganese introduced more iron than was found in the manganese-free alloys. In the latter it was of the order of 0·05 per cent., whereas in the manganese alloys it was 0·1–0·2 per cent. It is therefore possible that the retardation of the hardening process which has been noted in the case of some of the manganese alloys may in some measure be associated with the presence of iron.

SUMMARY.

1. A study has been made of the effect of quenching and tempering on the properties of copper and a variety of commercial copper alloys containing additions of nickel and aluminium.

2. It has been found that in order to obtain appreciable temper-

hardening effects the aluminium content should not be less than about 0·5 per cent. and the nickel content should be in excess of 2 per cent. The extent to which temper-hardening occurs is determined, apart from variations in the heat-treatment, by the composition of the alloy and the ratio and amounts of nickel and aluminium present. The optimum hardening occurs when the nickel is present to the extent of at least four times the aluminium content.

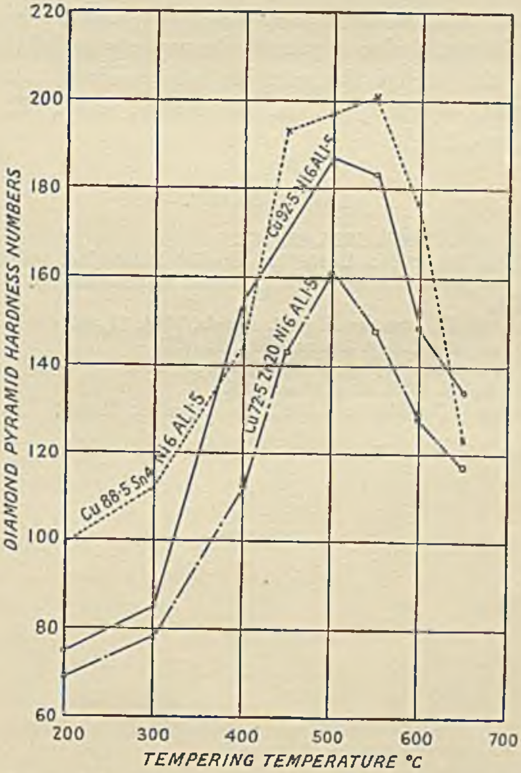

FIG. 7.—Effect of Tempering on the D.P. Hardness of Quenched Alloys.

3. The alloys are obtained in the softest condition by quenching from about 900° C., and can be appreciably hardened by tempering at about 400°–600° C., as shown by three typical temper-hardening curves in Fig. 7.

4. The exact conditions for obtaining maximum hardening vary with the composition, and for some of the alloys a detailed study has been made of the effects of quenching temperature, time and temperature of tempering, and also of tempering cold-worked alloys.

5. A few typical alloys of each group, *i.e.*, copper, copper–zinc, copper–tin, copper–manganese, containing nickel and aluminium, have been produced in the form of either strip or rod, or both, and complete tensile tests carried out at room temperature and at elevated temperatures on alloys in various conditions.

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BIBLIOGRAPHY.

[1] R. Genders, *J. Inst. Metals*, 1930, 43, 163.
[2] W. B. Price, U.S. Patent No. 1,815,071; English Patent No. 369,094.
[3] W. B. Price, Alcunic Condenser Tubing, Scovill Manufacturing Co., Waterbury, Conn., U.S.A.
[4] A. A. Read and R. H. Greaves, *J. Inst. Metals*, 1914, 11, 169; *ibid.*, 1921, 26, 57.
[5] I. Iytaka, *J. Soc. Mech. Eng. Japan*, 1922, 25, (72).
[6] T. Ishikawa, *J. Soc. Mech. Eng. Japan*, 1928, 31, 215.
[7] T. Saito, *Suiyokaishi*, 1927, 5, 433 and 465.
[8] U.S. Patent Nos. 1,755,554 to 1,755,557. Canadian Patent Nos. 290,189 and 290,190.
[9] English Patent No. 386,017.

TABLE I.—*Copper–Nickel–Aluminium Alloys. Influence of Tempering Temperature after Quenching.*

No. of Alloy.	Nominal Composition.			Diamond Pyramid Hardness.								
	Copper, Per Cent.	Nickel, Per Cent.	Aluminium, Per Cent.	Quenched from 900° C. (1 Hr.)	Quenched from 900° C. (1 Hr.) and Tempered for 2 Hrs. at Temperatures of :—							Maximum Hardness Increment.
					300° C.	400° C.	450° C.	500° C.	550° C.	600° C.	650° C.	
1 : 1 Ni–Al Ratio.												
9	99	0·5	0·5	46	46	45	47	46	45	47	47	1
10	98	1·0	1·0	48	50	50	48	50	50	52	56	8
11	95	2·5	2·5	63	65	65	62	71	68	64	64	8
12	90	5·0	5·0	86	92	88	86	92	96	102	115	29
2 : 1 Ni–Al Ratio.												
5	99	0·66	0·33	46	50	46	50	50	46	52	45	6
6	98	1·32	0·66	49	52	50	48	50	49	53	53	4
7	95	3·3	1·65	64	69	69	67	72	67	67	67	8
8	90	6·6	3·3	76	81	88	101	121	131	133	109	57
3 : 1 Ni–Al Ratio.												
1	99	0·75	0·25	47	52	50	46	45	51	45	49	5
2	98	1·5	0·5	47	49	53	48	53	50	50	53	6
3	95	3·75	1·25	59	62	67	74	73	64	63	65	15
30	92	6·0	2·0	67	68	70	...	153	185	155	129	119
4	90	7·5	2·5	77	83	88	109	142	168	187	158	110
25	84	12·0	4·0	124	126	130	195	195	215	243	254	130
4 : 1 Ni–Al Ratio.												
31	99	0·8	0·2	44	44	45	...	46	45	44	44	2
32	98	1·6	0·4	46	46	47	...	46	47	47	46	1
33	95	4·0	1·0	55	60	114	...	100	76	64	58	59
27	92·5	6·0	1·5	75	85	155	...	187	183	149	134	112
34	90	8·0	2·0	69	70	86	...	124	168	186	184	117
26	87·5	10·0	2·5	94	120	185	...	227	240	227	218	146
6 : 1 Ni–Al Ratio.												
28	89·5	9·0	1·5	81	90	155	...	185	181	171	172	104
10 : 1 Ni–Al Ratio.												
35	95	4·55	0·45	48	49	52	...	52	68	49	48	20
36	90	9·1	0·9	64	88	155	...	172	181	162	150	117
37	85	13·65	1·35	75	90	172	...	192	206	229	230	155
" Aluminium–Bronze " containing Nickel.												
13	92	...	8·0	66	68	68	70	72	68	72	67	6
14	91	1·0	8·0	71	71	75	71	76	76	74	76	5
15	90	2·0	8·0	108	119	128	133	150	123	115	108	42
16	87	5·0	8·0	97	110	116	...	122	143	170	190	93
70 : 30 Cupro–Nickel containing Aluminium.*												
N11	70·0	30·0	Nil	84	...	86	...	82	82	85	87	3
N19	70·0	29·0	1·0	93	...	103	...	119	142	97	99	49
N20	70·0	28·25	1·75	96	...	98	...	124	183	197	168	101
N13	70·0	28·0	2·00	99	...	112	...	153	207	216	206	117
N21	70·0	27·25	2·75	95	...	134	...	179	212	266	282	187

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* The low temperature heat-treatment in this series was of 1 hr. duration.

TABLE II.—*Copper–Nickel–Aluminium Alloys. Influence of Time of Tempering at Different Temperatures.*

No. of Alloy.	Diamond Pyramid Hardness.											
	Quenched from 900° C. (1 Hr.).	Quenched from 900° C. (1 Hr.) and Tempered at 400° C. for Periods of :—			Quenched from 900° C. (1 Hr.) and Tempered at 500° C. for Periods of :—			Quenched from 900° C. (1 Hr.) and Tempered at 600° C. for Periods of :—			Maximum Hardness Increment.	
		15 min.	2 hrs.	20 hrs.	15 min.	2 hrs.	20 hrs.	15 min.	2 hrs.	20 hrs.	As Recorded in Table I.	Now Observed.
11	63	65	65	68	...	71	69	...	64	67	8	8
12	86	87	88	109	92	92	136	96	102	131	29	50
7	64	62	69	82	...	72	133	...	67	67	8	69
8	76	83	88	105	98	121	143	103	133	143	57	67
3	59	61	67	100	...	73	133	...	63	79	15	74
30	67	70	70	126	140	155	174	153	155	174	119	107
4	77	83	88	131	114	112	166	...	187	167	110	110
33	55	...	114	140	...	100	135	...	64	107	59	85
27	75	140	155	181	174	187	195	163	149	163	112	120
34	69	74	86	109	107	124	183	146	186	212	117	143
26	94	161	185	209	215	227	237	221	227	233	146	143
28	81	153	155	122	166	185	190	164	171	195	104	114
35	48	53	52	91	52	52	68	61	49	69	20	43
36	64	139	165	158	158	172	185	154	162	177	117	121
37	75	111	172	200	177	192	209	192	229	218	155	154
14	71	...	75	76	...	76	75	...	74	73	5	5
15	108	135	128	157	153	150	140	142	115	106	42	49
16	97	119	116	121	120	122	140	126	170	179	93	82

TABLE III.—*Copper–Nickel–Aluminium Alloys. Influence of Initial Quenching Temperature.*

No. of Alloy.	Diamond Pyramid Hardness.														
	Quenched from 800° C.	Quenched from 800° C. and Tempered 2 Hrs. at Temperatures of :—			Maximum Hardness Increment.	Quenched from 900° C.	Quenched from 900° C. and Tempered 2 Hrs. at Temperatures of :—			Maximum Hardness Increment.	Quenched from 1000° C.	Quenched from 1000° C. and Tempered 2 Hrs. at Temperatures of :—			Maximum Hardness Increment.
		500° C.	550° C.	600° C.			500° C.	550° C.	600° C.			500° C.	550° C.	600° C.	
12	103	101	109	115	12	86	92	96	102	16	80	81	87	83	7
8	85	137	142	100	57	76	121	131	133	57	68	119	139	121	71
30	79	155	177	160	98	67	155	186	155	119	70	158	185	160	115
4	86	133	195	181	109	77	142	168	187	110	69	122	188	170	119
33	54	110	78	64	56	55	100	76	64	45	54	100	78	65	46
27	74	185	183	140	111	75	187	183	149	112	66	183	179	145	117
34	74	124	193	183	119	69	124	168	186	117	64	139	212	203	148
26	101	224	250	243	149	94	227	240	227	146	69	215	243	240	174
36	66	178	183	162	117	64	172	181	162	117	57	160	182	162	125
37	88	246	252	240	164	75	192	206	229	154	76	206	212	230	154
15	116	134	124	119	18	108	150	123	115	42	96	119	110	90	23
16	179	179	183	185	6	97	122	143	170	73	81	94	112	114	33
N19	96	123	187	120	91	93	119 *	142 *	97 *	49	88	121	177	96	89
N20	99	139	189	206	107	96	124 *	183 *	197 *	101	82	134	162	172	90
N13	107	153	200	215	108	99	153 *	207 *	216 *	117	93	151	187	221	128
N21	215	233	259	292	77	95	179 *	212 *	266 *	171	94	221	239	250	156

* Tempered for 1 hr. only.

TABLE IV.—*Copper–Nickel–Aluminium Alloys. The Tempering of Hard-Rolled Strip.*

No. of Alloy.	Diamond Pyramid Hardness.								
	Hard-Rolled.	Hard-Rolled Material Tempered for 30 Minutes at Temperatures of :—							Maximum Hardness Increment.
		300° C.	400° C.	500° C.	600° C.	700° C.	800° C.	900° C.	
9	116	121	86	52	52	47	46	44	5
10	131	134	121	64	62	56	55	48	3
11	162	166	164	92	82	75	71	63	4
12	215	218	243	224	187	142	103	86	28
5	116	112	72	52	48	48	46	46	...
6	120	122	109	57	54	54	52	49	2
7	131	142	150	100	75	72	68	61	19
8	200	225	230	237	195	128	85	76	37
1	119	114	78	52	49	47	44	47	...
2	122	119	117	57	54	54	52	47	...
3	139	140	140	116	70	65	60	59	1
30	157	164	177	200	160	86	79	67	43
4	171	183	197	221	233	116	86	77	62
25	270	...	...	...	...	...	...	...	...
31	119	115	76	56	52	50	45	44	...
32	116	117	78	56	52	50	48	46	1
33	128	130	127	104	70	58	54	55	2
27	144	146	172	190	177	85	74	75	46
34	174	183	197	225	244	158	74	69	70
26	181	185	235	240	250	195	101	94	69
35	128	123	120	92	56	52	48	48	...
36	145	153	174	187	197	104	66	64	52
37	175	183	233	229	227	206	88	75	58
13	224	240	146	120	100	90	83	66	16
14	224	246	197	151	127	93	84	71	22
15	246	266	200	183	143	120	116	108	20
16	266	302	307	258	224	203	179	97	41
N19	206	212	220	211	209	103	96	93	14
N20	212	212	230	266	287	237	99	96	75
N13	218	218	250	280	305	243	107	99	87
N21	250	266	322	322	333	287	215	95	83

Table V.—*Copper–Nickel–Aluminium Alloys. Prolonged Tempering of Hard-Rolled Strip.*

No. of Alloy.	Diamond Pyramid Hardness.											
	Hard-Rolled.	Tempered at 300° C. for Periods of :—			Tempered at 400° C. for Periods of :—			Tempered at 500° C. for Periods of :—			Maximum Hardness Increment.	
		30 min.	20 hrs.	60 hrs.	30 min.	3 hrs.	20 hrs.	30 min.	3 hrs.	20 hrs.	As Recorded in Table IV.	Now Observed.
11	162	166	168	172	164	90	166	92	92	89	4	10
12	215	218	243	243	243	217	239	224	192	155	28	28
7	131	142	151	150	150	85	158	100	100	112	19	27
8	200	225	224	233	230	237	246	237	227	177	37	46
3	139	140	139	142	140	86	152	116	112	112	1	13
30	157	164	165	167	177	226	203	200	220	220	43	69
4	171	183	195	200	197	258	224	221	246	246	62	87
33	128	130	137	146	127	122	153	104	128	145	2	25
27	144	146	170	183	172	197	215	190	209	218	46	74
34	174	183	193	200	197	245	264	225	262	270	70	96
26	181	185	233	237	235	233	252	240	268	270	69	89
35	128	125	123	122	120	73	98	92	75	117	...	...
36	145	153	183	195	174	211	209	187	206	218	52	73
37	175	183	228	217	233	226	240	229	246	262	58	87
14	224	246	246	246	197	144	140	151	140	124	22	22
15	246	266	237	233	200	182	174	183	177	155	20	20
16	266	302	320	297	307	240	220	258	227	212	41	54
N19	206	212	218	221	220	228	292	211	254	258	14	86
N20	212	212	237	232	230	297	278	266	297	290	75	85
N13	218	218	221	246	250	300	307	280	294	302	87	89
N21	250	266	312	322	322	327	336	322	333	345	83	95

Table VI.—*Mechanical Properties of Copper* 92·5, *Nickel* 6, *Aluminium* 1·5 *per Cent. Alloy* (*L.S.*7) *in Rod Form, in the Softened Condition and after Tempering for* 2 *Hrs. at Various Temperatures.*

Condition.	Diamond Pyramid Hardness.	Limit of Proportionality, Tons/in.².	Proof Stress, Tons/in.².		Tensile Strength, Tons/in.².	Elongation, Per Cent. on 2 in.
			0·1%.	0·2%.		
Quenched from 900° C.	68	1·2	4·6	5·2	22·0	48
Quenched from 900° C. and tempered for 2 hrs. at the following temperatures :—						
300° C. . .	68	1·2	4·6	5·2	22·0	47
400° C. . .	125	4·0	9·3	10·9	29·0	36
500° C. . .	142	10·5	16·2	17·0	35·8	34
600° C. . .	194	17·9	23·0	34·0	44·3	20
700° C. . .	119	6·4	12·9	13·7	28·8	30
800° C. . .	80	1·6	4·9	5·4	22·0	48

Table VII.—*Mechanical Properties of Copper–Nickel–Aluminium Alloys in the Form of Extruded and Drawn Rod.*

No. of Alloy.	Condition.	Temperature of Testing.	Diamond Pyramid Hardness.	Limit of Proportionality, Tons/in.².	Proof Stress, Tons/in.².		Tensile Strength, Tons/in.².	Elongation Per Cent. on 2 in.
					0·1%.	0·2%.		
L.S.24 Copper 96·25; nickel 3·0; aluminium 0·75%	A. Cold-drawn (10% reduction)	normal	116	3·0	16·9	18·5	20·3	30
	B. Cold-drawn, followed by tempering at 450° C. for 20 hrs.	normal	145	15·3	22·7	23·7	31·1	25
	C. Quenched from 900° C.	normal	57	1·4	3·5	3·8	16·9	56
		400° C.	...	...	...	...	13·2	41
	D. Quenched from 900° C. and tempered at 450° C. for 20 hrs.	normal	111	3·3	9·4	10·3	25·7	36
		300° C.	...	...	...	...	17·6	24
		400° C.	...	...	...	...	17·1	8
L.S.23 Copper 95; nickel 4; aluminium 1%	A. Cold-drawn (10% reduction)	normal	112	2·8	19·2	20·8	21·9	28
	B. Cold-drawn or rolled, followed by tempering at 450° C. for 20 hrs.	normal	165	21·3	28·9	29·9	36·3	22
	C. Quenched from 900° C.	normal	61	1·2	3·6	3·8	16·2	51
		400° C.	...	...	...	...	13·4	28
	D. Quenched from 900° C. and tempered at 450° C. for 20 hrs.	normal	127	9·5	12·7	12·9	30·2	37
		300° C.	...	...	...	...	21·1	18
		400° C.	...	...	...	...	16·6	6
L.S.7 Copper 92·5; nickel 6·0; aluminium 1·5%	A. Cold-drawn (10% reduction)	normal	123	9·0	20·1	22·2	27·1	28
	B. Cold-drawn or rolled, followed by tempering at 500° C. for 2 hrs.	normal	224	21·0	30·1	32·9	47·1	15
		400° C.	...	...	...	...	22·0	0·5
	C. Quenched from 900° C.	normal	68	1·2	4·6	5·2	22·0	48
		400° C.	...	...	...	...	17·0	19
	D. Quenched from 900° C. and tempered at 550° C. for 2 hrs.	normal	194	17·9	23·0	34·0	44·3	20
		300° C.	...	...	...	...	23·6	11
		400° C.	...	...	...	...	20·2	5
		500° C.	...	...	...	...	16·0	4
L.S.8 Copper 85; nickel 13·5; aluminium 1·5%	A. Cold-drawn (10% reduction)	normal	146	11·2	21·2	23·1	28·8	28
	B. Cold-drawn or rolled, followed by tempering at 550° C. for 2 hrs.	normal	254	24·8	31·0	32·2	55·5	15
		400° C.	...	...	...	...	20·7	1
	C. Quenched from 900° C.	normal	80	1·4	3·6	4·2	24·8	43
		400° C.	...	...	...	...	21·0	12
	D. Quenched from 900° C. and tempered at 600° C. for 2 hrs.	normal	201	20·4	28·4	30·2	54·2	13
		300° C.	...	...	...	...	18·0	7
		400° C.	...	...	...	...	17·6	2
		500° C.	...	...	...	...	16·0	2
L.S.9 Copper 70; nickel 28·5; aluminium 1·5%	A. Cold-drawn (10% reduction)	normal	216	13·2	22·9	24·7	35·1	17
	B. Cold-drawn or rolled, followed by tempering at 550° C. for 2 hrs.	normal	296	31·4	36·4	38·1	58·2	12

TABLE VIII.—*Mechanical Properties of Copper–Nickel–Aluminium Alloys in the Form of Rolled Strip.*

No. of Alloy.	Condition.	Temperature of Testing.	Diamond Pyramid Hardness.	Limit of Proportionality, Tons/in.².	Proof Stress, Tons/in.²		Tensile Strength, Tons/in.².	Elongation, Per Cent. on 2 in.
					0·1%.	0·2%.		
L.S.20 Copper 95; nickel 4; aluminium 1%	A. Cold-rolled (50% reduction)	normal	150	16·0	26·3	28·5	31·6	8
	B. Rolled, followed by tempering at 450° C. for 20 hrs.	normal	160	15·3	25·5	27·4	33·4	14
	C. Quenched from 900° C.	normal	59	2·0	3·5	3·8	17·1	42
		400° C.	...	...	...	...	12·9	13
	D. Quenched from 900° C. and tempered at 450° C. for 20 hrs.	normal	126	5·6	11·8	13·5	28·1	28
		300° C.	...	...	...	...	19·0	9
		400° C.	...	...	...	...	16·4	3
L.S.10 Copper 92·5; nickel 6·0; aluminium 1·5%	A. Cold-rolled (50% reduction)	normal	151	14·8	27·3	30·5	31·3	5
	B. Cold-rolled, followed by tempering at 500° C. for 2 hrs.	normal	200	19·1	28·7	30·4	43·7	22
		400° C.	...	...	...	...	24·0	5
	C. Quenched from 900° C.	normal	61	1·8	3·9	4·3	19·5	43
		400° C.	...	...	...	...	15·2	12
	D. Quenched from 900° C. and tempered at 550° C. for 2 hrs.	normal	174	17·5	23·3	24·1	40·0	25
		400° C.	...	...	...	...	20·0	4
L.S.11 Copper 85; nickel 13·5; aluminium 1·5%	A. Cold-rolled (50% reduction)	normal	188	14·2	31·0	35·1	36·5	4
	B. Cold-rolled, followed by tempering at 550° C. for 2 hrs.	normal	250	28·7	42·6	46·9	55·5	15
		400° C.	...	...	...	...	31·7	12
	C. Quenched from 900° C.	normal	73	3·2	5·5	6·0	24·2	48
		400° C.	...	...	...	...	16·8	12
	D. Quenched from 900° C. and tempered at 600° C. for 2 hrs.	normal	221	25·8	31·1	33·0	48·4	14
		400° C.	...	...	...	...	16·7	4
		500° C.	...	...	...	...	16·1	4
L.S.12 Copper 70; nickel 28·5; aluminium 1·5%	A. Cold-rolled (50% reduction)	normal	200	26·3	32·6	...	41·7	1
	B. Cold-rolled, followed by tempering at 550° C. for 2 hrs.	normal	270	43·3	52·8	...	58·0	7
		400° C.	...	...	...	...	44·3	2
	C. Quenched from 900° C.	normal	97	3·8	7·2	8·0	26·2	36
	D. Quenched from 900° C. and tempered at 600° C. for 2 hrs.	normal	206	12·8	20·5	23·5	41·8	17
		400° C.	...	...	...	...	21·6	1
		500° C.	...	...	...	...	18·2	2

TABLE IX.—*Properties of Copper–Nickel–Aluminium Wires* (0·064 *in. Diameter.*)

Condition.	Tensile Strength, Tons/in.².	Elongation, Per Cent. on 2 in.	Specific Resistance, (Microhms per cm. cube.)
Alloy L.S. 20. Copper 95, nickel 4, aluminium 1%.			
Cold-drawn	35·8	2	9·45
Cold-drawn, followed by tempering at 450° C. for 20 hrs.	36·8	5	7·61
Quenched from 900° C. . . .	19·9	30	9·33
Quenched from 900° C. and tempered at 450° C. for 20 hrs.	31·7	14	7·70
Alloy L.S.10. Copper 92·5, nickel 6, aluminium 1·5%.			
Cold-drawn	40·5	1	12·28
Cold-drawn, followed by tempering at 500° C. for 2 hrs.	49·0	16	8·88
Quenched from 900° C. . . .	22·7	29	11·55
Quenched from 900° C. and tempered at 550° C. for 2 hrs.	38·5	9	8·42
Alloy L.S.11. Copper 85, nickel 13·5, aluminium 1·5%.			
Cold-drawn	41·5	2	19·96
Cold-drawn, followed by tempering at 550° C. for 2 hrs.	54·4	19	15·23
Quenched from 900° C. . . .	22·4	20	18·94
Quenched from 900° C. and tempered at 600° C. for 2 hrs.	39·5	12	14·82

TABLE X.—*Mechanical Properties of Copper* 85, *Nickel* 13·5, *Aluminium* 1·5 *per Cent. Alloy in the Form of Extruded and Drawn Tube.*

Condition.	Extruded and Drawn Tube 0·75 in. Outside Diameter and 0·048 in. Wall Thickness.			
	Diamond Pyramid Hardness.	Limit of Proportionality, Tons/in.².	Tensile Strength, Tons/in.².	Elongation, Per Cent. on 2 in.
Cold-drawn	159	5·9	33·8	7
Cold-drawn, followed by tempering at 500° C. for 2 hrs..	233	10·6	52·7	15

TABLE XI.—*Copper-Zinc-Nickel-Aluminium Alloys. The Influence of Tempering Temperature after Quenching.*

No. of Alloy.	Nominal Composition.				Diamond Pyramid Hardness.								
					Quenched from 900° C. (1 Hr.).	Quenched from 900° C. (1 Hr.) and Tempered for 2 Hrs. at Temperatures of :—							Maximum Hardness Increment.
	Copper, Per Cent.	Nickel, Per Cent.	Aluminium, Per Cent.	Zinc, Per Cent.		300° C.	400° C.	450° C.	500° C.	550° C.	600° C.	650° C.	
					Aluminium-Brasses with Nickel Additions.								
A5	77·0	...	2·0	21·0	48	48	50	49	52	51	49	53	5
A4	76·5	0·5	2·0	21·0	49	49	50	49	54	50	52	52	5
A3	76·0	1·0	2·0	21·0	52	53	52	52	53	54	58	53	6
A2	76·0	2·0	2·0	20·0	53	52	53	54	58	64	86	75	33
A1	73·0	5·0	2·0	20·0	82	83	128	155	177	160	143	138	95
17	70·0	10·0	2·0	18·0	92	101	160	172	220	195	188	175	128
					Gilding Metals and Brasses with Nickel and Aluminium Additions.								
					3 : 1 Ratio.								
41	84·0	4·5	1·5	10·0	65	66	73	100	116	74	72	69	51
42	80·0	7·5	2·5	10·0	77	80	102	117	157	193	193	143	116
					4 : 1 Ratio.								
40	85·0	4·0	1·0	10·0	57	57	60	88	116	61	60	58	59
59	80·0	8·0	2·0	10·0	72	74	93	123	153	193	190	157	121
61	72·5	6·0	1·5	20·0	69	78	112	143	161	148	128	117	92
45	60·0	4·0	1·0	35·0	151	155	193	153	172	150	137	139	42
					10 : 1 Ratio.								
43	79·0	10·0	1·0	10·0	65	67	78	91	131	139	134	71	74
62	65·0	13·5	1·5	20·0	87	92	137	143	190	168	160	148	103
					Nickel Silvers with Aluminium Additions.								
18	60·0	20·0	...	20·0	79	88	86	83	81	78	83	81	9
19	60·0	20·0	0·5	19·5	80	92	103	108	112	116	121	92	41
20	60·0	20·0	1·0	19·0	82	95	108	121	131	146	150	124	68

TABLE XII.—*Copper–Zinc–Nickel–Aluminium Alloys. Influence of Time of Tempering at Different Temperatures.*

No. of Alloy.	Diamond Pyramid Hardness.											
	Quenched from 900° C. (1 Hr.).	Quenched from 900° C. (1 Hr.) and Tempered at 400° C. for Periods of :—			Quenched from 900° C. (1 Hr.) and Tempered at 500° C. for Periods of :—			Quenched from 900° C. (1 Hr.) and Tempered at 600° C. for Periods of :—			Maximum Hardness Increment.	
		15 min.	2 hrs.	20 hrs.	15 min.	2 hrs.	20 hrs.	15 min.	2 hrs.	20 hrs.	As Recorded in Table II.	Now Observed.
A5	48	49	50	50	49	52	48	49	49	48	5	4
A4	49	50	50	52	51	54	54	50	52	49	5	5
A3	52	52	52	54	53	53	65	52	58	71	6	19
A2	53	54	53	88	53	58	96	55	86	101	33	48
A1	82	84	128	155	126	177	166	153	143	142	95	95
17	92	109	160	224	193	220	224	200	188	137	128	132
41	65	67	73	122	89	116	139	85	72	70	51	74
42	77	84	102	157	143	157	187	127	193	157	116	116
40	57	58	60	114	90	116	155	92	60	63	59	98
39	72	74	93	155	126	153	193	130	190	191	121	121
43	65	66	78	116	78	131	150	92	134	143	74	85
45	151	156	193	183	154	172	170	150	137	122	42	42
18	79	81	86	92	82	81	83	84	83	80	9	13
19	80	92	103	123	107	112	119	106	121	112	41	43
20	82	100	108	131	124	131	142	143	150	143	68	68

TABLE XIII.—*Copper–Zinc–Nickel–Aluminium Alloys. The Influence of Initial Quenching Temperature.*

No. of Alloy.	Diamond Pyramid Hardness.									
	Quenched from 800° C.	Quenched from 800° C. and Tempered 2 Hrs. at Temperatures of :—			Maximum Hardness Increment.	Quenched from 900° C.	Quenched from 900° C. and Tempered 2 Hrs. at Temperatures of :—			Maximum Hardness Increment.
		500° C.	550° C.	600° C.			500° C.	550° C.	600° C.	
A2	58	58	63	81	23	53	58	64	86	33
A1	96	165	158	143	69	82	177	160	143	95
17	143	212	197	170	69	92	220	195	188	128
41	74	110	78	72	36	65	116	74	72	51
42	116	159	178	174	62	77	157	193	193	116
40	66	66	66	66	0	57	116	61	60	59
39	81	157	202	195	121	72	153	193	190	121
43	72	146	148	143	76	65	131	139	134	74
45	103	131	130	130	28	151	172	150	137	21
18	82	83	82	84	2	79	81	78	83	4
19	90	122	127	111	37	80	112	116	121	41
20	98	140	166	151	68	82	131	146	150	68

Table XIV.—*Copper–Zinc–Nickel–Aluminium Alloys. The Tempering of Hard-Rolled Strip.*

No. of Alloy.	Diamond Pyramid Hardness.								
	Hard-Rolled.	Hard-Rolled Material Tempered for 30 Minutes at Temperatures of :—							Maximum Hardness Increment.
		300° C.	400° C.	500° C.	600° C.	700° C.	800° C.	900° C.	
A5	187	197	103	91	76	64	53	48	10
A4	183	200	112	104	80	65	54	49	17
A3	202	221	206	145	127	69	57	52	19
A2	205	232	225	164	142	94	58	55	27
A1	212	237	233	174	145	131	96	82	25
17	227	262	278	251	185	164	143	92	51
41	177	187	203	190	106	78	74	65	26
42	193	212	233	250	212	174	116	68	57
40	153	158	161	158	81	71	66	65	8
39	195	197	211	246	246	139	81	72	51
43	162	164	160	187	179	81	72	65	25
45	209	230	230	183	162	140	103	151	21
18	203	206	207	153	108	93	82	77	4
19	212	218	230	224	197	97	90	78	18
20	209	224	233	240	237	170	98	82	31

Table XV.—*Copper–Zinc–Nickel–Aluminium Alloys. Prolonged Tempering of Hard-Rolled Strip.*

No. of Alloy.	Diamond Pyramid Hardness.											
	Hard-Rolled.	Tempered at 300° C. for Periods of :—			Tempered at 400° C. for Periods of :—			Tempered at 500° C. for Periods of :—			Maximum Hardness Increment.	
		30 min.	20 hrs.	63 hrs.	30 min.	3 hrs.	20 hrs.	30 min.	3 hrs.	20 hrs.	As Recorded in Table XIV.	Now Observed.
A2	205	232	233	193	225	162	162	164	160	148	27	28
A1	212	237	248	220	233	170	162	174	164	154	25	36
17	227	262	290	287	278	232	206	251	204	172	51	63
41	177	187	193	193	203	195	187	190	183	139	26	26
42	193	212	221	230	233	264	262	250	250	209	57	71
40	153	158	166	170	161	120	151	158	177	151	8	24
39	195	197	203	221	211	272	270	246	274	252	51	79
43	162	164	172	179	160	214	212	187	209	197	25	52
45	209	230	240	230	230	176	162	183	169	153	21	31
18	203	206	221	224	207	200	185	153	121	114	4	21
19	212	218	233	240	230	233	237	224	233	227	18	28
20	209	224	233	240	233	238	250	240	252	240	31	43

TABLE XVI.—*Mechanical Properties of Copper–Zinc–Nickel–Aluminium Alloys in the Form of Rolled Strip.*

No. of Alloy.	Condition.	Diamond Pyramid Hardness.	Limit of Proportionality, Tons/in.^{2}.	Proof Stress, Tons/in.^{2}. 0·1%.	Proof Stress, Tons/in.^{2}. 0·2%.	Tensile Strength, Tons/in.^{2}.	Elongation, Per Cent. on 2 in.
61 Copper 72·5; nickel 6·0; aluminium 1·5; zinc 20·0%	A. Cold-rolled (50% reduction)	198	11·1	30·8	...	39·7	6
	B. Cold-rolled, followed by tempering at 500° C. for 2 hrs.	240	25·0	31·0	...	46·6	11
	C. Quenched from 900° C.	69	4·4	5·3	5·7	22·8	61
	D. Quenched from 900° C. and tempered at 500° C. for 2 hrs.	161	17·2	22·0	23·0	36·6	29
62 Copper 65·0; nickel 13·5; aluminium 1·5; zinc 20·0%	A. Cold-rolled (50% reduction)	227	12·1	23·3	...	45·7	6
	B. Cold-rolled, followed by tempering at 500° C. for 2 hrs.	278	29·0	36·0	...	55·5	6
	C. Quenched from 900° C.	87	4·2	9·0	9·3	24·1	58
	D. Quenched from 900° C. and tempered at 500° C. for 2 hrs.	190	17·7	24·4	25·3	36·7	33

TABLE XVII.—*Diamond Pyramid Hardness of Copper–Tin–Nickel–Aluminium Alloys in Various Conditions.*

No. of Alloy.	Nominal Composition. Copper, Per Cent.	Tin, Per Cent.	Nickel, Per Cent.	Aluminium, Per Cent.	Quenched from 900° C. (1 hr.).	Quenched and Tempered.	Cold-Rolled (50% Reduction).	Cold-Rolled and Tempered.
1T	91·5	4	3	1·5	93	107	187	201
2T	88·5	4	6	1·5	99	201	217	281
3T	79·5	4	15	1·5	106	213	196 *	288 *
4T	87·5	8	3	1·5	101	129	218	...
5T	84·5	8	6	1·5	119	218	234	246
6T	75·5	8	15	1·5	155	281	...	...
7T	83·5	12	3	1·5	117	174	...	...
8T	80·5	12	6	1·5	131	227	...	...
9T	71·5	12	15	1·5	196	310	...	...

* After 25 per cent. reduction.

TABLE XVIII.—*Copper–Tin–Nickel–Aluminium Alloys. Influence of Tempering Temperature After Quenching.*

No. of Alloy.	Nominal Composition. Copper, Per Cent.	Tin, Per Cent.	Nickel, Per Cent.	Aluminium, Per Cent.	Diamond Pyramid Hardness. Quenched from 900° C. (1 Hr.).	Quenched from 900° C. (1 Hr.) and Tempered 2 Hrs. at:— 300° C.	400° C.	450° C.	500° C.	550° C.	600° C.	650° C.	Maximum Hardness Increment.
1T	91·5	4	3	1·5	93	99	96	100	104	107	98	94	14
2T	88·5	4	6	1·5	99	112	144	193	197	201	175	123	102
7T	83·5	12	3	1·5	117	144	167	...	174	...	145	...	57
8T	80·5	12	6	1·5	131	150	187	...	227	...	202	...	96
9T	71·5	12	15	1·5	196	215	248	...	305	...	310	...	114

TABLE XIX.—*Mechanical Properties of a Copper–Tin–Nickel–Aluminium Alloy in Various Conditions.*

No. of Alloy.	Condition of Test.	Condition of Material.											
		Quenched from 900° C.			Quenched from 900° C. and Tempered at 550° C. for 2 Hrs.			Quenched from 900° C. and Cold-Worked (50%).			Quenched from 900° C. Cold-Worked and Tempered at 550° C. for 2 Hrs.		
		Tensile Strength, Tons/in.^{2}.	Elongation, Per Cent. on 2 in.	D.P. Hardness (10 Kg.).	Tensile Strength, Tons/in.^{2}.	Elongation, Per Cent. on 2 in.	D.P. Hardness (10 Kg.).	Tensile Strength, Tons/in.^{2}.	Elongation Per Cent. on 2 in.	D.P. Hardness (10 Kg.).	Tensile Strength, Tons/in.^{2}.	Elongation, Per Cent. on 2 in.	D.P. Hardness (10 Kg.).
2T	Room temperature	25·3	55	99	44·0	21	201	46·2	4	217	57·4	11	281
,,	400° C.	14·4	7	...	12·2	1	...	27·6	1	...	30·3	1	...

TABLE XX.—*Copper–Manganese–Nickel–Aluminium Alloys. Influence of Tempering Temperature after Quenching.*

No. of Alloy.	Nominal Composition.				Diamond Pyramid Hardness.								
	Copper, Per Cent.	Nickel, Per Cent.	Aluminium, Per Cent.	Manganese, Per Cent.	Quenched from 900° C. (1 Hr.).	Quenched from 900° C. (1 Hr.) and Tempered 2 Hrs. at Temperatures of:—							Maximum Hardness Increment.
						300° C.	400° C.	450° C.	500° C.	550° C.	600° C.	650° C.	
MA.1	87·5	6	1·5	5	74	95	101	103	124	125	101	98	51
MA.2	80·0	13·5	1·5	5	86	115	134	151	171	203	203	179	117

TABLE XXI.—*Mechanical Properties of Copper–Manganese–Nickel–Aluminium Alloys in the Form of Extruded and Drawn Rod.*

No. of Alloy.	Condition.	Temperature of Testing.	Diamond Pyramid Hardness.	Limit of Proportionality, Tons/in.².	Proof Stress, Tons/in.².		Tensile Strength, Tons/in.².	Elongation, Per Cent. on 2 in.
					0·1%.	0·2%.		
L.S.15 Copper 87·5; nickel 6·0; aluminium 1·5; manganese 5·0%	A. Cold-drawn (10% reduction)	normal	125	7·0	17·2	19·2	26·0	40
	B. Cold-drawn, followed by tempering at 500° C. for 20 hrs.	normal	185	18·8	25·6	26·4	36·6	25
		400° C.	...	...	...	...	23·6	2
	C. Quenched from 900° C.	normal	75	3·4	5·6	6·0	22·0	53
		400° C.	...	...	...	...	19·1	38
	D. Quenched from 900° C. and tempered at 500° C. for 20 hrs.	normal	152	16·3	17·9	18·1	33·7	25
		300° C.	...	...	...	...	28·8	34
		400° C.	...	...	...	...	20·7	3
L.S.16 Copper 82·5; nickel 6·0; aluminium 1·5; manganese 10·0%	A. Cold-drawn (10% reduction)	normal	145	6·0	16·8	19·2	27·0	43
	B. Cold-drawn, followed by tempering at 600° C. for 2 hrs.	normal	160	14·0	17·6	18·4	30·2	32
		400° C.	...	...	...	...	22·2	6
	C. Quenched from 900° C.	normal	77	2·0	6·4	7·2	24·5	62
		400° C.	...	...	...	...	19·8	39
	D. Quenched from 900° C. and tempered at 600° C. for 2 hrs.	normal	92	6·4	9·6	10·2	26·2	49
		300° C.	...	...	...	...	23·5	37
		400° C.	...	...	...	...	19·0	25
L.S.17 Copper 80; nickel 13·5; aluminium 1·5; manganese 5·0%	A. Cold-drawn (10% reduction)	normal	157	8·0	20·9	22·5	30·9	36
	B. Cold-drawn, followed by tempering at 600° C. for 2 hrs.	normal	240	31·2	37·2	38·0	49·0	21
		400° C.	...	...	...	...	24·9	1
	C. Quenched from 900° C.	normal	100	5·6	8·4	8·9	25·5	40
		400° C.	...	...	...	...	19·4	23
	D. Quenched from 900° C. and tempered at 600° C. for 2 hrs.	normal	221	22·0	27·2	28·0	37·6	7
		300° C.	...	...	...	...	28·4	4
		400° C.	...	...	...	...	26·4	1
L.S.18 Copper 75; nickel 13·5; aluminium 1·5; manganese 10·0%	A. Cold-drawn (10% reduction)	normal	190	13·2	23·8	25·6	34·2	38
	B. Cold-drawn, followed by tempering at 600° C. for 2 hrs.	normal	235	24·8	31·0	32·2	44·9	21
		400° C.	...	...	...	...	18·0	2
	C. Quenched from 900° C.	normal	110	5·2	9·4	...	22·2	45
		400° C.	...	...	...	...	18·3	20
	D. Quenched from 900° C. and tempered at 600° C. for 2 hrs.	normal	168	16·4	20·0	...	28·0	13
		300° C.	...	...	...	...	25·9	7
		400° C.	...	...	...	...	22·4	5

JOINT DISCUSSION ON BROWNSDON, COOK, AND MILLER'S AND JONES, PFEIL, AND GRIFFITHS' PAPERS.

Mr. W. T. Griffiths,* M.Sc. (Member): I would like to direct attention to a difficulty and to make a suggestion. The difficulty is the old one of nomenclature, and is illustrated by the three papers which have so far been presented this morning. In the first Dr. Rosenhain referred to "age-hardening" and also mentioned "precipitation-hardening." In the second the authors have described the same general phenomenon as "temper-hardening," whilst we, in the third paper, have called it "precipitation-hardening." It is now obvious that the treatment giving this type of hardening is applicable to a wide range of alloys, and it would undoubtedly simplify matters if there could be some uniformity of nomenclature.

The difficulty extends also to the individual operations producing the hardening. When we first wrote our paper we used the word "temper" to refer to the reheating operation, but, on further consideration, we came to the conclusion that, in its established usage in steel treatment, it gave an impression of softening rather than hardening. We therefore employed the simple word "reheating," although undoubtedly a term more descriptive of the effect of the operation would be preferable.

The suggestion I wish to make is that the subject is worthy of immediate consideration by the Institute, and that a ruling be given regarding a nomenclature which could be employed uniformly.

The President: It will be better not to discuss this now. I suggest that the matter be referred to the Council for their consideration.

Professor D. Hanson,† D.Sc. (Vice-President): These papers are two of the most important that have been published on the age-hardening of copper alloys. They are full of new information, and they are most stimulating, because of the very promising nature of the results which have been achieved. The alloys described are not by any means the first of the copper alloys which have been found to be amenable to this type of treatment, and I am sure that they will not be the last. A few of the simple copper alloys, for instance, those containing iron or beryllium, exhibit this phenomenon, but in the present work we have a case in which it is apparent only when two elements are added to the copper. We have parallels in the case of aluminium alloys. There are huge possibilities in the combination of two elements at a time in copper, but when we consider the addition of three, or even four elements at a time, it can be readily realized that there is an immense field of investigation, which may be justified by the achievement of important results. I wish to refer to two general aspects of the question. The earlier heat-treated copper alloys suffered because they mostly possessed rather low elastic limits, the beryllium alloy being an exception. It is a very notable advance that these particular series, by simple heat-treatment, can be obtained in a condition in which they attain a very considerable elastic limit. That elastic limit may be still further improved by the application of a small amount of cold-work followed by still further heating, or perhaps by cold-work before the tempering or reheating process. I would suggest that there is room for still further work on the increase of the elastic limit of these alloys while maintaining the greatest possible degree of ductility. Dr. Brownsdon and his colleagues have carried out a certain amount of work in that direction which is most promising, but I am sure that they will agree that their experiments by

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† Professor of Metallurgy, The University, Birmingham.

no means exhaust the possibilities in that direction, and I suggest that a most useful further study could be made.

These two papers emphasize the need for knowing *why* these things happen. Both papers give us a great many facts, which are rather difficult to correlate. Mr. Jones, in introducing his paper, referred to the variation which was found when the different proportions of the added constituents were added to the alloy. These workers will, I am sure, admit that they are rather groping in the dark at present. I feel that the wrong policy would be adopted if work of this kind were allowed to be carried too far without discovering the ultimate causes and the constituents responsible for the phenomena produced, and also what are the changes in solubility, &c., which govern the heat-treatment.

It is very important to know this if certain types of development are to be brought about with speed and certainty. For instance, in some of these systems an alloy might be produced which would have a very high degree of strength associated with high electrical conductivity. To bring about such a condition the minimum amount of hardening agent must be added; if two elements are involved, they must be present in just the right proportion, and the heat-treatment must be such as to bring about the maximum degree of precipitation. All those results will be achieved much more intelligently if it is known just what the alloy is. We do not want to know that it is an alloy of copper, nickel, and aluminium; we want to know in what particular form those elements are combined to bring about these particular results.

The time and temperature of heat-treatment in alloys of this type require a great deal of investigation. Up to the present, attention seems to have been directed principally towards obtaining the result in the minimum of time. I suggest that that is not necessarily the best direction in which to go. It has been shown in the case of many aluminium alloys that certain results are produced by tempering periods of long duration which differ materially from the results produced by short heat-treatments, even though the mechanical properties of the alloys may be very similar. A good deal more attention should be paid to the properties of these alloys, particularly the physical properties apart from the mechanical properties, by varying the periods of time.

Dr.-phil. **Eugen Vaders** * (Member): I investigated the precipitation-hardening of aluminium–nickel–copper alloys as long ago as 1927, a German patent application being filed in the same year.† My original investigation was confined to sand-casting alloys, but last year workable alloys were studied.

In the paper by Dr. Brownsdon and his colleagues the maximum aluminium content permissible in nickel–copper alloys is stated to be about 3 per cent. This does not seem to be correct in all cases. We have found that aluminium–nickel–copper alloys can easily be cold-rolled if, with the presence of 3 per cent. aluminium, the nickel content does not exceed 15–20 per cent. If the aluminium content increases to 4·5 or even to 6 per cent., the nickel content must be reduced to 10 per cent. or less. Aluminium–nickel–copper alloys containing about nickel 10, aluminium 5, and copper 85 per cent. have a Brinell hardness of 70 when quenched; they can be rolled in the cold and in the hot conditions without difficulty. The authors state that they have established the conditions of heat-treatment to secure the greatest improvement in the properties. This refers particularly to the ternary system aluminium–nickel–copper. Of more complex alloys, only those containing zinc, tin, and manganese have been investigated. We have found that an addition of iron to aluminium–nickel–copper alloys may be useful. In some patents dealing

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* Hirsch Kupfer- und Messingwerke, A.G., Finow/Mark, Germany.

† This application has now been granted; see D.R.P. No. 586,338.

with hardening aluminium–nickel–copper alloys there is mentioned, it is true, the presence of a small iron content, but this amounts to only 1 to 2 per cent., whilst we have investigated alloys with 5–15 per cent. iron. An alloy with nickel 10, aluminium 5, and copper 85 per cent. shows marked temper-hardening effects if 10 per cent. of iron is added, whereas the alloy free from iron possesses no hardening tendencies.

The solubility of aluminium in nickel–copper alloys seems to be advantageously influenced by the iron. When quenching alloys containing iron, more aluminium is held in solid solution than with alloys which are free from iron, and in consequence, the mechanical properties of these alloys are much higher than with the ternary aluminium–nickel–copper alloys. Certain iron–aluminium–nickel–copper alloys have a tensile strength of about 77 tons/in.^{2}, the elongation amounting to 3–4 per cent. on 2·5 in. It might be thought that the alloys were badly influenced by the iron as regards the rolling properties, but this is not the case. We have cold-rolled an alloy with 10 per cent. iron from 6 mm. to 0·5 mm. in thickness without annealing. The elongation of this alloy in the soft, *i.e.*, quenched, condition was about 50 per cent. on 3 in.; in others it was more than 60 per cent.

As for the ratio of nickel and aluminium, we were unable to observe that the figures 4 : 1 gave the best hardening effects in all cases. With higher nickel contents this ratio cannot be the right one. Alloys containing 20 per cent. or more nickel become very hard with an aluminium content which would correspond with this ratio.

From the results we have obtained it appears that the nickel and the aluminium contents are dependent on each other, inasmuch as a low nickel content permits a high aluminium content, whereas a high nickel content, on the other hand, requires a lower proportion of aluminium.

In the paper by Messrs. Jones, Pfeil, and Griffiths, it is stated that with increasing aluminium content a higher temperature is necessary to give the best precipitation-hardening. This is correct only for alloys which are free from iron and which have a low nickel content. With increasing nickel content, and the more so if iron be added, the annealing temperatures must be higher, the aluminium content having less effect. With regard to the nickel content, the authors come to the same conclusion, as is stated on p. 145.

The aluminium–nickel–copper alloys containing iron are of interest not only because of their high tensile strength, but also by reason of their magnetic properties and good resistance to heat. An addition of only 5–10 per cent. of iron is sufficient to make the alloys strongly magnetic. The permeability, susceptibility, &c., have, however, not yet been investigated. It may be that these properties render the alloys useful for electrical purposes, the more so as they are absolutely rust-proof.

As for the heat-resistance, certain alloys of this range are not seriously attacked even if heated to 900° C. for 3 hrs. They retain practically all their bright and smooth appearance.

Mr. S. L. ARCHBUTT * (Member): Have Dr. Brownsdon and his colleagues found any changes in the elastic modulus in connection with the raising of the elastic properties—the limit of proportionality—in some of these copper alloys, and particularly in the copper-rich alloys?

Mr. E. H. BUCKNALL,† M.Sc. (Member): I note that on etching the age-hardened copper–nickel–aluminium alloys a black residue was left behind,

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whereas on etching the quenched alloys no such residue remained. A somewhat similar behaviour is exhibited by copper–nickel–silicon alloys, the quenched material dissolving completely in a 20 per cent. solution of nitric acid in water, whilst with aged material a residue remains which consists of nickel oxide and silica. The weight of residue increases but slightly, however, with the duration of tempering until the maximum hardness has been reached and passed, when it increases rapidly to a constant value. It would be interesting to learn to what extent the phenomenon was studied by Dr. Brownsdon and his colleagues and how far their experience was parallel.

In amplification of Professor Hanson's remarks, it is my very strong opinion that more prolonged investigation of a number of the alloys might be extremely profitable. In Table II of the paper by Dr. Brownsdon are set out certain values for the attained hardness increment. The values, being simply the maximum arrived at in a comparatively small number of experiments, probably do not represent the true maxima of hardness–time curves. Indeed, the effect of composition on the increment appears more pronounced than our knowledge of other age-hardening copper alloys would lead us to expect. I refer particularly to the alloys of copper with beryllium and with titanium, in which the major effect of increase in alloy content beyond the minimum which will cause hardening appears to be in shortening the time in which maximum hardness is attained at any particular temperature.

Mr. N. F. S. Hubbard,* B.Sc. (Member): In dealing with these alloys to a limited extent on a practical scale, I have noticed the very marked brittle range at low temperatures, somewhere about 300° C. The authors have not mentioned this, and it is important, because it may greatly limit the sphere of usefulness of the alloys. The existence of this brittle range should be known to those who wish to use these materials in practice.

Mr. Archbutt asked whether the precipitation treatment had any effect on the elastic modulus. It has very little effect indeed on certain alloys, such as those containing nickel 10, aluminium 3, and nickel 7·5, aluminium 7·5 per cent.

A Japanese firm exploited alloys of this character a good many years ago, but I do not know what commercial success they met with.

Mr. A. J. Murphy,† M.Sc. (Member): In their second paper, written in 1921, Read and Greaves went fairly deeply into the properties which could be obtained by heat-treatment of these alloys. My impression is that they were able to increase the Brinell hardness by something like 60 or 70 per cent. in alloys with about 5 per cent. each of nickel and aluminium.

I should like to support Professor Hanson's remarks about investigation of the constitution. I know that practical exploitation cannot be held up until the last word is written on the constitution of alloys, but I entirely agree that there is a great danger of missing very valuable possible developments if a little side-tracking into the question of constitution is not done.

The material which is precipitated on heat-treatment has always interested me very much. When Austin and I did some work primarily on the liquidus of the copper–aluminium–nickel alloys about 1923, we considered that we obtained evidence to suggest that the β-phases of the copper–aluminium and nickel–aluminium alloys were isomorphous and formed a continuous series of solid solutions. In that case the constituent which is precipitated is possibly a mixed β-phase of copper–aluminium and nickel–aluminium, but opposed to that there is the fact that in the cast alloys a curious cruciform constituent is

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† J. Stone and Company, Ltd., Deptford.

obtained which looks more like a nickel–aluminium compound than a solid solution.

Have the authors of either of these papers found serious distortion during heat-treatment? That, I understand, has threatened to be a serious disadvantage in copper–beryllium heat-treatable alloys.

Finally, I think that we ought to realize that if an alloy depends for heat-treatment on the attainment of certain mechanical properties, as things are to-day those properties must really be exceedingly good to justify the expense, time, and close control which are necessary in the commercial production of the final heat-treated alloy.

Dr. MAURICE COOK (*in reply*): With regard to Professor Hanson's remarks, we quite appreciate that the experiments on the improvement of the elastic limits by a combination of heat-treatment and cold-working are only preliminary, and certainly feel that the work could be very usefully extended in this direction. We are optimistic about obtaining even better values than those which we have recorded in the paper. We all realize, of course, that it is very desirable to know the underlying mechanism which has given rise to the improvement in the properties of the alloys which has been recorded. Professor Hanson's remarks in this connection have been echoed by Mr. Bucknall and Mr. Murphy, but in carrying out the work we had not the opportunities of making any extended study in this connection, and although we have some ideas on the subject, we have carefully refrained from any premature expression of opinion in the paper.

Concerning the question of minimum time and the effect of time and temperature, our experiments were not altogether directed to finding out the minimum time required to accomplish the maximum hardening. It may be, of course, although there is no evidence from our results to suggest it, that a long ageing period at lower temperatures might yield improved qualities.

Regarding Dr. Vaders' remarks, it is stated in our paper that when the aluminium content exceeded about 3 per cent. difficulties were experienced in fabricating the alloys. This observation applies to methods of cold-working, such as cold-rolling and cold-drawing. We know that by hot-working, extrusion, hot-rolling, and so on, alloys with an aluminium content of up to about 5 per cent. can be readily worked. In that connection, Messrs. Jones, Pfeil, and Griffiths in their paper state that in the preparation of their alloys the ingots, which were ¾ in. thick, were, after softening by quenching, cold-rolled down to a thickness of ¼ in., a reduction of 66 per cent. From our experience that would be an extraordinarily difficult thing to accomplish, especially in alloys of high aluminium content, exceeding, say, 4 per cent. Tables I, II, and III of their paper show that these alloys, even in the quenched condition, *i.e.*, in their softest possible condition, had a Brinell hardness in excess of 200. I should like to ask whether those alloys were cold-rolled to 66 per cent. thickness, since no remark is made to the contrary in the paper.

As no time is available now, we will reply in writing to the other points raised in the discussion.

Mr. W. T. GRIFFITHS (*in reply*): I agree that a further knowledge of the constitution of the nickel–copper–aluminium alloys and information regarding the true cause of the precipitation-hardening phenomenon would be of great value, but suggest that the complex and lengthy investigations entailed are perhaps more suited to University laboratories or those of our large research institutions. For such studies to be of the greatest value it would be necessary to take into account the effect of the presence of impurities and additional elements such as deoxidizers which, it is already known, play an important part in the precipitation-hardening phenomenon. Dr. Vaders has pointed out how the addition of iron affects the matter, and in our earlier paper * on the copper–nickel–silicon system we showed how manganese, added primarily for purposes of deoxidation, affected the hardening of alloys.

Information regarding precipitation-hardening must, to a large extent, be obtained by inference, and in point of fact one of the best methods of studying precipitation-hardening phenomenon lies in determinations of the hardening effects producible in the alloys. While we have considered the fundamental aspects of the problem, we felt, in preparing our present paper that, in the absence of proof, speculation would be of doubtful value, our aim being to place on record some of the results obtained during the past five or six years with a view to stimulating the interest of others in the precipitation-hardening of the nickel–copper–aluminium alloys.

Dr. Cook is correct in his statement that the cold-rolling of alloys containing more than 4 per cent. aluminium is difficult. We attempted to produce wrought products from alloys containing up to about 7 per cent. aluminium, but those containing more than about 3½ per cent. aluminium cracked badly on cold-rolling, owing probably to the difficulty of producing the soft condition. Attempts to produce strip by hot-rolling also failed in the majority of the high aluminium alloys, and it should have been pointed out in the paper that the alloys SX referred to in Table I, and TT referred to in Table III, were hot-rolled and not cold-rolled. It should be added that the hot-rolled strips were by no means free from cracks.

CORRESPONDENCE.

Messrs. Jones, Pfeil, and Griffths (*in further reply to the discussion*): We fully appreciate the possibility pointed out by Professor Hanson, and referred to also by Mr. Bucknall, that the relation between time and temperature in the precipitation-hardening heat-treatment was well worthy of study, and might lead to the development of useful properties differing from those described in the paper. We have not ignored this matter altogether, but so far as mechanical properties are concerned we found that the best all-round results, taking into account the probable cost of the heat-treatment, were given by short-time treatment at a relatively high temperature.

Dr. Vaders suggested that only in the case of low-nickel alloys was it correct to state that with increasing aluminium content a higher temperature is necessary to give the best precipitation-hardening. Our results, however, over the range 10–45 per cent. nickel dealt with in the paper, definitely point to a higher temperature being necessary the higher the aluminium content. Similarly we found that higher temperatures are necessary for the complete softening of the precipitation-hardened alloys the higher the aluminium content, whilst the temperature required for softening is nearly independent of the nickel content. It is necessary to distinguish between alloys hardened by precipitation and alloys hardened by cold-working. In the latter case a higher annealing temperature is required the higher the nickel content.

In our view the high heat-resistance of the copper–nickel–aluminium alloys is due essentially to the aluminium and nickel contents and, so far as our experiments indicate, additions of iron and a number of other elements have no substantial effect in this connection.

The effects of iron in obtaining high mechanical properties referred to by Dr. Vaders, are interesting, and we are inclined to suggest that these are probably due to a reduction of the rate of diffusion in the alloys. In the ternary alloys it appears difficult to retain all the aluminium in solution by

* *Loc cit.*

quenching when the content of that element is in excess of about 4 per cent. With iron present the separation of the hardening constituent is possibly made more difficult, as is also the growth of the particles of the precipitated phase, so that the hardening effect on reheating may be greater. In this connection, however, it should be mentioned that by the simultaneous use of the effect of cold-work and precipitation-hardening even better combinations of properties can be obtained than those given by Dr. Vaders.

Mr. Hubbard referred to brittleness at 300° C. We have encountered brittleness at a temperature somewhat higher than this, *viz.* 350°–500° C., in copper–nickel–aluminium alloys of high aluminium content, but in the more generally useful alloys of the series containing about 1·5 per cent. aluminium elongations of 10–15 per cent. were obtained in tensile tests at 350° C.

Mr. Murphy raised the question of distortion on heat-treatment, which is a serious disadvantage in some heat-treatable alloys. In the copper–nickel–aluminium alloys of relatively high aluminium content, cracking sometimes occurs on heat-treatment, but in the case of the readily forgeable compositions, in which commercial interest principally lies, cracking and distortion does not occur. In some cases in our experiments tensile test-pieces were heat-treated after machining without distortion being detected, even by a test so critical as the determination of limit of proportionality, using the Martens mirror apparatus.

Dr. F. Johnson * (Member): The authors state, on p. 154, that "So far as the authors are aware, it has not been recorded that copper–zinc alloys containing additions of aluminium and nickel exhibit temper-hardening properties." This has caused me to look up some old lecture-notes in which there was a reference to work by Irresberger,† who obtained the following results with a brass containing copper 60·5, zinc 33·65, aluminium 2·8, and nickel 2·96 per cent.:

	As Cast.	Heated to 789° C., Quenched in Water, and Annealed at 450° C. for 30 minutes.
Tensile strength, tons/in²	36·0	45·5
Elastic limit, tons/in.²	16·7	27·8
Elongation, per cent.	19·0	18·0
Brinell hardness number	125	272

These figures indicate that a brass, fortified by the addition of aluminium and nickel, will respond, even in the cast state, to the kind of heat-treatment adopted by the authors. I have not seen the original paper by Irresberger, so that I cannot state whether the quenching treatment results in softening, which would have brought the results definitely under the category of "temper-hardening," to use the authors' term. Alloys of this type, however, should repay investigation as regards possibilities of age-hardening (a term which I prefer) as well as regards ordinary heat-treatment.

Dr. Brownsdon, Dr. Cook, and Mr. Miller (*in reply*): As regards a suitable nomenclature to indicate the improvement in strength and hardness which takes place when alloys of this type are reheated after quenching, we agree with Mr. Griffiths that it is very desirable for some suitable expression to be generally adopted. We consider that "age-hardening" should be

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† See abstract, this *J.*, 1923, 30, 479.

reserved for those alloys which harden at normal temperatures. This leaves us with a choice between "precipitation-hardening" and "temper-hardening" from the expressions which are now in use, and after due consideration we adopted the latter. In so doing we have been influenced to some extent by the views expressed in Professor Portevin's May Lecture. While the word "tempering" is one which is commonly associated with the heat-treatment of steels, "temper-hardening" is an entirely different word, and describes exactly what happens, namely, a hardening which results from a process of "tempering" which is a reheating. This expression, moreover, has the advantage of not making any assumptions regarding the mechanism of the process.

Dr. Vaders' experience with alloys of this type goes to show that both the aluminium contents and the nickel : aluminium ratio can be modified considerably still giving alloys showing temper-hardening properties. Reference to Table I in our paper confirms his findings, and in this connection we would wish to make it clear that in carrying out our experimental work we always had in mind the obtaining of temper-hardening in copper alloys with as little interference as possible to their original properties and methods of working. In other words, our main object was to obtain an age-hardening copper, brass, or copper–nickel alloy with a minimum addition of aluminium, for with increased quantities of aluminium not only is the nature of the basic metal or alloy very much modified, but difficulties in working arise. Dr. Vaders' work on the addition of iron to these alloys is of considerable interest, but in the absence of further knowledge of their properties we are unable to assess their value. We are surprised to hear that Dr. Vaders did not obtain temper-hardening properties with an alloy containing copper 85, nickel 10, and aluminium 5 per cent., this alloy being not very different from Alloy No. 25 in Table I, which contained nickel 12 and aluminium 4 per cent., and the hardness of this alloy was doubled by suitable heat-treatment.

With regard to Mr. Archbutt's question, we have not any evidence which shows that the modulus of elasticity is sensibly affected by tempering the soft- or hard-worked alloys. The elastic modulus values for the alloys are of the order of 19×10^{-6} lb./in.^{2}.

In reply to Mr. Bucknall, no experiments of a quantitative nature have yet been carried out on the residues obtained when the heat-treated alloys are dissolved in acids, but realizing, since the observation was first made, that useful data may be obtained from a study of such residues, we are continuing this line of investigation.

The possibility of a brittle range in these alloys referred to by Mr. Hubbard has not been specially investigated, but figures given in the paper indicate a falling off of elongation with increase in temperature, the elongation in the temper-hardened alloys being at 300° C. only about half of what it is at normal temperatures, but we would scarcely consider this as indicating a brittle range.

Mr. Murphy refers to distortion on heat-treatment, and some preliminary tests that have been made indicate that this is not serious. The question as to whether the improved physical properties obtained by heat-treatment are economically worth while depends so much on circumstances that it is only possible to come to a useful conclusion when considering the use of such alloys in some specific application.

Finally, Dr. Johnson directs our attention to some results obtained on a 60 per cent. copper–zinc alloy, indicating that such an alloy containing aluminium 2·8 and nickel 2·96 per cent. hardened after quenching and tempering. We made one or two experiments with alloys of 60 : 40 type plus additions of nickel and aluminium, but failed to obtain any appreciable hardening by suitable heat-treatment, and for this reason we confined our experimental work to the richer copper alloys.

FURTHER OBSERVATIONS ON THE DISTRIBUTION OF POROSITY IN ALUMINIUM AND COPPER INGOTS, WITH SOME NOTES ON INVERSE SEGREGATION.*

By N. P. ALLEN,† M.Met., Member.

Synopsis.

Three copper ingots and four aluminium alloy ingots cast in a specially tapered mould have been examined. In all cases the distribution of porosity followed the probable form of the isotherms in the cooling mass, and was much influenced by the mould taper. The type of microstructure also had an influence on the distribution of porosity, the nature of which is discussed. The inverse segregation of two aluminium-copper alloy ingots has been found to be closely related to their porosity.

Introduction.

In a previous paper [1] observations on the distribution of porosity in works' copper ingots have been reported, as the result of which a certain "typical" porosity distribution was deduced. The present work was undertaken:

(*a*) To confirm the existence of this "typical" distribution;
(*b*) To study the effect upon it of the mould taper;
(*c*) To determine to what extent this distribution is common to all ingots, or to what extent it is peculiar to tough-pitch copper.

The last point is important in deciding the processes which are at work, since if the distribution is peculiar to copper, it is clearly useless to attempt to explain it in terms of processes which are common to all solidifying metals, whilst if it is found in a wide variety of other metals and alloys, it cannot be accounted for by means of reactions which occur in copper alone.

Scope of the Work.

The following is a list of the examples studied.

Example 23. An extremely porous casting of electrolytic copper.

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Examples 24 *and* 25. Fire-refined tough-pitch copper: two ingots from the same charge cast in the same mould, one with the wide end upward, the other with the narrow end upward.

Examples 26 *and* 27. Aluminium–silicon alloy (10·3 per cent. silicon): two ingots—cast wide end upward and narrow end upward respectively.

Examples 28 *and* 29. Aluminium–copper alloy (6·7 per cent. copper): two ingots cast wide end upward and narrow end upward respectively.

The aluminium alloys were chosen because gas porosity can be readily produced in them, and the aluminium–silicon alloys have the further advantage that quite wide variations in the silicon content have very little effect on the density (see Table I). The aluminium-copper alloys have not this advantage, and, moreover, are known to be liable to inverse segregation when chill-cast. It was necessary, therefore, to determine the extent of this segregation and to take account of it in the interpretation of the results.

TABLE I.—*Density of Aluminium–Copper and Aluminium–Silicon Alloys.*

Copper, Per Cent.	Density.		Silicon, Per Cent.	Density.	
	Slater.[*]	Edwards.[†]		Slater.[*]	Edwards.[†]
4	2·772	2·784	4	2·693	...
8	2·866	2·865	8·4	...	2·680
12	2·952	...	10·3	2·663	...
24	3·243	...	15	2·642	2·652
Change for 1% addition	0·0223	0·0202	...	0·0047	0·0042
Mean	0·0213		...	0·0045	

[*] Private communication from Dr. I. G. Slater.

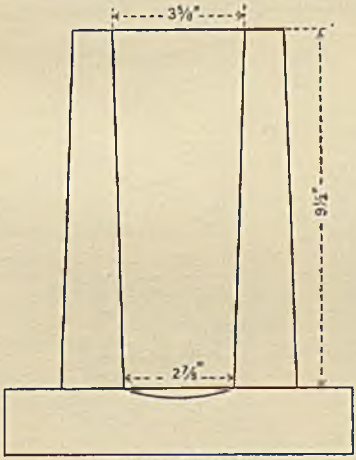
[†] J. D. Edwards, *Chem. and Met. Eng.*, 1923, 28, 165.

EXPERIMENTAL METHODS.

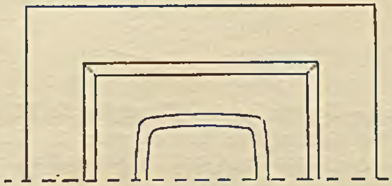
The experimental methods were the same as those employed in the previous work. Pieces were cut out of the ingots in a systematic manner, and their densities determined by Archimedes's method, the figures reported being the apparent densities in water at room temperature. Occasionally pieces with large cavities open to the surface were encountered. In these cases the sample was weighed (w_1 grams) and the cavities were filled with plasticine. It was then re-weighed in air (w_2 grams) and in water (w_3 grams). The density of the piece was taken to be $\frac{w_1}{w_2 - w_3}$.

The accuracy of measurement was well within ± 0·01 for the copper specimens, and about ± 0·001 for the aluminium.

All the ingots were cast in the same mould, a diagram of which is given in Fig. 1. It was made in two pieces, of solid copper, and was unusually heavy, so that the chilling effect on the metal was severe. The ingots were square in cross-section, 9½ in. long, and tapered from 2⅞ in. square at one end to 3⅝ in. square at the other. The mould thickness was substantially increased at the narrow end, to encourage progressive solidification from that end. From each ingot a vertical section about ⅝ in. thick was taken, which, after macro-examination, was cut up in the manner shown in Fig. 2 (Plate XLVIII).



VERTICAL SECTION



HALF PLAN

Fig. 1.—Copper Mould.

Details of Ingots.

Example 23.—*Porous H.C. Copper Ingot.*

The metal was tough-pitch H.C. copper in the form of oily rolled strip, melted in a high-frequency electric furnace under an ample cover of charcoal, so that the metal became practically free from oxygen. Before casting, nitrogen was bubbled through the metal for 10 minutes to remove the gas which was present, but this was unsuccessful, for the metal when cast rose considerably in the mould, the ingot increasing in length at least 1 in. The mould was wide end upward.

The macrostructure of the ingot showed columnar crystals growing from the top, bottom, and sides, extending to a depth of $\frac{3}{4}$ to $\frac{1}{2}$ in. and enclosing a region of equi-axed crystals some $\frac{1}{16}$ to $\frac{1}{8}$ in. in diameter.

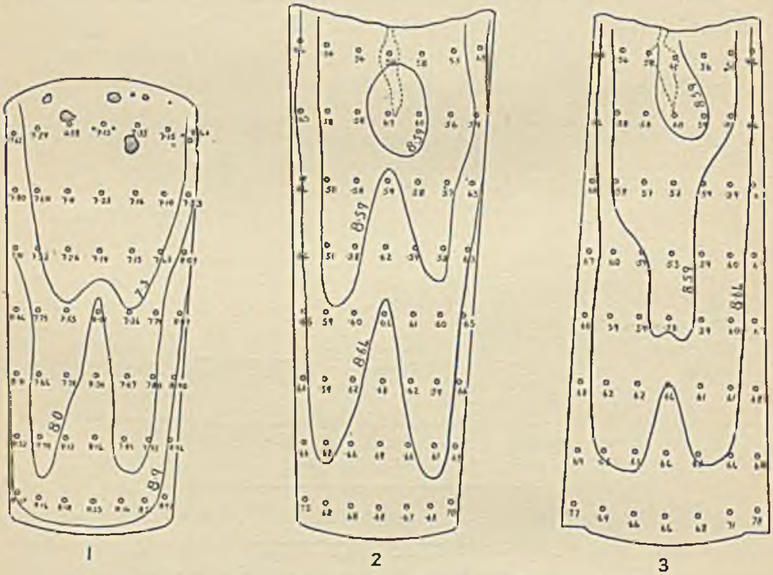


Fig. 4.—Copper Ingots. Examples 23, 24, and 25.

(1) Crucible melted electrolytic: low oxygen; (2) Tough-pitch: ingot cast wide end up; (3) Tough-pitch: ingot cast narrow end up.

The blow-holes were extremely numerous and very small, except near the top, where cavities up to $\frac{3}{8}$ in. in diameter were found. In spite of its very low average density, there was a border about $\frac{1}{4}$ in. thick round the bottom of the ingot quite free from blow-holes. The transition from this region to the porous region of the ingot is shown in Fig. 3 (Plate XLVIII). It is important to note how *the same crystal was sound at the beginning of its growth and porous at the end.*

The distribution of porosity is shown in Fig. 4(1), the most interesting features being: (*a*) the great variations in density; (*b*) the general tendency of the density contours to run parallel to the mould walls except for the very marked sound cone in the bottom centre of the ingot; (*c*) the great porosity of the material exuded when the metal "rose" in the mould.

Examples 24 *and* 25.—*Tough-Pitch Fire-Refined Copper.*

These two ingots were cast from the same charge of reverberatory furnace copper under so far as possible identical conditions, with the exception that whereas Example 24 was cast with the wide end of the mould uppermost, Example 25 was cast with the narrow end up. The details are summarized in Table II, and Fig. 5 (Plate XLIX) shows the macrostructure, which presented no unusual features. The furnace was at the time engaged in the production of a variety of sizes of wedge bar, which set perfectly level, but, on account of the small size of the ingots and relatively great weight of the mould, these ingots solidified with a decided sink, and, on being cut up, were found to be piped to a depth of about 1½ in. The pipe was filled with water during the density determinations, so that the density figures recorded were not affected by the pipe.

TABLE II.—*Casting Conditions.*

Ingot.	Nature.	Composition, Per Cent.	Melting.	Casting Temp., ° C.	Wide or Narrow End up.	Mould Temp., ° C.	Mould Dressing.
23	H.C. copper	0·001 O_2	H.F. furnace	...	wide	...	bone ash
24 25	Fire-refined copper	0·02 As 0·04 Ni 0·01 Pb 0·0005 Bi 0·07 O_2	Reverberatory furnace	1120	wide narrow	120 70	bone ash ,,
26 27	Aluminium–silicon alloy	10·3 Si	Coke-fired crucible: stirred with stick	660 650	wide narrow	100 90	none ,,
28 29	Alloy "3L11"	6·67 Cu	Coke-fired crucible: stirred with stick	760 720	wide narrow	90 80	none ,,

Fig. 4 (2 and 3) shows the results. The density contours were similar in form to those exhibited by Example 23, but the actual density differences were very much less. In spite of the much greater mean density of the ingots, there was no border region absolutely free from blow-holes: in short, whereas in Examples 24 and 25 gas was evolved immediately solidification began, in Example 23 a certain amount of solidification took place before any gas was given off, although, apparently, the amount of gas subsequently generated was very much greater. The effect of altering the taper of the mould was felt chiefly in the axis of the ingot. When the casting was wide end up, the axis was everywhere comparatively sound. In the ingot cast with the narrow end upward, the axis was the least sound part of the ingot in the upper two-thirds and relatively sound in the lower third. An interesting feature was found in the neighbourhood of the pipe, where a perceptible local increase of density occurred. It seems that towards the end of solidification there took place in the centre of the ingot a decrease of pressure, under the influence of which the comparatively porous region in the centre of Example 25 was produced, and oxidized metal from the surface was drawn into the centre of the ingot. Fig. 6 (Plate L) shows such an oxidized stream drawn into the space between two dendrites situated just below the contraction cavity in Example 24. Where this metal was able to enter, it caused a local increase of the density of the casting, but where it could not penetrate, the lower hydrostatic pressure in the ingot resulted in an increased amount of porosity, as is shown by the prolonged inter-dendritic cavity in Fig. 7 (Plate L), taken from a position a little lower down in the ingot than Fig. 6. It is probable that this lowering of pressure was produced by the contraction on solidification when the metal was so far frozen across the top of the ingot that feeding was interfered with. This would account for its effects being much more obvious in the ingot cast with the narrow end upward.

Examples 26–29.—*Aluminium–Silicon and Aluminium–Copper Alloys.*

Examples 26–29 are two pairs of ingots, one cast with the wide end up, and the other with the narrow end up, of aluminium–silicon alloy and aluminium–copper alloy, respectively. The material was good-quality scrap, and in each case enough metal for the two ingots was melted in a Salamander crucible in a coke-fired furnace. To ensure that gas should be present, the metal was stirred at about 750° C. with a wooden stick. The wide-end-up ingot was cast first. While the mould was being cooled and reversed, the metal was returned to the furnace and kept warm, and the narrow-end-up ingot was then cast. All the ingots were fed as long as possible, and evolved gas fairly liberally during solidification. Other details are reported in Table II.

In none of the ingots was the layer of columnar crystals more than ¼ in. deep, and the succeeding equi-axed crystals were very fine and uniform. The visible porosity in the copper alloy ingots (Examples 28 and 29) was slight and evenly distributed. The silicon alloys (Examples 26 and 27) showed, besides uniformly distributed pores, serious inter-dendritic porosity just below the surface in the wide-end-up ingot, but deep into the ingot in the other, which also showed an appreciable primary pipe. These cavities are illustrated in Fig. 2 (A and B) (Plate XLVIII). The microstructures of the aluminium–copper alloy ingots were characteristic of alloys of their composition. Those of the silicon alloy ingots showed a little primary silicon in a ground-mass consisting of a few small dendrites of aluminium, surrounded by a coarse, unmodified eutectic.

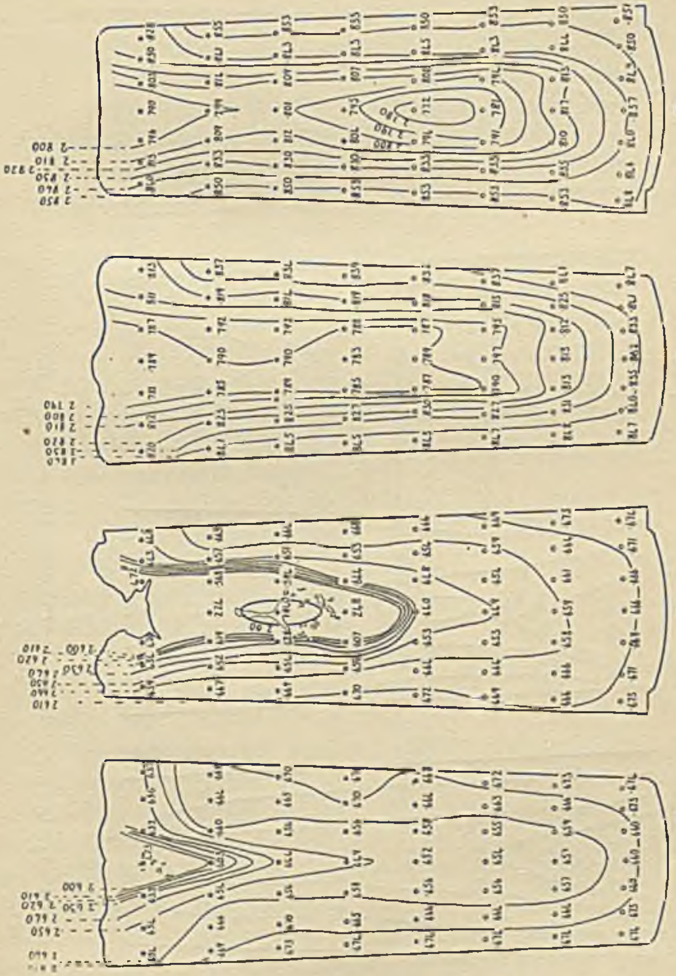


FIG. 8.—Density Distribution in Aluminium Alloy Ingots. Examples 26, 27, 28, and 29.

In order to estimate the effect of segregation in the aluminium-copper alloy ingots, copper determinations were made in the positions shown in Fig. 9 (E and F), where also the figures obtained are recorded. Inverse segregation to the extent of some 1 per cent. on the average was present in both ingots, and the lines of equal copper content ran roughly parallel to the walls of the mould.

The results of the density measurements are summarized in Fig. 8 (A to D) and the figures for the aluminium–copper alloy ingots, corrected for copper segregation, in Fig. 9 (G and H). For this purpose the mean value for the effect of copper on the density of the alloy arrived at in Table I is used, and the densities are given as they would have been if the copper content of the ingots had been uniformly 6·67 per cent. Any density changes consequent on the solution or precipitation in the solid state of $CuAl_2$ are quite negligible.

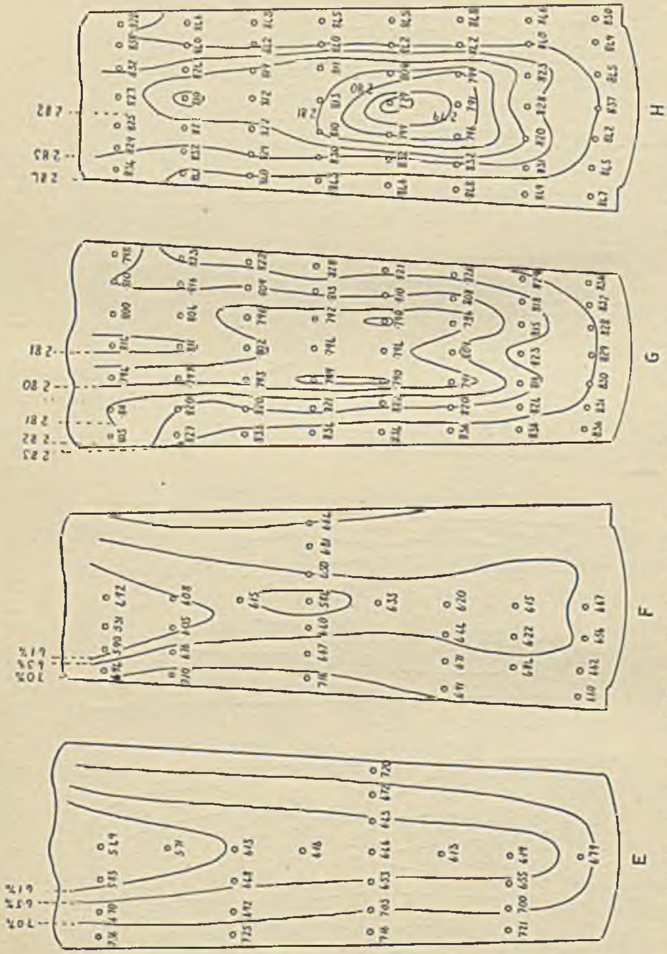


Fig. 9.—Copper and Corrected Density Distribution in Aluminium–Copper Alloy Ingots. E and G, Example 28; F and H, Example 29.

The same orderly variations of porosity existed as were found in the copper ingots. In all cases the general tendency of the density contours to run parallel to the mould walls was marked, indicating that the flow of heat was the most potent factor. There was a certain tendency for the contours to flatten out at the top of the ingot, due probably to bubbles of gas being trapped below the surface of the metal, but this was a quite minor phenomenon. The sound cone, so prominent in the copper ingots, was definitely absent in the aluminium–silicon alloy ingots. There was a trace of it in the aluminium–copper alloy ingot, Example 29, and it was definitely present in Example 28. It was difficult to detect in the uncorrected density figures, but the corrections for copper segregation brought it up sharply. The top region of enhanced density found in the copper ingots Nos. 24 and 25, and attributed to feeding, was absent in Examples 26 and 27, but quite marked in Example 28 (copper–aluminium alloy ingot wide end up, Fig. 9, G). Otherwise the porosity was determined chiefly by the order of solidification: the metal was soundest where it solidified first, and least sound where it solidified last, and it is noteworthy that the porosity of the "gassy" metal was influenced in the same way by the shape of the mould as the piping would have been had the metal been gas-free; *i.e.* it tended to be confined to the top when the wide end was up, and drawn more deeply into the ingot when the top was the narrower. The curves for Example 29 might almost be a diagram from a text-book illustrating the formation of primary and secondary pipe. This is considered to be evidence in favour of the close connection between gas porosity and contraction on solidification argued in the author's paper on "The Influence of Pressure on the Evolution of Gases from Metals." [2]

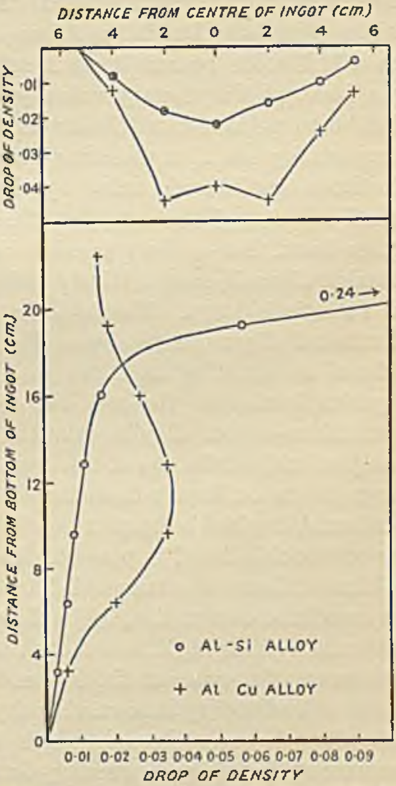


FIG. 10.—Comparison of Al–Cu and Al–Si Ingots.

There was an important difference between the two alloys in the rate at which the amount of porosity varied as the solidification proceeded. This is shown by the spacing of the density contours, and further illustrated in Fig. 10, in which the decrease of density (corrected in the case of copper alloy) along vertical and horizontal sections is plotted for the wide-end-up ingots of each type. In the aluminium–copper alloy the decrease of density was fairly rapid at first, and then slower, with an increase towards the top of the ingot, where feeding effects were felt; but in the silicon alloy it was at first slow, and then, as solidification became more nearly complete, extremely rapid. On the basis of the views previously expressed, the difference is to be related to the structural characteristics of the alloys. The aluminium–copper alloy has a long freezing range during which massive interlacing dendrites are formed, ended by the solidification of a comparatively small amount of the eutectic. The aluminium–silicon alloy, on the other hand, has a short freezing range; the primary crystallization consists of small, comparatively undeveloped crystals, and the quantity of eutectic is large. The solidification of the wide-end-up ingots is illustrated diagrammatically in Fig. 11, in which the process is considered as resulting from the gradual travelling of the solidus and liquidus isotherms through the mass. Fig. 11(*a*) represents the aluminium–copper alloy ingot at the point where the liquidus isotherm has just bridged the top of the ingot. On account of the long freezing range, there is a large volume included between the liquidus and solidus isotherms, in which a complex tangle of aluminium dendrites surrounded by copper-rich liquid is present. In such a mass, the advance of the solidus isotherm is accompanied by solidification of the eutectic with its associated contraction, and unless liquid metal travels from the top and centre of the ingot fast enough to compensate for this contraction, a decrease of pressure at the solidus face must result. The flow of this metal is hindered by its own viscosity, and the narrowness of the interdendritic channels through which it must pass; consequently the pressure at the solidus face readily decreases to a value below the internal gas pressure of the melt, and evolution of dissolved gas is promoted. Nevertheless, a considerable amount of downward and outward flow of feeding metal does occur, as consideration of the copper distribution shows. On the other hand, the aluminium–silicon alloy at the same stage (Fig. 11*c*) exhibits a narrow zone between the liquidus and the solidus, interspersed with relatively few granules of primary silicon and a few small aluminium dendrites. These interfere little with the feeding, practically no decrease of the hydrostatic pressure takes place, and gas evolution receives no assistance from the conditions within the ingot. When solidification approaches completion, conditions within

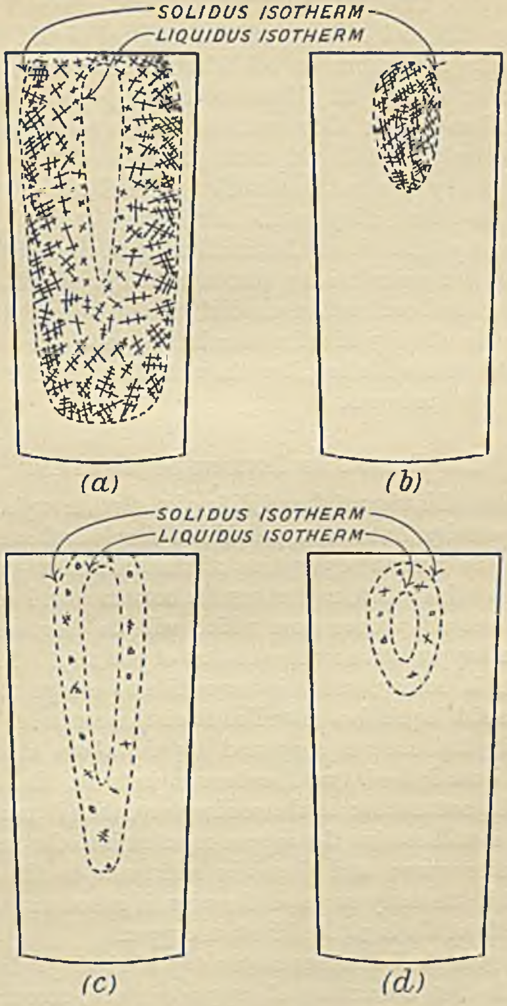


Fig. 11.

(*a*) Great distance between solidus and liquidus. Dendrites numerous and interlaced, interfering with feeding. Consequent rapid drop of pressure. Evolution of gas promoted.

(*b*) Metal completely solid on top. No further feeding. Small quantity of residual liquid. No great local increase of porosity.

(*c*) Small distance between liquidus and solidus. Few and small primary crystals, not interfering with feeding. Consequent small drop of pressure. Evolution of gas not promoted.

(*d*) Metal completely solid on top. No further feeding. Large quantity of residual liquid. Great local increase of porosity.

the ingot change. The bridging of the top of the ingot by the solidus isotherm (Fig. 11*b* and *d*) cuts off the residual liquid from further feeding, and the contraction on solidification must appear as cavities of some form or other. At this stage the region within the solidus of the aluminium–copper alloy contains large quantities of dendrites with comparatively little liquid entangled between them. The local increase of porosity due to the cessation of feeding is therefore slight. The aluminium–silicon alloy at the same stage encloses a large proportion of liquid within the solidus isotherm, and the cavities produced by its solidification are relatively numerous and large. The interaction of gas evolution and contraction on solidification is thus very successful in explaining the density distributions in the wide-end-up ingots, and a little consideration will show how the variations found in the narrow-end-up ingots are produced.

THE THEORY OF INVERSE SEGREGATION.

Not only does this view of the solidification give an explanation of the incidence of porosity, but it also provides a simple and satisfactory explanation for the inverse segregation of the aluminium–copper alloys. In Fig. 9 it is evident that, neglecting the bottom sound cone, which is due to some second phenomenon which will be discussed later, the distribution of copper is the reverse of that of porosity. Where cavities appear, copper is lacking, and it is impossible to escape the suggestion that a copper-rich liquid has travelled from the centre of the ingot to the outside in the manner suggested by the above description. If liquid metal does indeed travel outwards between the dendrites in response to the contraction at the solidus face, then it must be rich in copper, since it will receive the copper rejected into the residual liquid as the dendrites grow; and since the resistance to the flow of this liquid is least in the early stages of freezing, it is not surprising to find that the outside of the ingot is richest in copper.

In both ingots the behaviour at the top of the ingot is anomalous. There is at the top a decrease of copper content, accompanied by a decrease of porosity. This is due to the continuous addition of fresh liquid for feeding. Once dendrites begin to appear in this region, the liquid fed to the bottom of the ingot is a copper-rich concentrate: that added as liquid metal corresponds with the average of the alloy: the net result is a loss of copper. The addition of fresh liquid militates against the production of cavities, and this region is relatively sound. The local copper enrichment found near the centre of each ingot possibly represents eutectic liquid fed from the top of the ingot in the later stages of solidification.

This theory of inverse segregation is somewhat similar to that of Genders,[3] according to whom the impurity-rich residual liquid is blown to the edges of the ingot by gases generated at the centre. The evolution of gas in this way would certainly assist the movements of the feeding liquid, but the fact that alloys substantially free from gas show the segregation as severely as gas-containing alloys has in some quarters militated seriously against the theory. The recognition of the part played by contraction overcomes this objection, and the process envisaged by Genders may be considered as a particular case of a general action. Several other theories of inverse segregation have been proposed, of which those based on the Ludwig–Soret effect, under-cooling, and movements of the primary dendrites have been attractive to metallurgists. The first is open to several objections—namely, that the effect is not large enough to account for inverse segregation, that it is too slow to establish itself to produce any change in the time in which an ingot solidifies, and that, although attempts have been made to produce the effect in molten alloys, they have not been successful; further, it does not explain the most prominent feature of inverse segregation, which is that it is produced only in alloys having a long freezing range.* Impressed by this fact, Watson[5] endeavoured to establish a connection between inverse segregation and the movement of the primary dendrites away from the chilling surface. He succeeded in proving that if a mixture of dendrites and liquid is suddenly chilled, the dendrites are repelled from the chilled side, but overlooked the fact that when a molten alloy is poured into a cold mould there are no dendrites present to be so repelled. The dendrites present in an ingot are produced by the action of the chill, and such dendrites cohere together, and are not free to move: otherwise it would be impossible to produce a hollow shell by "bleeding" an ingot, or to make satisfactory "slush" castings. Moreover, Rosenhain and Archbutt[6] have shown that the shell produced by "bleeding" a copper–aluminium alloy casting itself presents inverse segregation: the phenomenon cannot therefore be due to dendrites which are not connected to the shell. Thus, whilst the effect described by Watson certainly exists, its bearing on the ordinary inverse segregation which occurs in a casting cannot be considered to be proved. The amount of under-cooling necessary to explain the phenomena on the under-cooling theory has not yet been observed in metals.

* Benedicks[4] has established a connection between the Ludwig–Soret effect and the *slope of the liquidus curve*, but this is not identical with the *freezing range* with which inverse segregation is related. If the slope of the liquidus curve were the determining factor, a 50 per cent. silver–copper alloy would show much the same amount of segregation as a 70 per cent. silver–copper alloy, which is not the case.

The movement of the residual liquid under the influence of contraction on solidification leads not only qualitatively to the phenomena of inverse segregation (in showing the necessity for a freezing range, and a temperature gradient, which are the conditions for the existence of a zone of dendrites separated by liquid channels, and for a structure in which the dendrites differ much in composition from the liquid solidifying last), but the extent to which the segregation should occur can also be roughly estimated. Consider the case of an aluminium–copper alloy containing 6·67 per cent. copper, and assume that in the border zone the feeding was perfect (*i.e.* that the metal froze without any cavities), which was very nearly true in the ingots studied. The solidification contraction of this alloy is about 4 per cent. by volume.[7] If this were compensated for by the infiltration into the border zone of eutectic liquid, 100 grm. of the border material would gain (allowing for the higher density of the eutectic) about 5 grm. of eutectic liquid. The composition after solidification would be $\frac{100 \times 6{\cdot}67 + 5 \times 33^{*}}{105} =$ 7·91 per cent. copper. This calculation assumes that the whole of the contraction takes place when the eutectic freezes. Actually, this is not the case: each stage of solidification is accompanied by a portion of the contraction, and the liquid thereby drawn into the border region varies in composition from 6·67 per cent. of copper (which is the composition in equilibrium with the first nucleus to appear) to 33 per cent. copper (the composition in equilibrium with the solid separating last). Taking 20 per cent. copper as the average composition, and adjusting the weight of metal drawn in to 4·5 grm. to allow for its less average density, the final composition becomes $\frac{100 \times 6{\cdot}67 + 4{\cdot}5 \times 20}{104{\cdot}5} = 7{\cdot}24$. This agrees very well with the values found (6·91 — 7·36), and although one cannot be too confident about either the contraction value employed or the mean composition of the liquid drawn into the border region, the calculation shows that the causes invoked are adequate for the effects observed.

Similar calculations to the above were made with regard to the silver–copper alloys by Phelps[8] in discussing Smith's[11] well-known paper on this subject, and he also concluded that contraction was sufficient to account for the segregation. Moreover, he showed (and Smith confirmed) that the alloys of silver with bismuth (which expand on solidification) segregate in the opposite way to the alloys of silver with lead. Gulliver[9] came to the same conclusion in discussing Reader's work on inverse segregation in bronzes, and directed attention to the

[*] CuAl eutectic = 33 per cent. copper.

presence of porosity in the regions low in tin. Masing and Haase,[12] and, later, Masing and Scheuer [13] have also studied the relation between volume contraction and inverse segregation, using the figures of Masing and Haase,[12] and Fraenkel and Gödecke [14] with respect to the systems copper–tin, aluminium–zinc, aluminium–copper, and silver–copper. In all cases the calculated amount of inverse segregation was of the same order of magnitude as that found, although the numerical agreement was not good. Other workers, notably Bauer and Arndt,[15] Iokibe,[10] Kuhnel,[16] and Price and Phillips,[17] whilst recognizing an outward interdendritic flow of the residual liquid as the cause of inverse segregation, have sought other explanations of the origin of the movement, but it is noteworthy that Iokibe, as a result of his later investigations of the tin–zinc alloys,[18] has come to the conclusion that solidification contraction is the most important cause. A summary of the theories of inverse segregation has recently been made by Masing and Scheuer,[13] whose conclusion is in favour of an interdendritic flow theory, with contraction on solidification as the primary cause when cooling is rapid, and gas evolution in the case of ingots cooled slowly.

SUMMARY.

Regarding the results as a whole, it appears that the production of cavities in an ingot is a regular sequence of events, in which the order and the manner in which the solid constituents separate out from the liquid, together with the contraction on solidification, play a greater part than the movements of gas bubbles. The porosity distribution previously considered "typical" of copper ingots is confirmed by the present copper ingots, but is not common to all ingots. It appears rather to be the result of two distinct processes, one of which causes the metal to become more porous as solidification proceeds, whilst the other produces a sound cone at the centre of the bottom of the ingot. Of these, the former has been found in every ingot yet examined and may be the result of

(*a*) The greater rate of cooling at the outside;
(*b*) The segregation of dissolved gas to the centre;
(*c*) The fall of hydrostatic pressure as solidification proceeds, on account of the increasing obstructions to feeding.

All three probably play their part, but information is lacking which would enable one to decide their relative importance. There is definite evidence for the part played by the contraction on solidification, particularly in alloys with a long freezing range, in which also the contraction determines inverse segregation. The relationship between inter-dendritic porosity and inverse segregation in such alloys may be stated thus: to the extent that inter-dendritic feeding is possible, contraction on solidification produces inverse segregation; to the extent that it is hindered, it promotes gas evolution and inter-dendritic porosity.

The second process sometimes occurs and sometimes does not. The form of density contour it produces would be consistent with the rise through the mass of light particles (or the fall of heavy ones), more time being allowed for the separation in the centre of the ingot. Ingots which give off gas early in the freezing process, or have a long freezing range, show the phenomenon more clearly than others.

The influence of the type of structure on the distribution of porosity is of practical importance in the foundry. If castings suffer from large cavities or localized spongy patches, the remedy is either better feeding, or the choice of an alloy with a longer freezing range, which will distribute the porosity. If, on the other hand, the trouble is extensive ramifying porosity, producing permeability under pressure, an alloy with a shorter freezing range, with more rapid cooling and less gas content, is likely to be better.

Acknowledgments.

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References.

[1] Allen, *J. Inst. Metals*, 1933, **51**, 277.

[2] Allen, *J. Inst. Metals*, 1932, **49**, 333.

[3] Genders, *J. Inst. Metals*, 1927, **37**, 241.

[4] Benedicks, *Trans. Inst. Min. Met.*, 1926, **35**, 316.

[5] Watson, *J. Inst. Metals*, 1932, **49**, 347.

[6] Archbutt, *J. Inst. Metals*, 1927, **37**, 241 (discussion).

[7] Edwards and Gammon, *Chem. and Met. Eng.*, 1921, **24**, 338.

[8] Phelps, *Trans. Inst. Min. Met.*, 1926, **35**, 304.

[9] Gulliver, *Trans. Inst. Min. Met.*, 1926, **35**, 327.

[10] Iokibe, *J. Inst. Metals*, 1924, **31**, 225.

[11] Smith, *Trans. Inst. Min. Met.*, 1926, **35**, 254.

[12] Masing and Haase, *Wiss. Veröff. Siemens-Konzern*, 1925, **6**, 113.

[13] Masing and Scheuer, *Z. Metallkunde*, 1933, **25**, 173.

[14] Fraenkel and Gödecke, *Z. Metallkunde*, 1929, **21**, 322.

[15] Bauer and Arndt, *Z. Metallkunde*, 1921, **13**, 497.

[16] Kuhnel, *Z. Metallkunde*, 1922, **14**, 462; 1926, **18**, 273.

[17] Price and Phillips, *Amer. Inst. Min. Met. Eng., Proc. Inst. Metals Div.*, **1927**, 80–88.

[18] Iokibe, *Sci. Rep. Tôhoku Imp. Univ.*, 1931, [i], **20**, 608.

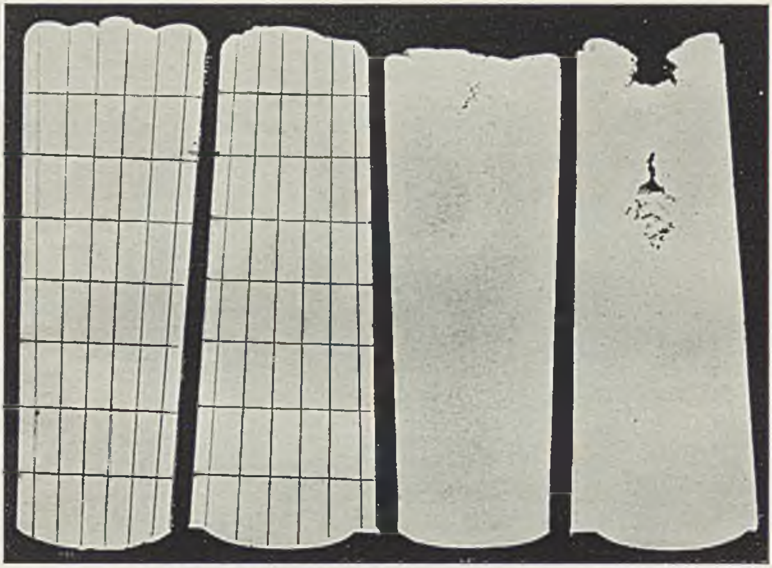

FIG. 2.—Aluminium Alloy Ingots showing Method of Sectioning.

FIG. 3.—Transition from Sound to Porous Regions in Copper Ingot. × 5.

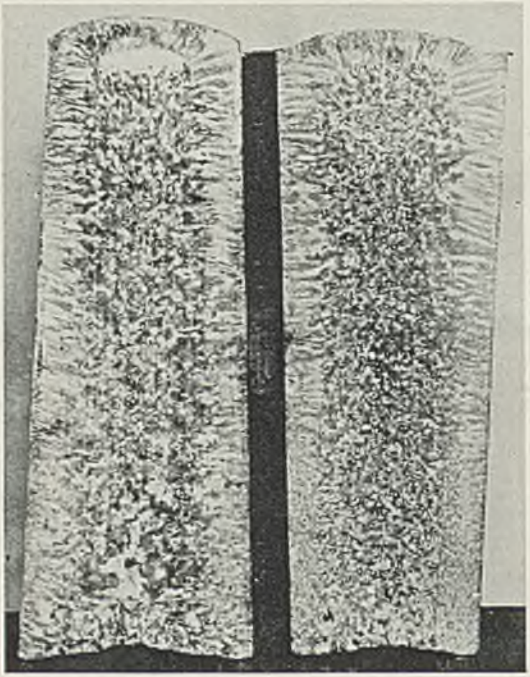

Fig. 5.—Macrostructures of Examples 24, 25.

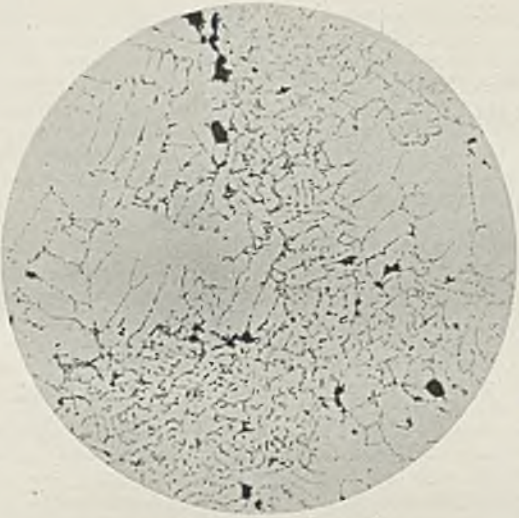

FIG. 6.—Oxidized Region near Pipe in Copper Ingot. × 100.

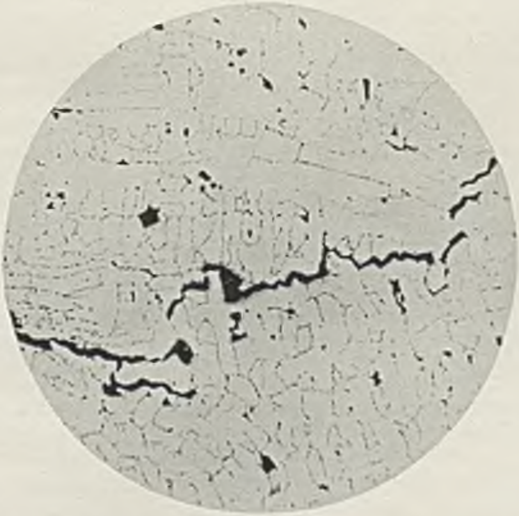

FIG. 7.—Inter-dendritic Cavity in Copper Ingot. × 100.

DISCUSSION.

Mr. H. Sutton,[*] M.Sc. (Member): This very careful record of observations on the ingots examined by Mr. Allen will be of value to those interested in the subject. There is no reference in the paper to the relative weights of the ingots and moulds, but I hope that Mr. Allen will be able to give those values. The Committee which is now studying steel ingots is making a practice of giving in all cases the relative weights of ingot and mould, and that has been in many instances of considerable interest.

I am glad that the author proposes to expand the portion of the paper dealing with inverse segregation. In the section on the theory of inverse segregation he makes one remark which seems to me scarcely in accord with practical observations on freezing ingots: "Since the resistance to the flow of this liquid is least in the early stages of freezing, it is not surprising to find that the outside of the ingot is richest in copper." Although bled ingots of aluminium-rich copper alloys show inverse segregation, that particular form of inverse segregation which in those alloys takes the form of exudations from the surface at the side seems to occur at a very late stage in freezing. I mention that because I have watched ingots freezing which have been stripped fairly soon, and have observed the exudation of liquid when it would appear from the head of the ingot that the whole thing was practically solid.

I have been very much impressed with the recent German work on inverse segregation, and I should appreciate the additions which Mr. Allen has mentioned. K. Iokibe[†] has studied the problem very intently, and in a recent publication states that he has found that inverse segregation occurs in tin–zinc alloys after dissolved gases have been removed by evacuation. Haase[‡] has studied the volume changes on reheating small chill-cast samples of copper–zinc alloys. The marked increases in volume observed are attributed by Haase to diffusion effects in the direction of equilibrium. It is apparent that the tempered specimens which he used have fissured very severely in the outer zones, and inverse segregation was very readily seen on the cross-sections through those samples, particularly after tempering. It seems inevitable that expansions occurring in such alloys must be recognized as a vital factor in relation to segregation. Haase also mentions that the phenomena are observed in vacuum-melted antimony–bismuth alloys. Since inverse segregation is observed in some cases where no solid solutions are known to be formed, it appears that the contraction may have the same effect as expansion and may result in a similar form of segregation.

At the Royal Aircraft Establishment at Farnborough we cast large aluminium alloy ingots for forgings with a hot-top or dozzle lined with sand, and this results in good feeding and appears generally beneficial. Inverse segregation, however, cannot be avoided in this way, and there is reason to suppose that it may be slightly increased.

Bohner[§] found that topping up fairly large aluminium alloy ingots during freezing had no effect of practical importance on segregation, and our experience has been in accord with that observation. The results obtained by Bohner on aluminium alloys indicate that both inverse and normal forms of segregation can be minimized by the use of very high or very low rates of cooling of the molten alloys, and this indication is also in good agreement with the view that inverse segregation is the result of volume changes.

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[†] K. Iokibe, *Sci. Rep. Tōhoku Imp. Univ.*, 1931, [i], **20**, 608.

[‡] C. Haase, *Z. Metallkunde*, 1932, **24**, 258–261.

[§] H. Bohner, *Hauszeit. V.A.W. u.d. Erftwerk*, 1932, **4**, 24–30.

In conclusion, I should like to say that it seems to me difficult to conceive of the eutectic, or liquid approaching eutectic composition, passing regions in which there are contraction cavities and leaving contraction cavities behind it on its way to the outer surface.

Dr. R. Genders,* M.B.E., M.Met. (Member): While one can agree substantially with Mr. Allen's views and his conclusions from his work, it must be borne in mind that certain important variables in the casting process have been entirely neglected, and consequently some of the more generalized statements which he has made must be subject to modification under certain conditions different from his own.

The horizontal variations in density which are shown by the copper–aluminium and aluminium–silicon ingots seem to be generally representative of a large variety of alloys. The brasses, which do not contain dissolved gas, so far as we are aware, show a very similar variation in density, and the decrease in density in the middle region of the ingot is greatest when the range of solidification is greatest. A 60 : 40 brass approximates in this respect to the aluminium–silicon alloy and a 70 : 30 brass to the copper–aluminium alloy, but this must not be taken to mean that the effect of gas is negligible. Gases can undoubtedly exert a very considerable effect under certain conditions.

As regards inverse segregation, the workers who have been referred to by Mr. Allen cannot complain that he has treated them other than fairly, and it seems to be fairly well agreed at the present moment that outward interdendritic flow of rich liquid must be responsible in some measure for inverse segregation. This outward flow is certainly due in some cases to the effects of gas pressure, and in that connection I should like to support Mr. Sutton's remarks, because it is difficult to understand why a liquid should move from the interior of an ingot to the outside, filling up cavities on the way and leaving cavities behind it, unless there is some actual pressure behind it. In the case of phosphor–bronze, one can visually observe the exudation of liquid on the outside of ingots and see that these small exudations are originally bubbles of gas which burst to form liquid nodules.

My own doubt, which has been previously expressed, that interdendritic flow of rich liquid to the outside could account completely for inverse segregation has been due partly to the fact that I made a different guess at the composition of the outward-flowing liquid for the purposes of calculation, and so obtained a figure different from that given by Mr. Allen; in passing, I should like to suggest to Mr. Allen that one cannot come to the conclusion which he gives in his section on the theory of inverse segregation (that "the calculation shows that the causes invoked are adequate for the effects observed"), when the figures in the calculation are not confidently obtained, or even confidently guessed. Another point in connection with this matter is that Iokibe showed some years ago that his porous alloys cracked the crucible in which they were solidifying; and that, of course, can hardly be a contraction effect.

There is another point which may be new and which is illustrated by the present results. If a small ingot of aluminium–copper alloy, containing about 6–10 per cent. of copper, be allowed to solidify in a small mould and closely observed during solidification, it will be seen that the dendrites growing at the mould surface are separated from each other by liquid, and float loosely against the mould. If the mould is tilted, these floating dendrites are easily detached and drift away into the liquid mass. It is clear, therefore, that the ingot surface next to the mould is not completely solid for some considerable time; it is separated by liquid channels which are quite wide in the early stages, and there is the possibility that the dendrites can sink by their own

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* Research Department, Woolwich.

weight into closer contact with each other, thus constricting the interdendritic channels. That would restrict the amount of interdendritic flow and the proportion of the effect which could be due to a plain contraction of the outer solid layer. If the effect occurred one would expect that consolidation of the outer layer would be evident in an ingot mould cast narrow end up, where the walls slope outwards and downwards, and the data given by Mr. Allen are in accordance with this view in showing that the inverse segregation is considerably less in the ingot with the narrow end up than in the ingot with the wide end up. It may also be noted that the former is actually the sounder of the two, although Mr. Allen has unfortunately not given us the complete density figures for the whole ingot; *i.e.* the density of the whole ingot taken as one specimen. There are grounds, therefore, for believing that the outward interdendritic flow of rich liquid by contraction is not the whole cause of inverse segregation.

In describing the copper mould shown in Fig. 1, Mr. Allen states "the mould thickness was substantially increased at the narrow end, to encourage progressive solidification from that end." That encouragement is, I think, quite insufficient to have any appreciable effect.

Dr. W. Rosenhain,* F.Inst.Met., F.R.S. (Past-President): I have read Mr. Allen's paper with very great interest and with considerable appreciation of the work done and of the strenuous efforts made to find a rational interpretation of the results. I am afraid that I cannot agree that those efforts have been entirely successful, because the facts which he quotes do not unfortunately by any means tally with the facts which are frequently found in the production of ingots of various sizes under other conditions.

I must criticize Mr. Allen's use of the word "feeding." Most of us will understand by "feed metal" hot metal which is added to the mould during the process of solidification. I gather that has not been done in this case, and that the so-called feed metal is merely the residual liquid which he believes flows down into the cavities of the ingot. He does not explain, however, how it selects which it is going to fill and which it is going to leave.

I find a difficulty in understanding just how Mr. Allen arrived at his conclusions. He speaks in one place of a negative pressure being formed in the upper part of the ingot when a solid crust has formed on the outside surface which prevents downward sagging of the ingot externally. In a perfectly gas-free metal that may occur, but I am inclined to doubt if it ever does, because it is extremely difficult to obtain a metal which is sufficiently gas-free. Moreover, if there were really a negative pressure and liquid channels leading from the liquid interior through the interdendritic interstices to the outside, under a negative pressure that liquid would be forced in by atmospheric pressure and would not be allowed to flow outwards under gravity against such a negative pressure. I feel, therefore, that if Mr. Allen wishes us to accept his view that it is rich, interdendritic liquid which is flowing outwards, he will find it difficult to reconcile that with the existence of a negative pressure on the inside of the ingot. I do not think that it matters a great deal, except from the point of view of the argument, because I doubt very much whether a negative pressure ever really exists except very transiently indeed.

Mr. Allen and others who speak of this flow of rich interdendritic liquid as causing inverse segregation are, I think, inclined to ignore or neglect one point. If a sufficiently high figure be assumed the desired result can be obtained, but it means that a very large amount of a richer liquid has to flow outwards, unless the interdendritic spaces of the outer layers are large compared with the dendrites themselves, and that we have yet to prove. There

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* London.

is the further fact that this idea of an interdendritic liquid flowing outward implies the existence of a much more fusible liquid in the alloy. Now, where there is a eutectic in the alloy with primary crystals of fairly high freezing point, those conditions might be realized, but I think that it will be found that inverse segregation occurs in solid solution types of alloys in which there is no eutectic whatever and in which the freezing range is comparatively small. It is certainly in favour of the argument that a larger freezing range helps to produce inverse segregation, but inverse segregation does occur in gold–silver alloys in which the freezing range is small, and in gold–copper alloys still more so. Those cases are very well known—in fact I think that the phenomenon was first discovered in those alloys.

I will not occupy further time on the question of inverse segregation. It is a very large question, and there are many view-points about it. I agree with Dr. Genders that in many cases gas pressure within the ingot has a great deal to do with it, particularly those exudations from the surface with which we are all familiar, but inverse segregation can occur in the practical absence of gas, and therefore other causes must be at work as well as gas pressure.

The other point to which I wish to refer is the method which Mr. Allen has adopted in studying the distribution of porosity and inverse segregation in these ingots and in discussing his results. I think that he has rather assumed—I admit it is difficult to avoid the assumption, but it is not a true one—that his ingot mould has been filled with liquid metal at rest before solidification began. That is very far from being the case. Solidification must begin, in a heavy copper mould such as he used, the moment the stream of metal commences to enter it, and there must be a great deal of turbulence and disturbance while that stream of metal is being poured in. That is bound to affect the beginnings of crystallization, and there is good reason to believe it affects the general structure and the distribution of gas and also the segregation in an ingot. The study of steel ingots has brought this out quite clearly, and I have seen examples of a good many ingots in which there is no doubt whatever that the method of filling the mould makes an immense difference. The difference between a Durville cast ingot and an ordinary chill-cast ingot in which the metal is poured in as a jet is very marked in that respect, and we shall have to await some further work in which this question of filling the mould has been adequately considered before we can generalize on the information, in itself most useful and interesting, which Mr. Allen has given us.

Dr. F. JOHNSON * (Member): I have one or two brief remarks to make on this paper. The first refers to an ingot of copper which, as made by Mr. Allen, showed a considerable rise in the mould after being melted in a highly reducing atmosphere. I am glad to see that result published, because it disposes, so far as I can see, of the argument that electrolytic copper cannot be "over-poled." I think that that is a definite case of "over-poling" electrolytically-produced copper.

Another point arises from the remarks of Dr. Genders with regard to exudation. In a paper published by American investigators † in which exudations of copper were shown in the case of a copper ingot rather rich in cuprous oxide, the exudations were copper–cuprous oxide eutectic and showed no gas at all. They were not hollow bubble exudations, but solid blobs of eutectic, which seemed to show that the pressure behind them had been very considerable. They occurred, if I remember rightly, at the side of the ingot as well as at the top.

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† W. H. Bassett and J. C. Bradley, *Trans. Amer. Inst. Min Met. Eng.*, 1926, 73, 700–705.

Another point refers to inverse segregation, and I think Dr. Rosenhain has rather anticipated what I had to say there with respect to one case which occurred in my own experience and has been placed on record in the proceedings of the Institute, Admiralty gun-metal, in the form of a small chill-cast ingot, showed high tin content in the outer shell, low tin content in the centre, almost complete absence of the low melting point interdendritic constituent in the outer shell and a preponderance of it in the centre. It was a very clear case of inverse segregation, but one which could not, as far as I can see, come into line with Mr. Allen's explanation of the internal pressure forcing a low-melting-point constituent into the interdendritic spaces.

Dr. A. G. C. GWYER * (Vice-President): I am glad to see that Mr. Allen has broadened the basis of his work, because the subject of inverse segregation is one which is exercising us, I think, a great deal to-day, and it is very gratifying to find that he has extended it to metals other than copper. He has referred to the fact that he has rather cut down his remarks on other work, and I should be glad if in his reply he would consider the recent work of Masing and Scheuer. Their theory is rather different; they regard the process as being due not so much to contraction pressure, which they regard as a supplementary factor, as to the growth of the primary crystals forcing the nuclei apart, while interstitial metal flows in the spaces. It would be interesting to have Mr. Allen's views on that.

There are one or two details which it is perhaps important to have. I am not clear about the question raised by Dr. Rosenhain with regard to the feeding—whether these ingots were or were not fed. If they were fed separately, a few particulars about the temperature of the feeding metal and also the pouring temperature would be useful, as these factors are of importance. There is also the question of turbulence, as to whether they were poured quietly or not.

The AUTHOR (*in reply*): I will give the relative weights of the ingots and mould in my written reply.

The copper ingots were not fed, and the aluminium ingots were fed. Naturally the use of the word "feeding" for the interdendritic flow from the centre to the outside of the ingot is questionable, because the idea is not of sufficiently long standing to have had a word allocated to it, but "feeding" is a good word, since the process is a continuation of the process that is carried out when extra metal is poured into the top of the ingot.

With regard to exudations on the surface of a casting and the effect of gas generally, I do not think that there is really much doubt that when exudations come out on the surface of the casting gas must be the cause.

It is interesting to hear that the behaviour of 70 : 30 and 60 : 40 brasses with regard to the distribution of their porosity follows the general lines indicated in this paper.

The method of calculation I have employed is not, I believe, so arbitrary as Dr. Genders appears to think. It is similar to that employed by Masing and Haase. The figures for contraction on solidification are of course a little doubtful, but they are not more than 20 per cent. out, and similarly the mean figure for the liquid that feeds into the interstices is not out as much as that, and all I have claimed is that the volume changes are enough to give the type of effect observed. I do not wish to place any insistence on the second and third decimal places.

Dr. Rosenhain has raised the question of the pressure inside the ingot. I have dealt with that subject to some extent in a previous paper. He neglects,

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I think, the possibility that there may be variations of pressure in the liquid metal from side to centre of the ingot.

Referring to Fig. A, which represents an ingot in the process of solidification, at some stage or other there must be in the ingot an outer zone, *A*, which is completely solid, a zone, *B*, which is partly liquid and partly solid, and possibly a zone, *C*, which is completely liquid. Atmospheric pressure, *p*, exists outside the ingot, but since the zone *A* can sustain a difference of pressure, there is no reason why the pressure in the liquid at the solidus face should not be considerably less (*p–a*). Atmospheric pressure exists in the liquid in the top of the ingot, and in the centre, in accordance with this hypothesis, the pressure is less (*p–b*). There is no reason, however, why *a* should be equal to *b*, and it only requires *a* to be less than *b* for liquid metal to travel both from the feeder head to the centre of the ingot and from the centre of the ingot to the outside.

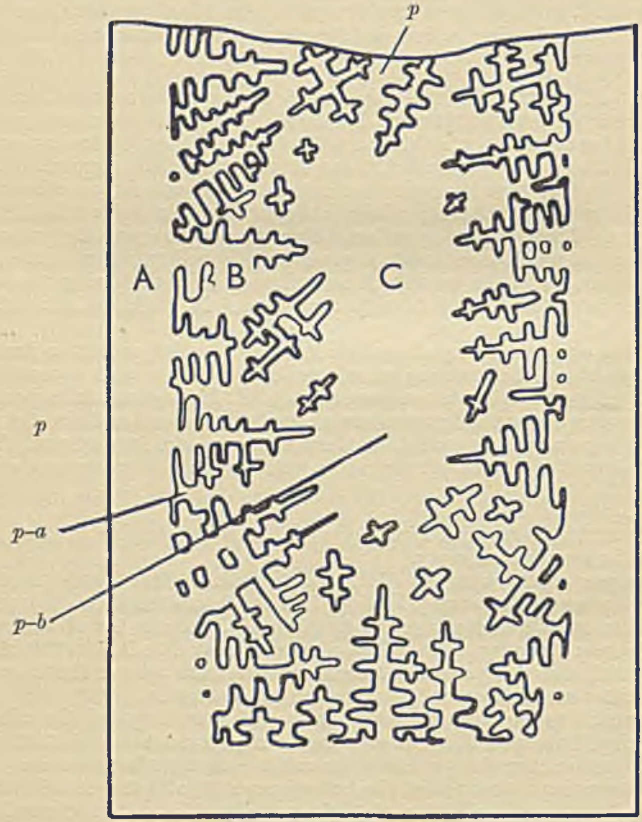

FIG. A.

I cannot deal with all the points mentioned in the discussion, but I should like to refer to the extraordinarily fine paper by Masing and Scheuer, which is a very balanced summary of the present state of the subject of inverse segregation. I do not entirely agree with Dr. Gwyer's statement of what those authors say. I believe they practically commit themselves to the interdendritic flow theory, with a reservation that in some cases under-cooling may be a factor. They say there are several possible causes for interdendritic flow, and place them in the order: (1) contraction on solidification; (2) the effect of gases; (3) the crystal thrust on account of diffusion; (4) the squeezing action of the contracting solid crust on the interior of the metal. They regard the first two as important, but the third and fourth as relatively unimportant. They do not say that any one of them is the sole cause of inverse segregation, and I entirely agree with that interpretation on the evidence as it stands at present.

CORRESPONDENCE.

The Author (*in further reply to the discussion at the meeting*): The weights of the copper ingot mould and ingots were as follow:

Total weight of mould	116 lb.
Weight of copper ingots	26–27 lb.
Weight of aluminium alloy ingots . . .	8·3–8·9 lb.

I thank Mr. Sutton for directing attention to the recent work in Germany. His recent very valuable summary * makes it unnecessary for me to expand my very brief treatment of the subject of inverse segregation to any considerable extent. The terms "late" and "early" as applied to stages in the solidification process are only relative. I have described as "early" any stage before the solidus isotherm has travelled deeply into the ingot. Mr. Sutton will probably agree that at the time exudations appear, liquid metal still exists in the skin of the ingot, but, on account of the appearance of the head of the ingot, this appeals to him as being "late" in the process. The experiments of Haase on volume changes accompanying diffusion are very important, but the phenomenon described by him takes place over a period of hours, whereas inverse segregation is established in a few seconds, and it seems rather dangerous to connect the two. The difficulties experienced by Mr. Sutton, and also by Dr. Genders, in conceiving the interdendritic flow of residual liquid may be overcome by contemplating the sinking of the mercury in the stem of a thermometer when the temperature is falling. The mercury travels towards the bulb in response to the contraction taking place there, leaving a cavity behind it. There is no pressure in the stem driving it down: the necessary force is provided by the negative hydrostatic pressure produced by the contraction of the mercury in the bulb. Surface tension (being the resistance to the formation of a new surface) provides the reason why no contraction cavity forms in the bulb. If this resistance be overcome, by the introduction of a bend, as in a clinical thermometer, or by the evolution of gas bubbles, as may happen in a solidifying metal, a new mercury-free gap begins to form in the capillary, and, if the process is repeated often enough, there is no reason why any number of such gaps may not be produced, without the bulb ever being other than completely filled with mercury. Similar conditions exist in the interdendritic spaces of a solidifying ingot. Iokibe has now come to the conclusion that the expansions occurring in his copper–zinc alloys had no bearing on their inverse segregation: indeed, the very fact that the alloys cracked the crucible in which they solidified tends to show that the expansion occurred *after* and not *during* solidification, it being characteristic of a solid material that when it expands it insists on maintaining its former shape, and will break its container in order to do so, while a plastic

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* *Metallurgist* (Suppt. to *Engineer*), 1933, 9, 22–24.

mass which contains any appreciable proportion of liquid will during expansion accommodate its shape to that of the vessel in which it finds itself.

With regard to the method of pouring the ingots mentioned by Dr. Rosenhain and Dr. Gwyer, this was done from the melting crucible with ordinary care, the crucible lip being just above the top of the mould, and the feed metal was supplied from the same crucible. The question of possible turbulence effects is important, and, if opportunity offers, I shall investigate it.

The contribution made by Dr. Johnson is very interesting: there is every reason to suppose that high pressures, such as might cause exudation of the eutectic, can be generated within ordinary tough-pitch copper ingots. The curious distribution of interdendritic constituent observed by him in Admiralty gunmetal is certainly the reverse of what would be expected from the considerations put forward in this paper. Work on the segregation of bronze ingots is going forward at Birmingham University, and this matter will be given attention.

Mr. O. W. Ellis,* M.Sc. (Member): The facts so lucidly presented by Mr. Allen in this paper constitute a most important contribution to our knowledge of the distribution of porosity in ingots. His explanations of this phenomenon and, in particular, of its relationship to the distribution of copper in ingots of aluminium–copper alloys are of special interest to me in view of the fact that I recently attempted to explain a somewhat similar relationship which appears to exist between the distribution of porosity and the distribution of tin in ingots of copper–tin alloys.

When considering the phenomenon of inverse segregation in copper–tin alloys, I was faced with this question: Does viscosity play the important part which many workers apparently believe it to play in delaying the flow of liquid through the system of capillaries which may be imagined as existing in ingots of alloys of wide freezing range during the last stages of freezing (stages of freezing such as are well depicted in Figs. II (*a*) and II (*b*) of Mr. Allen's paper)? I was led to answer this question in the negative, mainly because I was unable to conceive how inverse segregation could become more marked in bronze ingots, the greater their rate of cooling, if viscosity were so potent an agent in prohibiting the movement of tin-rich liquid through the system of capillaries which I had visualized.

Mr. Allen believes that viscosity is a most important factor in determining that "the pressure at the solidus face" decreases "to a value below the internal gas pressure of the melt," and hence that "evolution of dissolved gas promoted." His acceptance of this somewhat general view leads him to the point where he must of necessity say: "*Nevertheless*, a considerable amount of downward and outward flow of feeding metal does occur, as consideration of the copper distribution shows." It would appear that Mr. Allen has arrived at the same *impasse* as that reached by myself when studying this interesting problem in so far as it related to the bronzes. Having reached this *impasse*, I set myself this problem: What forces are there that might cause movement of tin-rich liquid from the central (hotter) parts to the peripheral (cooler) parts of the system of capillaries existing in a bronze casting during the later stages of its freezing? My answer to this question is summed up in paragraph 49 of my recent paper on "The Mechanism of Inverse Segregation" (see reprint, *Met. Ind.* (*Lond.*), 1933, **43**, 226): "It is suggested, therefore, that the phenomenon of inverse segregation is occasioned by the tendency for such contraction cavities as form in a rapidly cooled casting, in which a high-temperature gradient exists, to do so in those portions of the capillary system where the least surface energy is required for their formation. The fact that the vapour pressure of the melt at the ends of the capillaries is

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always less than that at the centre of the system decreases the likelihood of the formation of contraction cavities in its more constricted portions. The result will be that the tin-rich liquid in the system will become concentrated in the peripheral capillaries, while the central capillaries become filled with contraction cavities." This theory is developed somewhat more fully in the paragraphs preceding that just quoted.

It is pleasing to note the emphasis which Mr. Allen places on the coincidence of centre porosity and inverse segregation. My experience with bronze castings has already led me to the view that "inverse segregation is always coincident with pronounced incipient shrinkage, but that incipient shrinkage is not of necessity accompanied by inverse segregation" (see paragraph 17 of the paper referred to above). This well-established fact must be recognized in any attempt to explain the phenomenon of inverse segregation.

A somewhat interesting side-line that might be followed by the author in connection with this investigation would be a study of the relationship, if any, which exists between the distribution of porosity and the distribution of hardness in the ingots he has worked with. That Brinell hardness and density appear within certain limits to go hand in hand in the case of bronze castings I have referred to in paragraph 28 of the above-mentioned paper. Co-ordination of these two properties should be even closer in the alloys which were the subject of the author's test. It is believed that plots of the hardness numbers similar to those of the density values in Figs. 4 and 8 of Mr. Allen's paper would bring out still more clearly certain of the points which he has already presented.

Mr. I. E. Gorshkov * (Member): Mr. Allen's new paper is as interesting as his previous one on the same subject, but in neither does he point out the difference between the gas and the shrinkage porosity.

The method for determining these two kinds of porosity which I proposed in my note on the author's previous paper † has been somewhat modified since, and is now applied in the following way:

(1) First, the density of a cast specimen γ_1 is determined (the volume of 100 grm. of alloy is $V_1 = \frac{100}{\gamma_1}$).

(2) The specimen is then heated for a short time to the temperature near its melting point, the density usually decreasing in consequence of a partial gas expansion in the blow-holes, but chiefly because of the liberation of gas from the solid solution with blow-hole formation. Let the density after this anneal be γ_2 (the volume of 100 grm. of alloy $V_2 = \frac{100}{\gamma_2}$).

(3) The specimen is afterwards subjected to compression effected on all sides of it by means of a cylinder and punch put into a press up to the constant density γ_3 (the volume of 100 grm. of alloy $V_3 = \frac{100}{\gamma_3}$).

The specimens brittle at room temperature and more plastic at elevated temperatures, are subjected to compression at these elevated temperatures and cooled down again to room temperature, the pressure being constant.

(4) An anneal at a temperature a little higher than that of recrystallization is applied to determine the change in density produced by work-hardening. The resulting density, say, γ_4 (the volume of 100 grm. alloy $V_4 = \frac{100}{\gamma_4}$), lies in the neighbourhood of γ_3.

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† "The Distribution of Porosity in Copper Ingots," *J. Inst. Metals*, 1933, 51, 301.

(5) Finally, a second short time anneal is carried out at the temperature near the melting point as in stage 2, and the density γ_5 is determined (the volume of 100 grm. of alloy $V_5 = \frac{100}{\gamma_5}$).

All our experiments were carried out under the following conditions:

A specimen of 2 cm.^{3} volume was taken for this purpose.

The pressures in compression were applied above the yield-point of the material.

The compression was performed on a press for mechanical testing and of proper capacity.

After each operation, before determining the density, the specimens were ground with emery paper on all sides.

The calculation of the gas quantity and of the volume of shrinkage cavities in the specimens was carried out by referring them to 100 grm. metal in the following manner:

$$V_{\text{gas}} = V_5 - V_4 \text{ (cm.}^3\text{)}.$$

The gas volume was reduced to normal conditions (1 atm., 0° C.)

$$V_{0\text{ gas}} = \frac{p \,.\, V_{\text{gas}} \,.\, 273}{(273 + t) \,.\, 1{,}033} \text{ (cm.}^3\text{)}$$

where t (° C.) = annealing temperature near the melting point in stages 2 and 5;
p (kg./cm.^{2}) = gas pressure in the blow-holes; $\approxeq$ yield-point of the material, both at the temperature t° C.;
$V_{\text{shrinkage}} = V_2 - V_5$ (cm.^{3}).

It will readily be seen that the difference $V_2 - V_1$ can even give an idea of the gas quantity contained in the solid solution.

A certain degree of inaccuracy in the determination of the gas volume may be due only to the gas diffusion through the metal in the solid state, but as the annealing time is rather short (within ½ hr.), no considerable diffusion is to be expected.

Mr. Allen's doubt about the weldability of shrinkage voids seems to be unjustified, as, generally speaking, no ingot is free from shrinkage cavities, whereas the same material obtained after mechanical working by pressure shows no shrinkage porosity. It is also well known that in producing iron plated with non-ferrous metals, even heterogeneous metals are welded together, owing to the rolling process, which circumstance justifies the conclusion that through alternation of mechanical- and heat-treatment, either subsequently or simultaneous, shrinkage cavities become thoroughly welded.

As to Mr. Allen's further doubts about the unweldability of gas cavities in non-ferrous metals, they are also disproved by everyday experience when such cavities in an "as rolled" and annealed metal are swollen and show "blisters." Even if such cavities under pressure become partially welded, *i.e.* the gas enters the solid solution (which would explain the first failure in Mr. Allen's application of my method) such gas nevertheless becomes liberated again under a high-temperature anneal.

The above procedure is being successfully applied to both the ingots and the sand-castings. The latter in the following cases: (1) for castings used under high hydraulic and air pressures; (2) for testing and choosing casting methods; (3) for controlling castings in mass production and the like.

Dr. S. W. Smith,* C.B.E., A.R.S.M. (Member): In his interesting remarks on so-called "inverse segregation," Mr. Allen refers to Watson's work in

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* Chief Assayer, The Royal Mint, London.

establishing a connection between this phenomenon and the movement of the "primary dendrites" away from the chilling surface.

The use of the word "dendrites" as descriptive of the primaries tends, perhaps, to lead to some confusion of thought when discussing the earlier stages of solidification and certainly so in the case of copper-rich silver alloys. This appears to be borne out by Mr. Allen's comment that Watson "overlooked the fact that when a molten alloy is poured into a cold mould there are no dendrites present to be repelled." By "dendrites" Mr. Allen evidently visualizes the material which forms the solid shell, whereas, of course, the first formed primaries of which Watson was speaking are discrete, isolated particles, formed at a still earlier stage which, as he has clearly demonstrated, are free to move in the still molten matrix. In the case of the copper-rich silver alloys these primaries are usually globular in form, and not arborescent.

The movements of such primaries clearly occur at an earlier stage than that at which a solid shell begins to form against the chilling surface. When these outer portions actually become rigid, they are made up of both primaries and eutectic, but the average composition of this shell is lower in copper content than the average composition of the whole mass.

It is of this second or later phase of solidification that Mr. Allen is speaking when he says, "The dendrites present in an ingot are produced by the action of the chill and such dendrites cohere together and are not free to move: otherwise it would be impossible to produce a hollow shell by bleeding."

He then refers to the experiment by Rosenhain and Archbutt, who showed that the 12 per cent. copper–aluminium alloy exhibits liquation (or "inverse segregation") in an ordinary chill casting, even in respect to a difference of composition between the outer and inner portions of a cylindrical shell formed by "bleeding" or pouring out the unsolidified portions as soon as a convenient thickness of shell has formed. The outer portions of this shell were poorer in aluminium than the inner portions, and the average of the shell was poorer than the average of the whole mass, showing clearly, on the view taken by Watson, that some of the aluminium primaries which were formed in the very early stages of chilling had already moved inwards, and had become more concentrated towards the hotter portions of the mass.

Watson's work is therefore entirely consistent with the results of this experiment.

The AUTHOR (*in reply*): I have read Mr. Ellis's recent paper on "The Mechanism of Inverse Segregation" with great pleasure, and his contribution is very welcome. We are agreed as to the general nature of the processes at work, but differ in the difficult task of assessing the relative importance of the very numerous factors involved. The effect of increased rate of cooling in enhancing inverse segregation follows naturally when it is considered that interdendritic flow does not begin until a more or less rigid shell has formed around the outside of the ingot. Before this has happened, contraction results in a sinking of the level of the metal in the mould, and consequently, the sooner a rigid shell forms (*i.e.* the greater the rate of cooling) the greater is the proportion of the total contraction occupied in the production of inverse segregation. There is no contradiction involved in the view that although viscosity effects are felt, interdendritic flow still occurs, for it is part of the essential nature of viscosity that it never entirely prevents the movement which it hinders and, indeed, it is quite impossible for any considerable lowering of pressure to occur at the solidus face without there being a movement of liquid towards that face, if viscous resistance be assumed to be the only resistance to the movement. Nevertheless, surface energy has its importance, for if a liquid were not reluctant to produce new surfaces interdendritic flow would be much less, and the number of contraction cavities much greater.

I have not neglected the distinction between gas cavities and contraction cavities, as Mr. Gorshkov complains, so much as denied its reality in many cases, and while agreeing that his method of examining castings may give valuable insight into differences existing between them, I cannot accept the claim that the results give either the volume of contraction cavities or the amount of gas present in the sample. It cannot be denied that shrinkage cavities frequently weld in hot-working, nor that gas cavities occasionally do not, but Mr. Gorshkov's method required that shrinkage cavities shall *always* weld, and that gas cavities shall *never* do so, and of this he has offered no proof.

The close attention which Dr. S. W. Smith has given to the detailed phenomena of solidification is very necessary to the complete understanding of the process which we seek but cannot yet claim to have found. It is probable that Watson's experiments have been misinterpreted. Examining Fig. 5 of his paper,* one sees two sets of " primaries," one coarse and not obviously dendritic (although a close examination reveals that they had simple, branched forms) corresponding with the material which was solid before the chilling action was applied, the other fine and arborescent, produced by the chill. Watson's evidence shows quite clearly that the former moved when the chill was applied, but it shows equally clearly that the latter did not, for if the fine primaries had been produced in the interstices between the coarse ones, and had then taken part in their movement, they would have been found intermixed with them in the final sample. One of the most remarkable things about Watson's photographs is the almost complete absence of such intermixture. The question of the form and freedom to move of the primaries is immaterial; the evidence showing that the primaries produced by the chill actually stayed where they were formed is really quite strong.

* *J. Inst. Metals*, 1932, 49, 353.

EXPERIMENTS IN WIRE-DRAWING. PART III.—ANNEALING OF H.C. COPPER WIRES DRAWN TO VARYING DEGREES OF HARDNESS.*

By W. E. ALKINS,† M.Sc., Member, and W. CARTWRIGHT,† O.B.E., M.Sc., Member.

Synopsis.

Copper wires drawn with widely varying amounts of reduction have been annealed at different temperatures for periods up to 24 hrs. The greater the amount of the cold-work done on the wire, the lower is the temperature at which it begins to lose its work-hardness and the greater the rate of loss at any temperature, but the higher is the tensile strength of the "fully annealed" material.

1. Introduction.

A survey of a large number of observations on the annealing of cold-worked copper, the majority of them quite unrelated, which have come sporadically over a period of 10 or 12 years within the knowledge of one or both of the authors, has convinced them of the need for a thorough and detailed investigation of the whole question. They have been much influenced in their decision to attempt such an investigation at the present time by the introduction into commerce of oxygen-free and silver-bearing high-conductivity coppers and by a realization of the possibilities so opened up.

They do not propose to offer here any review of previous work, for they feel that, since none of it appears to them to have envisaged the detailed inquiry which they regard as necessary, the customary review may well be waived in the interests of economy.

2. Scope of the Present Paper.

The present paper is devoted to the description of experiments on a series of wires of silver-free high-conductivity copper, drawn to the same diameter but to widely varying degrees of hardness. It is hoped that it will be possible at a later date to extend the work on

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wire to oxygen-free and to silver-bearing copper, to ascertain whether the behaviour on annealing is in any way dependent on the diameter of the wire, and to examine the annealing phenomena in the case of sheet and strip; enough work has been carried out on the microstructure of the wires dealt with in the present contribution to disclose the interesting results which may be expected from more complete work. Breaking load only is considered in the present paper.

3. MATERIAL.

A piece of about 250 lb. weight was selected from a $\frac{9}{16}$-in. diameter rod, hot-rolled from a heavy wire-bar of good quality, silver-free, high-conductivity copper. The metal had the following composition:

	Per Cent.
Copper	99·95
Silver	nil.
Lead	nil.
Iron	0·003
Oxygen (by difference)	0·047

The oxygen content was confirmed by the appearance under the microscope of prepared sections of fully annealed wires.

The rod was cold-drawn after pickling without preliminary annealing; at appropriate stages during reduction pieces of about 20 lb. each were cut from the drawn wire, and these were all annealed together in an open furnace for about $\frac{3}{4}$ hr. at a temperature of approximately 650° C. They were then finished by cold-drawing after pickling, without any further annealing, together with the unannealed residue cold-drawn direct from the original rod, into wire of nominal diameter 0·104 in. (No. 12 S.W.G.), great care being exercised to see that the final diameter was kept constant throughout. There were thus prepared eleven coils of wire of the same diameter having breaking loads from 399 to 544 lb.; full details are given in Table I.

4. EXPERIMENTAL WORK AND METHODS OF TESTING.

The low-temperature annealing treatments, at 130°, 155°, 170°, 180°, 205°, 230°, 280°, and 330° C., were carried out in a Hearson electric oven, provided with temperature control (Hearson capsule), while the high-temperature treatments, at 450°, 650°, 750°, and 850° C., were given in an electric tube furnace. In both cases the efficiency of the control was thoroughly satisfactory. For all temperatures up to and including 280° C., treatments of 0·5, 1, 2, 6, 12, and 24 hrs. were given; for higher temperatures the results of $\frac{1}{2}$-hr. heatings alone are included here.

TABLE I.—*Preparation of Material.*

No. of Sample.	Diameter at Which Annealed, Inch.	Reduction in Area after Annealing, Per Cent.	Ratio : $\frac{\text{Annealing Diameter}}{\text{Finished Diameter}}$	Breaking Load, Lb.
1	0·128	35·9	1·25	399
2	0·160	59·0	1·56	457
3	0·186	69·6	1·82	474½
4	0·212	76·6	2·07	490
5	0·252	83·5	2·46	502
6	0·300	88·3	2·93	513½
7	0·348	91·3	3·40	520
8	0·400	93·4	3·90	537
9	0·450	94·8	4·39	544
10	0·500	95·8	4·88	544
11 (drawn from $\frac{9}{16}$-in. rod)	—	96·7	5·5	542½

Three test-pieces cut from each wire were used for each annealing treatment: the oven or furnace was heated up and kept at constant temperature, the series of 33 lengths was placed quickly inside and left for the necessary period. At the end of the annealing the test-pieces were withdrawn and either allowed to cool fairly rapidly in air or quenched in cold water. No difference in breaking load was found to result from the different methods of cooling, and no distinction is therefore shown in the sequel between series cooled in air and those quenched in water.

The breaking loads were determined on a 1000-lb. Dennison tensile testing machine reading in pounds, each determination taking not less than 2·5 and not more than 3 minutes. The load was applied quickly up to 2 or 3 lb. below the rupturing value, and then increased slowly by increments of 1 lb.: it became possible at an early stage to tell from the rate of fall of the beam whether the test-piece would break within the desired time or whether an increase in the load was necessary. In the great majority of cases, agreement to 1 lb. was shown by the first two tests on an individual wire: when the two did not differ by more than 2 lb., two determinations were regarded as sufficient, and the mean value was accepted. In a certain number of instances the first two results differed by more than 2 lb., and in all such cases the breaking loads accepted represent the mean of three or four tests.

Several of the annealing treatments were repeated on the whole range of wires after an interval of time: in some cases the same treatment was given a third time. The results were, with one exception, completely confirmatory. The exception arose in the case of the ½-hr. annealing at 205° C.: in this single instance the accepted results were the means of two complete series of determinations, *i.e.* of four tests on each wire.

Their experience in making the tensile tests has convinced the authors that a difference of 2 lb. between the mean breaking loads of different wires, or between those of the same wire after different treatments, is to be regarded as real and significant. The importance of this fact will be seen in the discussion, at a later stage, of the breaking load of the different wires after "complete annealing."

5. Presentation of Results.

Adequate presentation of the results of the experimental work has proved to be a matter of considerable difficulty, and the authors readily admit that charges of inadequacy from certain points of view may be sustained against their presentation. For the sake of economy, the tabulated data have been cut down to the absolute minimum, and the paper contains nothing more than the mean breaking load found for each wire after each annealing period at each temperature. This has involved the omission of all data bearing on the variability of the results, and also of all check determinations: some figures in illustration of both points would no doubt have been of value.

The authors have endeavoured to bring out the salient features of the results by graphical presentation. The relationships they have chosen are inevitably arbitrary, and by no means exhaust the possibilities: it is therefore hoped that interested readers will plot others for themselves. Typical diagrams only have been selected for publication, the number of illustrations having been cut down to the minimum. The authors strongly recommend that readers should construct additional similar diagrams to supplement those included in the paper.

The methods of plotting which the authors have adopted agree in the use of the breaking load in pounds as ordinate throughout. The load is plotted against (*a*) temperature; (*b*) time; and (*c*) the ratio $\frac{\text{annealing diameter}}{\text{finished diameter}}$.

(*a*) The first two diagrams show the relationship between breaking load and temperature for all the eleven wires when annealed for ½ hr. Fig. 1 brings out the general features of the way in which loss of strength proceeds with increasing annealing temperature. In Fig. 2, the ordinate scale is increased considerably in order to show the differences between the breaking loads of the various wires after annealing for ½ hr. at temperatures of 300° C. and upwards.

The four following diagrams (Figs. 3–6) give, for selected wires

(Nos. 2, 5, 8, and 11), the same relationship in the case of individual wires, all annealing periods being shown together.

(*b*) In the next four figures (Figs. 7–10) the changes in breaking load of individual wires with increasing annealing time are shown for the same four wires. The loads at each annealing temperature are plotted against the logarithm of the number of hours: the latter has been adopted in preference to the simple number of hours in order to give a more even spacing of the ordinates.

(If the same relationship—breaking load/(log) time—is plotted for all the wires at each annealing temperature, a series of diagrams is obtained, one for each temperature, which bring out well the differences in annealing behaviour of the various wires.)

(*c*) Finally, an attempt has been made to relate the annealing phenomena of the different wires with their original hardness. Plotting breaking load after heat-treatment against breaking load as drawn was useless, for the hardest drawn wires differed too little from one another in their original strength. It will, indeed, be shown later that the behaviour on annealing depends not nearly so directly on intrinsic hardness before annealing as on the cold-working treatment by which that hardness was conferred upon the wire. Percentage reduction of area subsequent to annealing gives poor spacing of the ordinates, and the difficulty has been overcome by the use of the quotient obtained by dividing the diameter at which the wire was annealed by the final diameter to which it was drawn—the latter value being, of course, constant for all wires. This quotient, *i.e.* the ratio $\frac{\text{annealing diameter}}{\text{finished diameter}}$, has been called for convenience the "work ratio," and has proved itself of great value (not merely, it may be said, for the preparation of clear diagrams).

The concluding diagram (Fig. 11) shows the relationship between breaking load and "work ratio" as just defined for ½-hr. annealings, a separate curve being shown for each temperature.

6. RESULTS.

The mean breaking loads of all the eleven wires after the different annealing treatments are tabulated in Tables II–IX; of these, all except the last relate to a single temperature, whilst Table IX sets out the results after ½-hr. annealings at temperatures of 330° C. and upwards. The changes in breaking load are illustrated in a variety of ways, as has been described above, in Figs. 1–11. No very detailed description of the features brought out by these diagrams will be attempted, but attention will be directed briefly to some of the more interesting points.

The relationship between breaking load and temperature for each wire conforms to the well-known form of softening curve, but the curves for the various wires differ to a remarkable extent.

The more lightly drawn wires show a definite increase in strength at low temperatures, the hardest-drawn wires an appreciable decrease after ½ hr. at 130° C. only. All wires up to and including No. 6 (perhaps No. 7) show an increase in breaking load; details of the maximum increase shown by each wire are as follows :

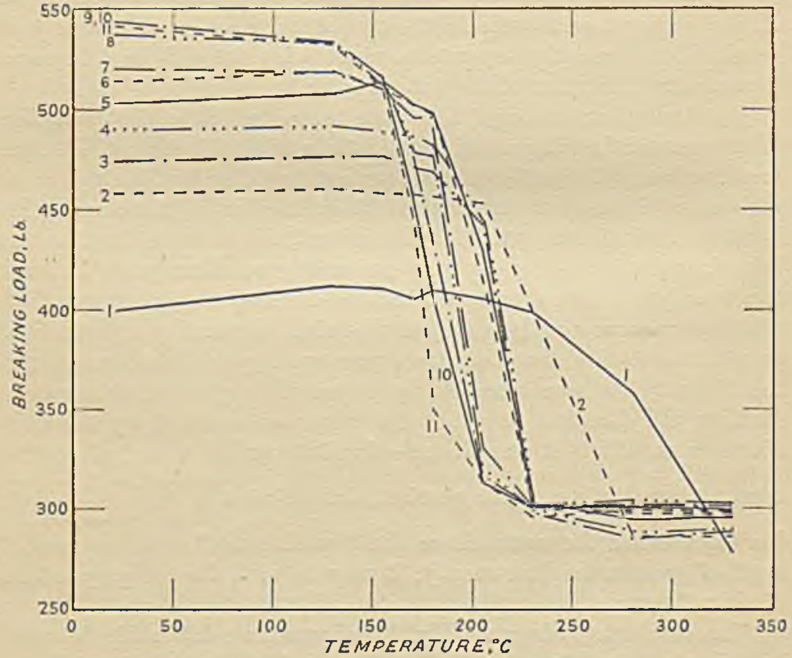

Fig. 1.—Relationship between Breaking Load and Temperature ; Half-hour Annealings.

No. 1.—399 lb. as drawn; 411 lb. after 1 hr. at 130° C.
No. 2.—457 ,, ,, 469 ,, 2 ,, ,,
No. 3.—474½ ,, ,, 483 ,, 2 ,, ,,
No. 4.—490 ,, ,, 493 ,, ½ ,, ,,
No. 5.—502 ,, ,, 510 ,, 1 ,, ,,
No. 6.—513½ ,, ,, 519 ,, ½ ,, ,,
(No. 7.—520 ,, ,, 521 ,, 1 ,, ,,)

The wires of low tensile strength retain their strength far better than the harder ones. Even after 24 hrs. at 180° C., No. 1 wire shows an increase of 3 lb. over its original strength; it loses 5 lb., or 1·25 per cent., after 24 hrs. at 205° C., 1 lb. after 1 hr. and 4 lb. after 2 hrs. at 230° C., and shows a loss of 41 lb., *i.e.* of just over

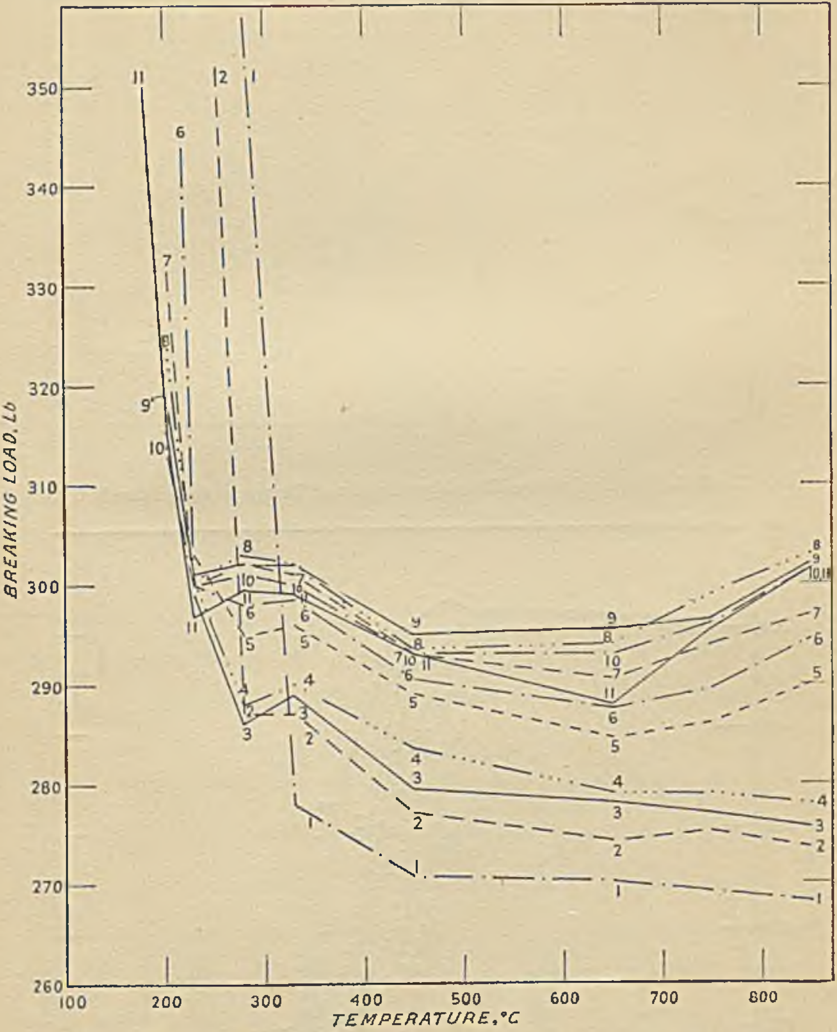

Fig. 2.—Relationship between Breaking Load and Temperature; Half-hour Annealings.

FIG. 3.—Relationship between Breaking Load and Temperature; Wire No. 2.

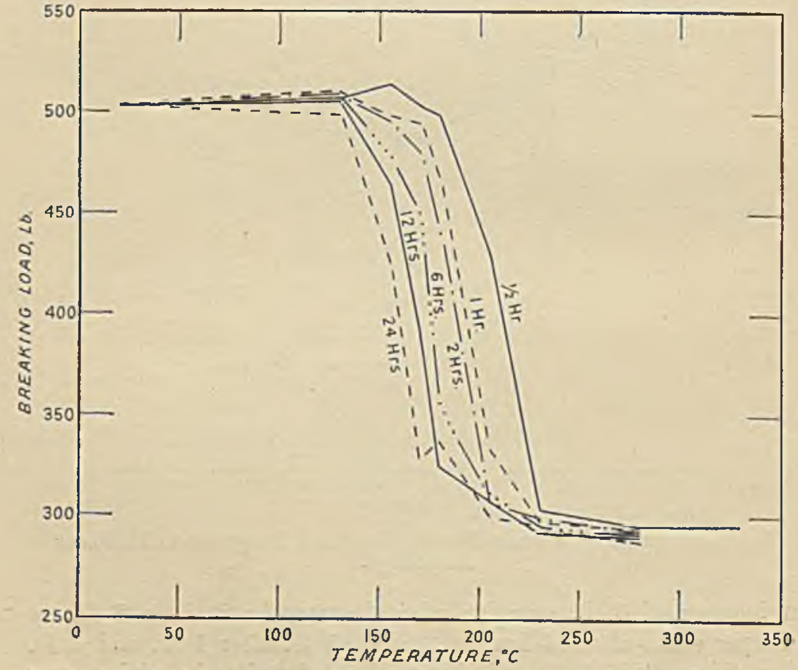

FIG. 4.—Relationship between Breaking Load and Temperature; Wire No. 5.

10 per cent. only, after ½ hr. at 280° C.—an annealing which suffices to reduce the breaking load of each of the other wires nearly to its minimum value (cf. Fig. 11). Wire No. 2 commences to soften

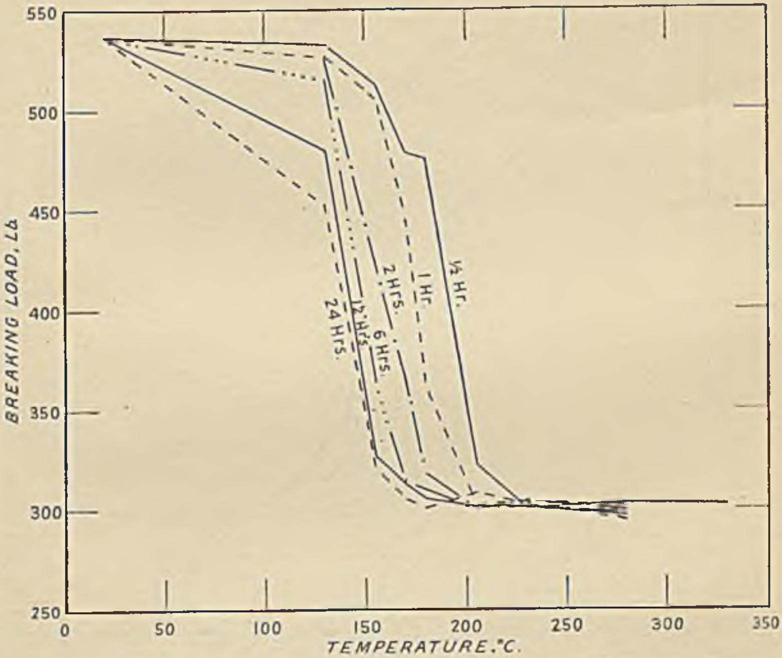

Fig. 5.—Relationship between Breaking Load and Temperature; Wire No. 8.

Table II.—*Annealed at* 130° C.

No.	Mean Breaking Load, Lb.					
	Annealing Period, Hours.					
	1/2.	1.	2.	6.	12.	24.
1	411	411	409	407	409	409
2	460	469	469	466	468	466
3	475·5	483	483	479	478	475
4	493	490	491	490	478	484
5	507	510	509	507	505	499
6	519	515	516	510	504	504
7	518·5	521	520	513	498	497
8	533·5	526	526	515	480	452
9	534	527	515	480	435	387
10	534·5	529	522	494	449	405
11	533	523	514	485	445	408

after 2 hrs. at 170° C.; No. 3 is unchanged after 2 hrs. at 155° C., but less hard after ½ hr. at 180° C.; No. 4 withstands without loss of strength ½ hr. at 155° C.; No. 5 12 hrs. at 130° C.; and Nos. 6 and 7

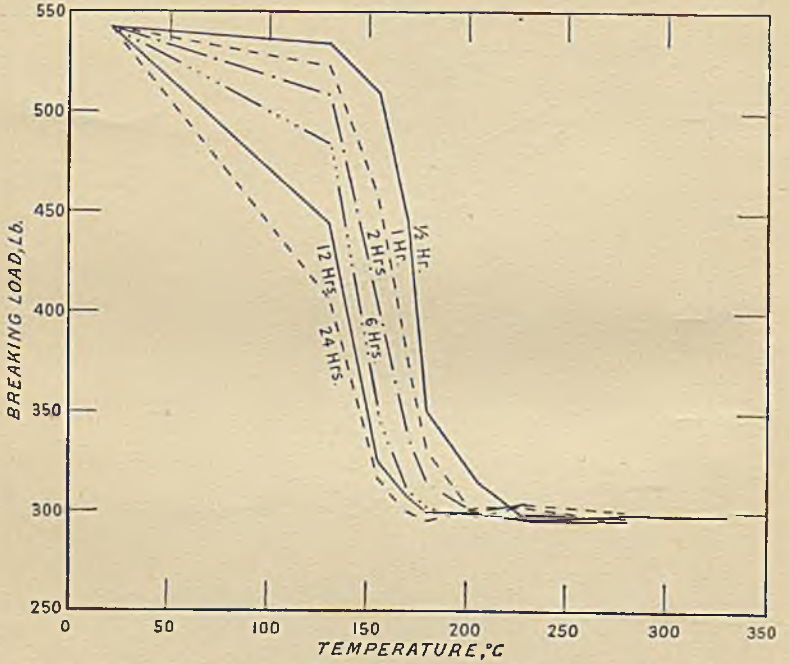

Fig. 6.—Relationship between Breaking Load and Temperature; Wire No. 11.

Table III.—*Annealed at* 155° C.

No.	Mean Breaking Load, Lb.					
	Annealing Period, Hours.					
	1/2.	1.	2.	6.	12.	24.
1	410	408	410	404	405	411
2	457	465	463	456	453	454
3	476	474	475	463	452	451
4	489	485	480	466	458	449
5	514	498	496	477	464	425
6	510	498	498	476	466	399
7	510	503	473	405	367	377
8	512	505	424	364	327	323
9	515	461	389	340	317	312
10	515	465	397	347	320	314
11	510	456	403	349	326	317

2 hrs. at the same temperature (it should be remarked, however, that No. 5 shows a decrease from its maximum strength—developed by annealing for 1 hr. at 130° C.—when kept at that temperature for 6

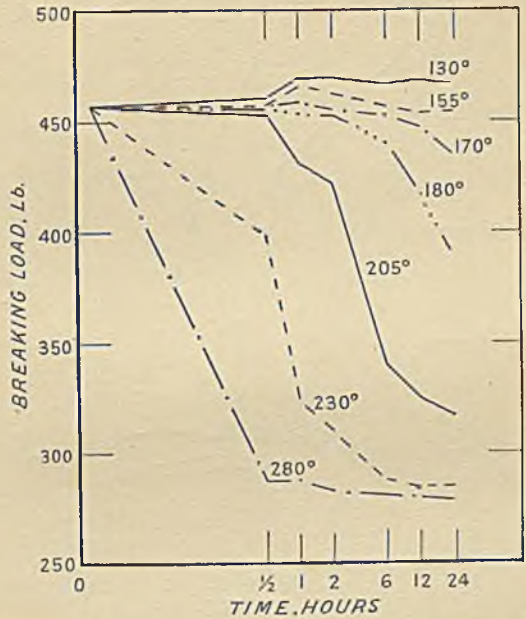

Fig. 7.—Relationship between Breaking Load and Time (Log. Hours); Wire No. 2.

Table IV.—*Annealed at* 170° C.

No.	Mean Breaking Load, Lb.					
	Annealing Period, Hours.					
	1/2.	1.	2.	6.	12.	24.
1	405	409	406	403	402	402
2	457	458	455	452	447	435
3	471	469	457	410	383	353
4	487	475	469	425	402	363
5	503	495	480	450	392	329
6	503	493	464	404	404	357
7	496	448	388	327	355	327
8	479	446	365	315	314	305
9	475·5	380	335	310	307	305
10	455·5	390	325	307·5	305	302
11	446	377	341	313	308	300

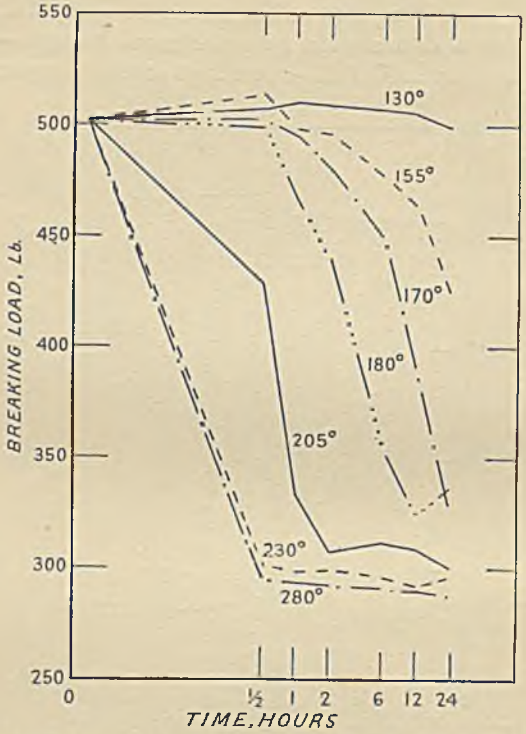

FIG. 8.—Relationship between Breaking Load and Time (Log. Hours); Wire No. 5.

TABLE V.—*Annealed at* 180° C.

No.	Mean Breaking Load, Lb.					
	Annealing Period, Hours.					
	1/2.	1.	2.	6.	12.	24.
1	409	404	405	403	402	402
2	455·5	453	453	440	416	390
3	469	455	425	356	347	313
4	483	465	440	365	325	312
5	498·5	467	440	356	325	337
6	499	423	426	311	334	300
7	497	445	409	325	318	302
8	476	364	318	310	305	300
9	431	346	312	307	304	301
10	405	321	305	302	302	300
11	350	333	316	303	300	296

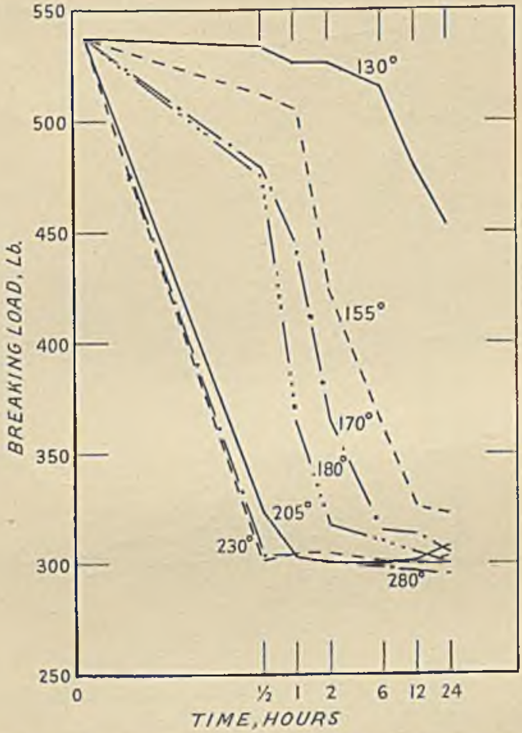

Fig. 9.—Relationship between Breaking Load and Time (Log. Hours); Wire No. 8.

Table VI.—*Annealed at* 205° C.

No.	Mean Breaking Load, Lb.					
	Annealing Period, Hours.					
	1/2.	1.	2.	6.	12.	24.
1	405	395	399	396	398	392
2	452·25	431	422	341	325	317·5
3	442	332	335	296	290	295
4	444	336	307	298	294	291
5	428·25	334	307	311	308·6	300
6	412·25	302	312	298	299	303·5
7	331·5	329	306	302	301	308
8	323·5	302	300	300	301	308
9	318	304	304	302	301	307·5
10	314	302	302	299	301	307·5
11	315·5	299	300	299	300	302

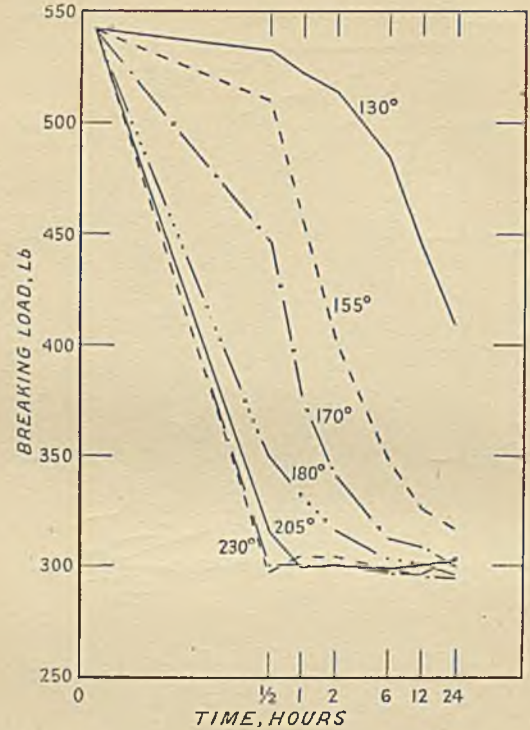

Fig. 10.—Relationship between Breaking Load and Time (Log. Hours); Wire No. 11.

Table VII.—*Annealed at* 230° C.

No.	Mean Breaking Load, Lb.					
	Annealing Period, Hours.					
	1/2.	1.	2.	6.	12.	24.
1	398	399	395	380	360	312
2	398	325	310	287	284	285
3	299	293	291	287	285	287
4	300·5	293	293	292	288	291
5	303	298	299	296	293	296
6	300	300	302	297	296	297
7	300	303	304	300	299	303
8	300·5	304	304	301	301	303
9	301	306	305	302	301	303
10	300	304	304	300	300	303
11	297	304	304	299	297	303

hrs.). The four hardest-drawn wires show a definite loss of strength after ½ hr. at 130° C. These differences are perhaps best shown in Fig. 11.

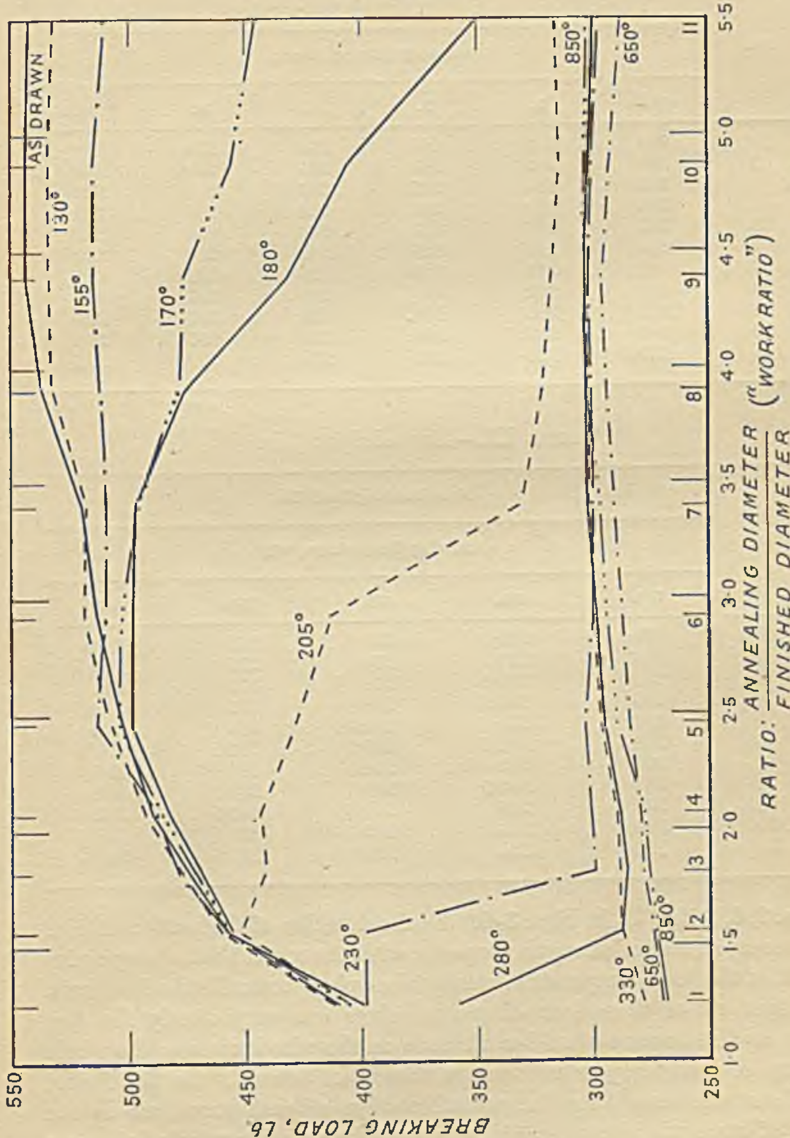

Fig. 11.—Relationship between Breaking Load and "Work Ratio"; Half-hour Annealings.

The effect of increase in the annealing period on the breaking load/temperature relationship is shown for four representative wires,

TABLE VIII.—*Annealed at* 280° C.

No.	Mean Breaking Load, Lb.					
	Annealing Period, Hours.					
	1/2.	1.	2.	6.	12.	24.
1	358	311	282	278	274	270
2	287	287	283	281	280	279
3	286	289	287	285	284	281
4	288	291	291	289	287	283
5	295	294	293	292	290	287
6	298	297	296	295	293	290
7	302	301	300	298	297	295
8	303	302	300	298	297	295
9	302	303	301	298	297	295
10	301	302	300	298	297	295
11	299·5	300	300	298	297	295

TABLE IX.—*Annealed for ½ hr.*

No.	Mean Breaking Load, Lb.				
	Annealing Temperature, ° C.				
	330.	450.	650.	750.	850.
1	278	270·5	270	269	268
2	287	277	274	275	273·5
3	289	279·5	278	277	275·5
4	290	283·5	279	279	278
5	296	289	284·5	286	290
6	298·5	290·5	287·5	289·5	294·5
7	301	293	290·5	294	297
8	302	293·5	294	299	303
9	302	295	295·5	296·5	302
10	300	293	293	296	301·5
11	299	293	288	295·5	301·5

Nos. 2, 5, 8, and 11, in Figs. 3–6. As the duration of the heat-treatment is increased, loss of strength proceeds, with the result that a progressive shift of the load/temperature curve takes place towards the load axis. Comparison of these four diagrams brings out very clearly the fact that, as the amount of cold-work done on the wire increases, the whole group of load/temperature curves moves in towards the load axis, while at the same time the central portion of each curve, where the loss of strength is most rapid, tends to become progressively nearer the vertical.

Figs. 7–10 show, for the same four selected wires, the influence of increasing annealing temperature (up to and including 280° C.) on the breaking load/(log) time relationship, and comparison of these diagrams among themselves illustrates the effect of increasing cold-work. With all wires, increase in the temperature results in progressively greater loss of strength, and all the softening curves have a marked resemblance (provided only that appreciable decrease of breaking load has taken place), but the distribution over the diagrams of the curves for the different temperatures changes in a very interesting way as harder and harder wires are examined. Thus, in the case of the first wire, the curves for all temperatures up to and including 205° C. lie very close together. Already in the case of wire No. 2 (Fig. 7) they have become quite well differentiated, and this differentiation of the curves for the lower temperatures proceeds with remarkable regularity as the amount of cold-work done on the wires increases. When the very severely worked wires are considered (cf. Fig. 10) the curves for 180° and 205° C. are found to have approached very close to those for 230° and 280° C. Thus the breaking load/time curve for 205° becomes displaced right across the diagram as the reduction by cold-drawing increases.

It should be remarked here that this progressive displacement across the breaking load/(log) time diagram of the load/time curves for 155°, 170°, and 180° C., with increasing cold-work, appears, if the evidence of the results now available is carefully examined, to be checked, and perhaps even slightly reversed, with extreme severity of drawing, at least in so far as those portions of the curves which relate to annealings of the longer periods are concerned. The effect seems to be too definite and persistent to be dismissed as an irregularity to be accounted for by experimental errors, but the authors are not prepared at present to offer any further comment upon the matter.

Undoubtedly the best summarized statement of the whole of the annealing phenomena examined is provided by a series of diagrams of the type of Fig. 11, in which breaking load is plotted against work ratio, one diagram being devoted to each annealing period. Each wire is represented by an ordinate, and the use of the work ratio as abscissa gives a convenient spacing of the wires; curves are shown for each temperature. In the authors' submission, such diagrams will well repay construction and careful examination, for so only, perhaps, can all the points commented on above be fitted in due perspective into a conception of the annealing phenomena as a whole.

Up to the present, attention has been directed to the commencement of softening and to the rate of loss of strength of the various wires, and no reference has been made to the values to which their breaking loads decrease after "complete" annealing. A glance at Fig. 1 shows that all the wires do not attain the same minimum breaking load. In Fig. 2 a much more open scale has been adopted for the breaking load (ordinate), and this diagram brings out at once the somewhat unexpected fact that the more lightly drawn wires anneal down to considerably lower strengths than the harder ones. It also suggests a rather sharp differentiation between the first four and the last seven wires: the load/temperature curves of the former fall gradually but steadily from 450° to 850° C., but those of the harder wires rise again quite sharply after passing through a minimum at 650° C. (it is further worthy of note that practically all the wires show a slight maximum in the load/temperature curves for ½-hr. annealings—at 330° in the case of wires Nos. 3–6 and at 280° in that of Nos. 7–11; Nos. 1 and 2, especially the former, must be regarded as not yet, at 330°, annealed to a degree comparable with that obtaining in the case of the other wires).

Even at 280° C., for all annealing periods from 2 hrs. upwards, there is a regular increase in the breaking load of the heat-treated wires with increasing original hardness, from No. 1 to No. 7 (the load values of Nos. 7, 8, 9, 10, and 11 are identical after 6, after 12, and again after 24 hrs. at 280° C.). The same is true after 12 and after 24 hrs. at 230° C., except that No. 1 wire, on account of its greater retention of strength, must be excluded from the comparison.

The influence of the amount of cold-work done on the wire on its tensile strength after an annealing which would ordinarily be regarded as "complete," *i.e.* for ½ hr. at a temperature of 330° or above, is best seen in Fig. 11; the results are essentially similar after longer annealings at lower temperatures. At each temperature there is an appreciable increase in the breaking load when any wire is compared with the next more severely worked until wire No. 8 is reached (No. 9 at 650° and 750°). It is remarkable that the increase, as from wire No. 1 to No. 8, is greatest at 850° C.: it varies from 23 lb. at 450° to 24 lb. at 650°, 30 lb. at 750°, and 35 lb. at 850° C., the last-mentioned increase being no less than 13 per cent. of the breaking load of the No. 1 wire after ½ hr. at 850° C.

Among the three or four most severely drawn wires, Nos. 8 (or 9)–11, the breaking load is generally fairly constant at all temperatures above 330° C., with the possible exception of 650° C.; in this case a distinct decrease in strength is suggested from wire No. 9 to No. 10 and again to No. 11.

In the light of these results it is clear that the tensile strength of a "completely" annealed high-conductivity copper wire is emphatically not a characteristic property of the material, but that it is directly related to the working treatment which the wire has undergone prior to its annealing. In a general way, the more severe has been the cold-working, the higher is the tensile strength of the completely annealed wire. It follows that any attempt to define "complete annealing" or "completely annealed wire" by the mere statement of a maximum tensile strength alone is entirely unsound. A satisfactory figure for a lightly drawn wire would be quite unattainable with a severely drawn sample, and a tensile strength representative of complete annealing in the case of a heavily drawn wire would represent partial annealing only of a lightly drawn one.

The authors are very much tempted to suggest that the only really characteristic tensile property of a ductile metal is the maximum tensile strength which can be conferred on it at any diameter by cold-working.

The results may thus be summarized in the statement that the greater the amount of cold-work done on the material, the lower is the temperature at which it begins to lose its work-hardness and the greater the rate of loss at any temperature, but the higher is the tensile strength characteristic of the fully annealed material. The last-mentioned clause is of vital importance in any attempt to arrive at a theoretical interpretation of the phenomenon of annealing of cold-worked metal, and, conversely, of that of work-hardening.

It is of interest to note that the differentiation of these wires into two groups suggested by the form of the breaking load/temperature curves, especially of Fig. 2, is confirmed by tensile tests made in May 1933, approximately two years after the material used in this work was drawn. The breaking loads of the various wires in 1931 soon after drawing and after two years' storage at (possibly rather high) room temperature were:

Wire No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Load, lb. 1931 .	399	457	474½	490	502	513½	520	537	544	544	542½
Load, lb. 1933 .	400	457	474½	490	502	504	511	532	533	532	536

The loss of strength in the case of all wires from No. 6 upwards is quite definite.

ACKNOWLEDGMENTS.

The authors wish to express to Messrs. Thomas Bolton and Sons, Ltd., and more especially to Mr. Thomas Bolton himself, their sincere thanks for the provision of facilities for carrying out the experimental work now described, and for permission to publish the results. They desire at the same time to put on record their appreciation of the great help they have received from a number of colleagues at Oakamoor.

DISCUSSION.

Mr. E. H. **Bucknall**,* M.Sc. (Member): There are several points which I feel should be emphasized in the discussion of this paper. The first is the one to which Dr. Rosenhain referred in his address,† and which has also been mentioned in connection with Mr. Allen's paper,‡ namely, that this is a subject on which 10, 20, 50, or even 500 or 1000 years ago metallurgists would have said that everything to be known was known—*i.e.*, that when a worked metal was put into the fire it was softened. More recently the position with regard to annealing has been summarized by R. W. Bailey in a paper read before this Institute. He showed that for copper and brass contours of equal Brinell hardness on a log. time/temperature curve are parallel lines crossing the curve at an angle.

Since Mr. Bailey summarized the position in that way, the field has been opened up in respect of the lower temperatures, partly by the work of the British Non-Ferrous Metals Research Association on locomotive stay-rods, in which I had the privilege to assist. We were able to show a marked stiffening of cold-worked materials on low-temperature annealing. This point, of course, has since been emphasized by Jones, Pfeil, and Griffiths in their paper on the age-hardening of alloys of copper, nickel, and silicon.§ The tensile strength values of the present authors, plotted by Bailey's method, instead of falling on parallel contours of tensile strength, appear to lie upon convergent lines—so the relation in this case is not logarithmic.

The authors, in discussing their results, state that a difference of 2 lb. in the tensile strength of the wires had a real significance. If that statement be accepted—and I see no reason why it should not be—then it would appear definite that the hard-drawn wires harden at the higher temperatures. For example, taking the figures given in Table IX, it will be found that the minimum tensile strength figure is usually attained by one of the intermediate temperatures of annealing, and not by the highest temperature. That is a very significant discovery. In the light of that and other data, it would appear very important and very enlightening to investigate the effects of annealings over shorter periods than half an hour at some of the elevated temperatures, as well as the effect of longer periods at lower temperatures, which was mentioned as a possible further line of investigation in the presentation of the paper.

Professor D. **Hanson**,|| D.Sc. (Vice-President): These results seemed to me, when summarized, to conform to the general laws of cold-working and annealing as we know them. The authors summarize them at the end of their paper, and state that they show that the greater the amount of cold-work the lower the temperature at which work-hardness begins to be lost and, they add, the higher the tensile strength in the fully-annealed material. To state the law of annealing a little more fully, we must add " the greater the initial cold-working the smaller the resultant crystal size." They do not refer anywhere to the crystal size of their material, so that the results cannot be fully interpreted, but we do know that, broadly speaking, the smaller the crystal size the greater the tensile strength, and the increase of tensile strength with the degree of cold-working to which they refer may be due to the smaller crystal size which we would expect in such material. I suggest that it might

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† See p. 55.

‡ This volume, p. 139.

§ *J. Inst. Metals*, 1931, 46, 423.

|| Professor of Metallurgy, The University, Birmingham.

be worth their while to attempt to give some measure, or at least estimate, of the crystal size in the resulting wires, because that might be a complete explanation of the phenomena, and a statement on that point might make the conclusions of the paper very much more complete and satisfying.

Dr. H. O'NEILL,* M.Met. (Member): The figures given in this paper will be of use to students and to those concerned with wire-drawing, and I hope that it may be possible to include values for reduction of area of the tensile test-pieces, if they have been measured.

A criticism might be made with regard to the method of preparing the copper before it was finally cold-worked. In order to secure a uniform diameter of test-piece in all cases after drawing, the metal was reduced to different diameters, then annealed, and then finally drawn. From Fig. 2 I take it that if copper which has been reduced by various amounts is annealed at 650° C. the breaking load will differ in the various specimens. Therefore, since the authors prepared their initial metal by this method of cold-drawing and annealing, their specimens were not necessarily in the same condition when they started the final drawing. If the values given in Fig. 2 can be applied backwards in that way, it would mean that the wires which they commenced to investigate had not all the same breaking load in the first place, and were not strictly comparable.

What is the objection to hot-working the original bolt down to the various sizes, then annealing to remove working strains, and finally cold-drawing? I should think that the same objection could not be taken to hot-working as to the preliminary cold-working. What precisely do the authors mean by the breaking load? In making these tests, did they record the maximum load or did they record the smaller breaking load? Did they run the weight back at all? Results can be obtained with copper showing a smaller breaking load than the maximum load, and it is important to know which values are reported here.

The increase in breaking load in worked specimens annealed at about 130° C. is an interesting effect. Increases in Brinell number are sometimes, but not always, obtained under similar conditions.

I am interested in the reduction of area values because I should imagine that the tensile reduction of area is smaller in those treatment regions which give increased breaking load. The increase in breaking load is due, I believe, to a decrease in ductility. The specimen does not "neck" so much, and therefore carries a bigger load. I should prefer to express the effect as a decrease of ductility rather than by trying to convey the impression of an increase of strength.

In our laboratory, Mr. Farnham has carried out some X-ray examinations of cold-rolled copper which had been annealed at 130° C. to produce this slight "hardening." The copper had not been drawn, but had been cold-rolled about 50 per cent. reduction, and showed a definite preferred orientation in the rolled condition. After heating at 130° C. the only change in the X-ray spectrum was a slight decrease in the intensity of the preferred orientation. The piling up of intensity was not so pronounced; it had become more diffused along the different lines. We also formed the impression that the lines were a little broader after the 130° C. treatment than before. If that is substantiated, it would suggest that the grain-size has become still more confused, and I suspect that perhaps within the distorted grains very tiny new grains are forming, and there is a mist of these scattered throughout the mass, which means more boundaries and generally greater stiffness and decrease in ductility. This may be the basis of the increase of breaking load which is reported.

* Senior Lecturer, Department of Metallurgy, The University, Manchester.

Dr. H. W. **Brownsdon**,* M.Sc. (Member of Council): The conclusion reached by the authors—namely, that the tensile strength of completely annealed high-conductivity copper is emphatically not a characteristic property of the material, is going somewhat too far in view of the fact that their observations are based on one material only, a silver-free copper. Early in their paper they mention that they hope at a later date to extend their work to oxygen-free and silver-bearing copper, and until they have done so the dogmatic conclusion in their present paper should be reserved until experiments on the other materials have been carried out.

Mr. J. S. **Glen Primrose** † (Member): The breaking load referred to is really the maximum breaking load in practice, and not the breaking load which the academic people may find when they run back; we never run back in practice. We find that this low-temperature annealing has a very remarkable effect on the lightly-drawn copper as well as other wire, namely that of releasing the sometimes small, sometimes large, amount of internal stress left in the skin due to the light drawing, which has left most of its work there and not penetrated to the centre. The low-temperature annealing simply relieves this internal stress and gives the true stress of the wire or other material recorded on the breaking load.

Some of the other questions seem rather more difficult of interpretation, except that what the authors have found as to light drawing giving the internal stress on the outer skin may be carried further in by the heavy drawing, and leave internal stresses inside which only the higher temperatures will relieve and give you the full value of the tensile and the breaking load to come out on the testing machines.

Practical people will appreciate these papers by Mr. Alkins as the results are most valuable in practice.

Mr. H. J. **Miller**,‡ M.Sc. (Member): The only point to which I wish to refer concerns the increase in strength which is obtained by annealing at the very highest temperatures, for this seems to be of fundamental importance. It seems notable that in Table IX the samples up to No. 4 behave in a perfectly normal manner, inasmuch as there is no increase in breaking load at the highest annealing temperatures, but from Nos. 5 to 11, *i.e.*, the materials which have been cold-worked to a much greater extent, there is a notable increase in the breaking load figure.

These results are associated, I believe, with the development of directional properties consequent on differential grain growth, for the factors involved are those which are known to be responsible for the development of directional properties in materials, namely, heavy amounts of cold-work followed by high annealing temperatures. About two years ago, Philipp and Bunn || published the results of some work upon the development of directional properties in some commercial coppers in strip or sheet form, making a study of the effect of work and annealing temperatures. One material with which they dealt, a deoxidized electrolytic copper containing traces of phosphorus and also of silver, gave results which closely resemble those of the present authors, for anomalous results were obtained when heavily cold-worked strip was annealed at the highest temperatures. When tested in the direction of rolling there was a definite increase in strength; when tested at right angles and at 45° to the direction of rolling the behaviour was quite normal, in that

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|| *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1931, 353.

there was continued softening with increase of temperature. Incidentally, I may point out that directional properties were developed to such an extent that the tensile strength in these two latter directions was only 85 per cent. of that obtained with the direction of rolling. With smaller amounts of cold-work and a wide range of annealing temperatures the properties in each direction were more or less equal.

I put forward this suggestion of directional properties to the authors for their consideration. They cannot examine their wires across the direction of rolling, and in that respect they have been unfortunate in the material chosen; if they had, like the American workers to whom I have referred, worked with strip they could have tested in all directions.

Mr. CARTWRIGHT (*in reply*): Mr. Alkins and I are, of course, acquainted with the work of R. W. Bailey. Two points had to be borne in mind in considering it: he made determinations of Brinell hardness, not tensile strength, and we know of cases in which the tensile strength can decrease while the Brinell hardness remains constant; we strongly suspect also that his test-pieces were not round. We chose to work with wires of a fairly small diameter in the hope that the work-hardening would penetrate to the centre. We agree that further work, using annealing periods of shorter duration, is likely to give interesting results; we have not now used heating periods of less than half an hour, mainly on account of the difficulty of allowing for the time taken by the test-pieces to reach the nominal temperature of experiment.

We hoped from his introductory remarks that Professor Hanson would give us some valuable information in the matter of crystal size. We have endeavoured to investigate this question, but we find there are serious difficulties in the way. Variation in grain-size over the section of the annealed wires renders useless the ordinary method of crystal-counting. We have not, indeed, worked out a satisfactory line of attack on the problem, which is one of great interest to us.

Regarding Dr. O'Neill's remarks, we have not made any measurements of reduction of area: accurate determination of this property is no easy matter with wires of one-tenth inch diameter. We have data for percentage elongation throughout, and hope to make them the subject of a short communication in the near future. Dr. O'Neill raised one point, with regard to the method of preparation of our wires, which is readily appreciated when our present results are available, but the force of which was not nearly so apparent when the work was being planned. Our primary object was the preparation of a set of wires, all of the same diameter but of widely varying hardness, and the method adopted furnished such a series satisfactorily. In any case, we are still quite unable to devise a means for preparing a suitable series of wires, within these conditions, which will not be liable to Dr. O'Neill's criticism.

We share to the full his interest in the possibility of correlating the increase in breaking load of the lightly drawn wires when annealed at low temperatures with a change in the orientation of the crystals as revealed by X-rays.

We thank Messrs. Miller and Primrose for their interesting contributions to the discussion. If and when we are able to extend our work to strip and sheet, we shall not fail to take into account possible directional effects of the methods of cold-working we adopt.

CORRESPONDENCE

Mr. W. E. Ballard * (Member): I am especially interested in the authors' conclusion that the greater the amount of cold-work the higher is the tensile strength characteristic of the fully annealed material. Some years ago I carried out a considerable amount of work on tube drawing, and noticed very similar results, and I give below a representative series of tests bearing out the contention of the authors.

Original material—ordinary commercial deoxidized copper tube $2\frac{3}{8}$ in. outside diameter × 2 in. inside diameter, carefully annealed; breaking load 15·72 tons/in.^{2}. Elongation 42 per cent. on 8 in. Samples were taken and given further cold-work in various stages with the following results:

	Reduction of Area, Per Cent.	Breaking Load, Tons/in.^{2}.	Elongation, Per Cent. on 8 in.
1	12	17·93	21
2	21	20·73	11
3	28	22·18	9
4	35	23·10	7
5	46·5	23·90	5·5

The tubes were then re-drawn without further annealing, with the following results:

	Total Reduction of Area, Per Cent.	Breaking Load, Tons/in.^{2}.	Elongation, Per Cent. on 8 in.
1	41·5	24·17	6·5
2	47	25·18	5·0
3	56	25·96	4·0
4	58	25·96	4·0
5	64	27·18	4·5

These heavily drawn samples were then annealed at 700° C. for 2 hrs. and tested.

		Breaking Load, Tons/in.^{2}.	Elongation, Per Cent. on 8 in.
1		15·72	42
2		15·72	42
3		15·75	42·5
4		15·99	41·5
5		16·52	41

The above figures are only representative of many tests taken, and with 70 : 30 brass the results were even more remarkable.

* Metallisation, Ltd., Dudley.

Some of the contributors to the verbal discussion seemed to attribute such results entirely to changes in grain-size, and while this appears to be the simple explanation, it has never seemed entirely satisfactory to me. Nevertheless, it is not my purpose to enter into any discussion of the underlying reasons of the noted facts, but rather to direct attention to their practical significance. It is often assumed in works practice that a long and thorough anneal will eradicate any mistakes in cold-working and leave the metal in a suitable state for further cold-working. In tube drawing the evils of heavy sinking cannot be disposed of so easily. I feel therefore that the authors are to be complimented on stressing the fact that " complete " annealing is not always complete, and I shall look forward with interest to any further work which deals with this point.

The AUTHORS (*in reply*) : We thank Mr. Ballard for his contribution, and for the confirmation of our results which he brings forward from his experience with tubes. We in turn can support his contention that the undesirable consequences of heavy sinking cannot be removed by the simple expedient of giving the tubes a long annealing.

THE EFFECT OF DIFFERENT ELEMENTS ON THE ANNEALING AND GRAIN-GROWTH CHARACTERISTICS OF ALPHA BRASS.*

By MAURICE COOK, Ph.D., M.Sc., Member, and HERBERT J. MILLER, M.Sc., Member.

ADDITIONAL CORRESPONDENCE.

Mr. W. B. Price, Ph.B. (Member): I have prepared two charts (Figs. A and B) showing the effect of the additions of aluminium and nickel to 70 : 30 and 80 : 20 brasses. These charts give direct comparisons between these brasses and the same alloys to which have been added approximately 2 per cent. aluminium and 1 per cent. nickel. They also show the remarkable effect that the combination of aluminium and nickel has on the physical properties and the annealing and grain-growth characteristics of the 80 : 20 and 70 : 30 alpha brasses.

The addition of aluminium and nickel to brasses, besides greatly increasing their corrosion-resistant properties, has a pronounced effect on the behaviour of the alloys on annealing. Strips of 70 : 30, 80 : 20 brasses and the same mixtures containing 2 per cent. aluminium and 1 per cent. nickel were cold-rolled 6# (B. & S.) hard (50·9 per cent. reduction) and annealed at temperatures from 200° C. to 800° C. for 2 hours to study the influence of nickel and aluminium on these alloys. All annealed samples were air-cooled.

Hardening occurs in all of the above alloys at temperatures below which recrystallization begins. The 70 : 30 and 80 : 20 brasses cold-worked the above amount, show the first traces of recrystallization at 275° C. and complete recrystallization at 400° C. Addition of the aluminium and nickel to 70 : 30 brass raises the recrystallization temperature to 400° C. and the temperature at which recrystallization is complete is 500° C. The same addition to an 80 : 20 brass raises the recrystallization temperature to 350° C. and the temperature at which recrystallization is complete is 450° C. The structure of the nickel–aluminium brasses annealed at 500° C. is very fine, and cannot be resolved into a clearly-defined constituent even at high magnifications. This fine microstructure persists with little change in grain-growth up to a temperature of nearly 600° C. This lag in grain-growth is accompanied by a stiffness of the material which is unusual for non-ferrous alloys in this range as shown by the charts. Above 600° C. grain-growth continues at a fairly rapid rate.

Alcunic G (copper 70, aluminium 2, nickel 1 per cent., balance zinc) after cold-working 4# to 6# hard, has a recrystallization temperature range of 425°–450° C. The fine structure obtained at this temperature persists with very little increase in grain-growth until a temperature of 650° C. is reached. From then on grain-growth is rapid.

No. 80 Alloy (70 : 30) after cold-working 6# hard is totally recrystallized at 375° C. and has a crystal size of 0·013 mm. at 400° C.

The age-hardening characteristics produced by the addition of aluminium and nickel to the alpha brasses is very clearly shown, and the retardation of

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* See *J. Inst. Metals*, 1932, 49, 247–261.

softening and increased tensile strength prior to the commencement of recrystallization is undoubtedly due to precipitation-hardening. This

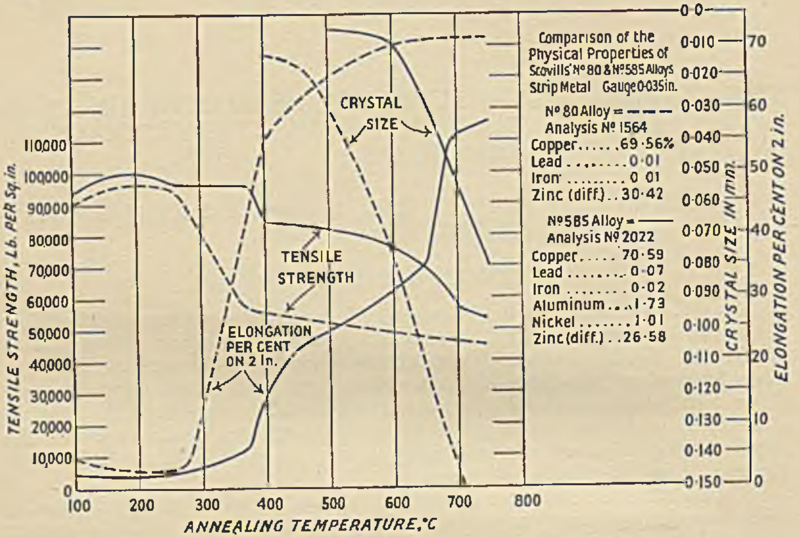

FIG. A.

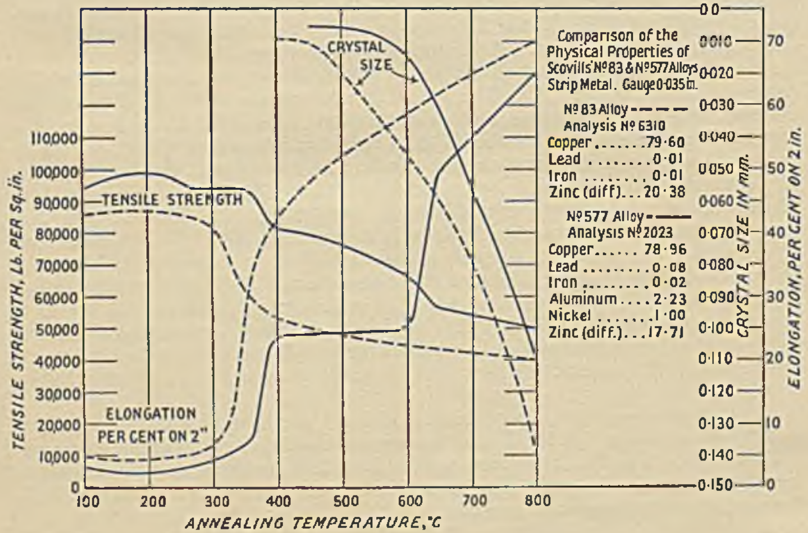

FIG. B.

persists in the 80 : 20 brass containing 2 per cent. aluminium and 1 per cent. nickel over a range of practically 200° C. from 400° to 600° C., as is shown by the elongation curve for No. 577 alloy on the chart.

The Authors (*in reply*): The curves which Mr. Price has illustrated in his interesting communication show, we agree, the marked effect which additions of aluminium and nickel can exert on the properties of alpha copper–zinc alloys. We have since published a paper, jointly with H. W. Brownsdon,* dealing with the effect of aluminium and nickel additions on copper, copper–zinc, copper–tin, and copper–manganese alloys, in which we have dealt at length with the age-hardening, or, to use a term which we prefer, the temper-hardening characteristics of these alloys. As a class the alloys possess this property in varying degrees, according to their composition. That hardening occurs at temperatures below that at which recrystallization commences we established for many of the alloys by showing that marked increases in hardness and strength of cold-worked alloys occurred when they were heated to comparatively low temperatures. We did not make a detailed study of the causes giving rise to the hardening effect which we observed, and, while it may be precipitation hardening, it does not seem to us that this conclusion regarding the precise nature of the hardening can be reached from Mr. Price's curves.

* See *J.*, this volume, p. 153.

OBITUARY.

William Cleland, B.Sc., a director and general manager of the Sheffield Testing Works, Ltd., died while playing golf at Sheffield on July 12, 1933.

Born at Coatbridge, in 1862, he was educated at the Coatbridge and Hamilton Academy. Later he joined the firm of Messrs. Murray & Patterson, Coatbridge, as an apprentice engineer. During this time he studied the engineering sciences at evening school and obtained a Winter scholarship at South Kensington. On his return from London, he was successful in obtaining an Exhibition at Glasgow University for three years, during which period he studied under Sir William Thomson (Lord Kelvin) and his brother, Mr. James Thomson. He obtained a Thomson Scholarship, and graduated as B.Sc. in engineering science. For a further three years he was a demonstrator in the Engineering Department of the Yorkshire College, under Professor Barr, and it was after this period that he was asked—in 1889—to undertake the management of the Sheffield Testing Works. At that time the firm undertook plain tensile and transverse tests of iron, steel, and cast iron. It had only a local reputation, but since then testing of all kinds, including refractories, chemical, and microscopical work, and investigations into the failure of all classes of materials have been undertaken.

Mr. Cleland was a member of the Institution of Mechanical Engineers, a member of the Iron and Steel Institute, and of the American Society for Testing Materials. A Freemason, he was a member of both the Britannia and University Lodges of Sheffield.

He was one of the oldest members of the Sheffield Caledonian Society and a trustee of the Society's Life Membership Fund. He was a keen golfer—a member of the Dore and Totley Club—and assisted the Caledonians in a number of matches.

Mr. Cleland was an original member of the Institute of Metals.

John Rolland died in London on July 27, 1933.

He was born in Glasgow, and was educated abroad as well as in England. He served his apprenticeship as engineer with Messrs. Swan Hunter and Wigham Richardson, Newcastle-on-Tyne, and for a short time went to sea. For a while he acted as surveyor to Lloyd's Register of British and Foreign Shipping, in Austria-Hungary and at Hamburg. In 1914, he was appointed Works Manager of the Turkish Arsenal at Constantinople, which was being reorganized by the Vickers-Armstrong group, but escaped from Turkey in November of that year when the Turks entered the War, and in 1915 was appointed Works Manager of a new factory at Lancaster for the manufacture of torpedoes for the British Government. In 1916–1917 he was transferred as Managing Director to the torpedo factory at St. Tropez, in the south of France, which also belonged to Messrs. Vickers-Armstrong, and was there engaged until the end of the War on the production of torpedoes and other armaments. He then returned to England, and up to 1921 acted as Works Manager at the Engineering Factory of Vickers, Ltd., Crayford, Kent.

Mr. Rolland then started a successful business of his own as consulting engineer and representative in Great Britain and Ireland of Benno Schilde Maschinenbau A.G., Hersfield, subsequently taking up the agencies of the

Lurgigesellschaft für Warmetechnik, Frankfort, and of Messrs. Fried. Krupp Grusonwerk A.G., Magdeburg.

He was a fluent German, Italian, and French linguist, and this accomplishment proved most useful to him in his very interesting and varied career.

Mr. Rolland was elected a member of the Institute of Metals on August 27, 1931.

JOSEPH KENT SMITH, O.B.E., died at Detroit, Michigan, U.S.A., on July 7, 1933. He had lived at Worksop, and went to the U.S.A. in 1925 to become consultant on the Hornsey Iron Process, a local discovery taken up by the United States Steel Corporation. He had resided in the United States before coming to Sheffield, where he was in practice as a metallurgical consultant and did valuable work for the refractories industry. Prior to his return to America in 1925, he was the guest at dinner of the Ganister, Compo and Refractories Associations of Sheffield, the members of which presented him with an illuminated address as a mark of their appreciation of his services to local industry.

Mr. Smith was made an Officer of the British Empire in March 1920, in recognition of his services to his country during the War. He was a member of the Committee of the Sheffield Local Section from its inauguration in 1918 until his departure for America in 1925. A much-esteemed, likeable, and active member, he contributed several papers to the Sheffield Local Section.

Mr. Smith was elected a member of the Institute of Metals on March 21, 1917.

Sir GILBERT CHRISTOPHER VYLE, K.B.E., died at his home in Moseley on September 7, 1933.

He was born at Hereford in 1870, and was educated in London, Glasgow, and Nottingham, and was then attached to the engineering branch of the Post Office as electrical engineer. He subsequently passed into the Colonial Service abroad, and on his return to England he was engaged in the manufacture of electrical apparatus, then practised as a consulting industrial engineer in Manchester, and finally came to Birmingham.

He joined the board of Messrs. W. & T. Avery, Ltd., in 1912, and became Managing Director in the following year.

During the War he manufactured and designed aircraft for the Admiralty, Army, and for the Air Force, and also made mine sinkers, projectiles, and munition factory equipment. He served on the Board of No. 4 area of the Ministry of Munitions, and was Chairman of the Finance Sub-Committee. He was also a member of the Royal Commission on Decimal Coinage, and served on the Water Power Resource Committee, the Safe-Guarding Enquiry Panel, the Special Enquiry into Fabric Gloves, and the Enquiry into Export Credits System. From 1923 to 1924 he was President of the Birmingham Chamber of Commerce, and assisted the Federation of British Industries in the Department Enquiry on Organization and in Lord Chelmsford's Committee, and later became Vice-President of the Federation. In 1926, he was President of the Association of the British Chambers of Commerce, and was also Chairman of the British Committee of Empire Trade. In addition to these activities, Sir Gilbert was also interested in the Development Council Department of Overseas Trade and the Travel Association of Great Britain and Ireland.

He was elected President of the British Engineers' Association for the year 1929–1930, was Vice-President of the Engineering and National Employers' Federation, and President of the Birmingham and District Engineering Employers' Federation.

Sir Gilbert Vyle was knighted in 1928, and the further honour of K.B.E. was conferred on him in the New Year list of 1932 in recognition of his services on many national and Government committees and also in the field of international and Imperial affairs. Thus, he was a Government adviser at Geneva on import and export restrictions, and was one of three official industrial advisers to the United Kingdom delegation at the Ottawa Economic Conference.

He also had many business interests, being Director of Radiation, Ltd., the Soho Automatic Machine Co., and the Soho Trust, and Chairman of the Birmingham Local Board of the Phœnix Insurance Co., Ltd., and of Messrs. Avery and Hardall and Southwell and Smith.

He was an active member of the Birmingham Business Club, the Birmingham Rotary Club, and the Birmingham Business Houses Sports Association. He was also a member of the Labour Advisory Committee of Birmingham and Smethwick.

His interest in education was shown by the fact that he was at one time Warden of the Guild of Undergraduates and a life Governor of the University of Birmingham. He himself wrote many articles on trade finance, industrial legislation and organization, and educational and postal matters.

Sir Gilbert Vyle was elected a member of the Institute of Metals on September 17, 1921.

INDEX TO AUTHORS AND SPEAKERS.

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