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OF THE
INSTITUTE OF METALS

VOLUME LIX

EDITED BY

G. SHAW SCOTT, M.Sc.

SECRETARY

LONDON
PUBLISHED BY THE INSTITUTE OF METALS
36 VICTORIA STREET, LONDON, S.W.1
1936

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

Form A. *(Membership Application)*

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

The INSTITUTE of METALS

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

Founded 1908. *Incorporated* 1910.

To the Secretary,
The Institute of Metals.

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

*Name of applicant in full ....

Address..

‡Business or Profession ....

Qualification..

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.

....
Chairman.

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

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

† For Qualifications of Members, see Rule 6, other side.
‡ Name and address of firm (or other body) should be stated, as well as position held.

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

59.

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.

Past-Presidents.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Harold Moore, C.B.E., D.Sc., Ph.D., F.Inst.Met., 1934–1936.

THE INSTITUTE OF METALS

OFFICERS AND COUNCIL,

ELECTED MARCH 11, 1936.

PRESIDENT:

W. R. BARCLAY, O.B.E.

PAST-PRESIDENTS:

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RICHARD SELIGMAN, Ph.nat.D.
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ENGINEER VICE-ADMIRAL SIR ROBERT DIXON, K.C.B., D.Eng.
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(Chairmen of Local Sections.)

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H. DUNFORD SMITH, M.Sc. (*North-East Coast*).
J. W. DONALDSON, D.Sc. (*Scottish*).
PROFESSOR J. H. ANDREW, D.Sc. (*Sheffield*).
ROOSEVELT GRIFFITHS, M.Sc. (*Swansea*).

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

ASSISTANT SECRETARY:

S. C. GUILLAN.

TELEGRAPHIC ADDRESS:
VICTORIA 2320, LONDON.

TELEPHONE:
VICTORIA 2320.

CORRESPONDING MEMBERS TO THE COUNCIL.

Australia.

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

Canada.

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Chemistry Building, McGill University, Montreal.

Egypt.

H. Norman Bassett, Egyptian State Railways, Bulak, Cairo.

France.

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

Germany.

Dr.-Ing. Max Haas, Waltraudstr. 1, Berlin-Zehlendorf-Mitte.

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India.

R. Mather, B.Met., Tata Iron and Steel Company,
24 Bruce Street, Fort, Bombay.

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

Japan.

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

South Africa.

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

Sweden.

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

Switzerland.

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

United States of America.

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

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Chairman : W. F. Brazener, The Mint (Birmingham), Ltd., Birmingham.

Hon. Secretary : J. W. Jenkin, B.Sc., Ph.D., Bromford Tube Co., Ltd., Erdington, Birmingham, 6.

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

North-East Coast.

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Hon. Secretary : C. E. Pearson, M.Met., Armstrong College, Newcastle-upon-Tyne, 2.

Scottish.

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

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

Sheffield.

Chairman : Professor J. H. Andrew, D.Sc., Department of Metallurgy, The University, St. George's Square, Sheffield, 1.

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

Swansea.

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

Hon. Secretary : K. M. Spring, 36 Beechwood Road, Uplands, Swansea.

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THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS.

AUTUMN MEETING.

THE TWENTY-EIGHTH AUTUMN MEETING of the Institute of Metals was held in Paris from September 14 to 18, 1936, by invitation of the Bureau International des Applications de l'Aluminium, with the co-operation of the Chambre Syndicale des Métaux à Paris.

Monday, September 14.

The meeting opened in the evening in the Grand Salle of the Maison de la Chimie, the President, Mr. W. R. Barclay, O.B.E., occupying the Chair, when Professor P. A. J. Chevenard, Corresponding Member to the Council for France, delivered the Fifteenth Autumn Lecture on "The Scientific Organization of Works." Over 400 members and visitors were present.

The PRESIDENT (in introducing the lecturer) said: It is my very great pleasure to-night to introduce to you Professor Chevenard, who is to deliver our Fifteenth Autumn Lecture.

We welcome Professor Chevenard this evening for many reasons. First of all, he is Corresponding Member to the Council for France, and I can assure our members that as an Institute we owe much to the devoted service of our Corresponding Members. Secondly, we welcome him as a metallurgist of international reputation, particularly in that very select field in which he has so brilliantly specialized, namely, the electrical and magnetic properties of the high-temperature alloys. We especially recall to-night his classical researches on dilatation and thermal changes, and their influence on these properties. May I add that I have a personal pleasure as a representative of the nickel industry in taking this opportunity to acknowledge Professor Chevenard's invaluable researches on the nickel-iron and nickel–chromium alloys.

Lastly, but by no means least, we appreciate the importance of the subject which he is to bring before us this evening, namely "The Scientific Organization of Works." It is a subject in which Professor Chevenard has previously exhibited interest, and I am sure that all those present to-night will listen with eagerness to what he has to say. Those of us who are not sufficiently acquainted with the French language to follow his native tongue will have the opportunity of reading the lecture in summary in English, and will have the further opportunity of reading the full text in a few days' time in the *Monthly Journal*.

At the conclusion of the lecture (which is printed in full on pp. 19–51 of this volume) the President proposed, Dr. J. L. Haughton, Member of Council, seconded, and Sir Robert Mond, M.A., LL.D., F.R.S.E. (Member) supported a hearty vote of thanks to Professor Chevenard for his lecture.

Members and visitors then adjourned for light refreshments, after which there was a display of cinematograph films of metallurgical interest.

Tuesday, September 15.

Morning.

At the morning session, held at the Maison de la Chimie, M. Dalmais, President of the Bureau des Applications de l'Aluminium, welcomed the members and their ladies to Paris, on behalf of the Institute's hosts.

M. J. Dalmais (*speaking in French*): We hoped very much that there would have been present to welcome you this morning the most honoured of our colleagues in the world of industry and science, Professor Henry Le Chatelier, but unfortunately he is absent from Paris. He writes: "I have received your kind letter asking me to open the first session of the Congress of the Institute of Metals in Paris. I am very flattered by the invitation and much appreciate the sympathy of my English colleagues, but to my great regret it will be impossible for me to accept. I am 85 years of age and I shall be in the South of France at the time, and I cannot make the journey; ten years ago I might have done so, but now it is impossible. I ask you, therefore, to apologize on my behalf and to tell my English colleagues how glad I should have been to show my appreciation of the welcome which I have always received in England."

In the absence of Professor Le Chatelier, I have great pleasure in offering you a cordial welcome in the name of the bodies participating in the invitation: The Bureau International des Applications de l'Aluminium, Aluminium Français, Aluminium Industrie A.G., Aluminium Werke A.G., the British Aluminium Company, Limited, Vereinigte Aluminium Werke A.G., and the Chambre Syndicale des Métaux. I regret that the President of the last-named is not able to be here to welcome you in person. It is thanks to the co-operation of these different societies, that we have been able to organize this Congress and the visits which will take place. We had hoped to arrange more receptions for you, but the month of September is a difficult one in which to hold such functions. At those which you do attend, however, you will see how glad our city is to welcome you. We trust that in addition to its scientific value you will carry away with you the happiest recollections of your visit to France.

The President: We desire, M. Dalmais, to thank you most heartily for your welcome this morning, and in particular to express our appreciation of the invitation which was so charmingly extended to us last year, accompanied by a promise—which already shows signs of being very abundantly fulfilled—of a most enjoyable meeting in Paris. This is the first time that we have met in this great country of France, and we are very glad that our first visit should be to its delightful capital. No gathering of metallurgists can possibly meet in this country and in this city without recalling with gratitude the debt we owe to the great French metallurgists, and particularly those who in the early days of the development of the science of metallography and physical metallurgy, have placed us all under such great obligations. This morning the names of Osmond, Le Chatelier, Guillet, Portevin, Chevenard, and many others come to our minds, and I am sure we all feel that here in Paris we are meeting in the right atmosphere.

I would especially take this opportunity—though we hope there will be others later—to say how deeply grateful we feel to the organization over which M. Dalmais presides for the immense amount of trouble which they have taken in connection with this meeting. It is not easy to organize a first meeting, when there are no traditions to serve as a guide. In this case, however, new traditions are being created, and, although we have been here so short a time, we have been made to feel thoroughly at home.

I regret more than I can say that I am not able to emulate some of my colleagues and address our hosts in their own language, but I have very great pleasure in asking Dr. Seligman, a Past-President of the Institute and one of its Fellows, to supplement my remarks.

Dr. **Richard Seligman**, Past-President : Monsieur, notre Président m'a chargé d'ajouter quelques mots en français au discours qu'il vient de prononcer et je me livre à la tâche qu'il m'a imposée.

Permettez-moi, d'abord, M. Dalmais, de vous demander de transmettre à nos collègues, les chimistes français, nos félicitations du succès de leurs efforts que représente cette Maison de la Chimie. En Angleterre nous avons suivi ces efforts avec grande sympathie. Nous sommes heureux qu'ils aient réussi et nous autres de l'Institute of Metals sommes peut-être même fiers qu'un de nous, notre membre bien respecté, Sir Robert Mond, les ait facilités par sa munificence. Nous regrettons infiniment que chez nous une entreprise analogue ait pour le moment échouée.

C'est avec grand plaisir que je vois siéger l'Institute of Metals dans la Maison de la Chimie. Ce n'est pas la première fois que j'assiste à des conférences dans cette salle et chaque fois que je l'ai visitée je me suis dit combien je serais heureux si une de nos conférences pouvait y avoir lieu. Voilà que mon désir se réalise et je tiens à offrir et de la part de l'Institut et de la mienne nos remerciements les plus sincères à ceux qui nous ont permis de tenir nos séances dans ce noble, cet historique bâtiment, autrefois le palais du Comte d'Auvergne, maintenant consacré à la mémoire d'un des plus fameux chimistes français—Marcelin Berthelot.

J'espère, M. Dalmais, que vous voudrez bien exprimer nos plus vifs remerciements à la Société de Chimie Industrielle pour leur hospitalité.

Qu'on me permette ensuite de souligner quelques-unes des paroles de M. Barclay. Il vous a dit quelle inspiration il y a pour nous de nous trouver dans le pays des grands savants français. Il n'est peut-être pas surprenant que quelqu'un comme moi, attaché dès son enfance métallurgique à l'industrie de l'Aluminium, rapelle à cet égard et à ce moment les noms de St. Claire Deville, de Henri Moissan, de Paul Héroult, noms de savants français devant lesquels doivent s'incliner, tous ceux qui comme vous, M. Dalmais, et comme moi, tirent les bénéfices de leurs travaux.

Ce que je désire faire ce matin surtout c'est d'insister sur l'esprit qui nous anime, mes collègues et moi, en vous rendant visite pour notre séance d'automne. Parmi ceux qui assistent à cette cérémonie inaugurale il y en a plusieurs que nous sommes enchantés de voir quoiqu'ils nous connaissent à peine. Peut-être justement parcequ'ils nous connaissent à peine.

Qu'ils sachent, M. Dalmais, comme vous le savez, que l'Institute of Metals est une Société scientifique devouée uniquement à l'avancement de la science métallurgique. Elle ne connait ni la politique ni les politiciens.

Cependant ceux qui ont organisé l'Institute, il y a maintenant presque 28 ans, ont bien reconnu que la science possède un pouvoir énorme qui lui permet de panser non seulement les blessures du corps mais aussi les blessures de l'esprit humain.

C'est pour cela que nous avons tenté, et tenté avec succès, de rassembler sous notre égide, à côté de nos compatriotes, les métallurgistes de toutes les nations. Dans nos séances, dans notre Journal, dont nous sommes toujours si fiers, il n'y a Français, ni Anglais, ni Italiens, ni Allemands, mais seulement des métallurgistes, chacun visant au même but, chacun cherchant à achever les mêmes tâches.

A plusieurs réprises nous sommes sortis de chez nous pour nous rassembler, soit en Belgique, soit en Allemagne, ou en Suisse et maintenant chez vous.

Nous croyons pouvoir par ce moyen resserrer plus étroitement les liens qui nous attachent les uns aux autres et éviter les malentendus qui surviennent si facilement si on ne se voit pas de temps en temps, si on n'a pas l'occasion de causer avec son vis à vis, de comprendre ses idées et surtout de reconnaître que les motifs qui l'activent sont au moins aussi dignes que les nôtres.

Les conférences auxquelles nous allons assister, les visites que vous avez si bien arrangées et surtout les belles fêtes auxquelles vous avez eu l'amabilité de nous inviter avec les membres de nos familles nous donneront en pleine mesure les occasions que nous cherchons. C'est à nous de les saisir et d'en profiter et pour ma part je n'ai aucun doute que nous ne le ferons avec succès.

En nous permettant de nous rassembler chez vous, M. Dalmais, vous nous avez rendu avec vos collègues un service pour lequel nous vous témoignons notre chaleureuse gratitude.

The President then extended a hearty welcome to the members attending the meeting from overseas; in addition to those from the British Isles, there were members present from Australia, Belgium, Denmark, Germany, Holland, Italy, Luxemburg, Sweden, Switzerland, and the United States of America.

The Minutes of the General Meeting held in London on May 6, 1936, were taken as read, and signed by the Chairman.

NOMINATION OF OFFICERS FOR 1937–1938.

The SECRETARY (Mr. G. Shaw Scott, M.Sc.) read the list of members nominated by the Council to fill vacancies as Officers for the year 1937–1938, as follows:

President.

W. R. BARCLAY, O.B.E.

Vice-Presidents.

Engineer Vice-Admiral Sir ROBERT DIXON, K.C.B., D.Eng.
Lieut.-Colonel the Hon. R. M. PRESTON, D.S.O.

Members of Council.

W. T. GRIFFITHS, M.Sc.
STANLEY ROBSON, M.Sc., D.I.C.
A. J. G. SMOUT.
D. STOCKDALE, M.A., Ph.D.

The PRESIDENT: I would remind members that in accordance with the Rules other nominations may be made at this meeting provided that they are signed by ten members. Should there be any other candidates, a ballot will be held and the result announced at the General Meeting to be held in London in March next.

Of the nominees brought before you to-day, Mr. Griffiths and Mr. Smout have already served the Institute as Members of Council, and we are indebted to them for a good deal of service rendered outside the Council. Mr. Stanley Robson is a very experienced worker in connection with such societies as ours, and is just completing his second year as Chairman of the Chemical Engineering Group of the Society of Chemical Industry. Those of you who know anything of the work of that Group will know something also of the keen interest which its members take in our own subject. I am sure that Mr. Robson will strengthen our Council on that side. Dr. Stockdale is well known to us for his brilliant research work at Cambridge.

Election of Members and Student Members.

The Secretary read a list of members and student members elected on July 2 and August 27, 1936, as follows:

Members Elected on July 2, 1936.

Green, Willie Dunstan Theodore	Edinburgh.
Robinson, Lyell Bryant	London.

Members Elected on August 27, 1936.

Alexander, Paul	St. Helens.
Anjaneyulu, Nadimpalli	Phirangipuram (Guntur), India.
Binstead, William Victor	London.
Dodd, Francis George	Walsall.
Doucet, Jacques Michel	Le Havre, France.
Eastlake, William H.	Montreal, P.Q., Canada.
Farlie, John Burke	Sutton.
Germinet, Emile	Paris, France.
Gould, George Herbert	Coventry.
Hobrock, Raymond Henry, Dr.-Ing., M.Sc.	Detroit, Mich., U.S.A.
Jackson, Henry Herbert	Wembley.
Jansson-Follin, Carl Gustaf Ingemar	Finspong, Sweden.
Lönnegren, Arvid Emil	Finspong, Sweden.
Mallam, Peter Gillespie, B.Sc.	London.
Pfann, Ernst, Dr.-Ing.	Düsseldorf, Germany.
Pihl, Gunnar	Stockholm, Sweden.
Risinger, Charles, Dr.Sc.	Prague, Czechoslovakia.
Spire, Jean Paul Etienne, Ph.D.	Billancourt (Seine), France.
Sykes, Charles, M.Sc., Ph.D.	Timperley, Cheshire.
Unckel, Hermann August	Finspong, Sweden.
Watson, James Bernard	London.
Worner, Howard Knox, M.Sc.	Melbourne, Australia.

Student Members Elected on August 27, 1936.

Beverley, Laurence Theodore	Birmingham.
Rivett, Francis Antony	London.

Future Meetings.

The President announced that the Annual General Meeting of the Institute would be held in London on March 10 and 11, 1937, and that an invitation had been received to hold the Autumn Meeting in Sheffield.

Communications.

Communications by the following authors were then presented and discussed: G. Gauthier; Marquis R. de Fleury and H. Portier; Professor A. von Zeerleder and R. Irmann; and N. D. Pullen. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried unanimously.

In the morning a ladies' visit was arranged to the Musée du Louvre.

Afternoon.

Members visited by invitation the following works: Babcock and Wilcox, Tréfileries de Vitry (Compagnie Générale d'Electrometallurgie) and Câbleries de St. Maurice (Tréfileries et Laminoirs du Havre), the Etablissements Marchal à Pantin and Société des Alliages d'Etain et Dérivés à Montreuil-sous-Bois. Ladies visited the Etablissements Julien Damoy.

Evening.

Members and their ladies were the guests of the Bureau International des Applications de l'Aluminium at a Banquet at the Maison de la Chimie.

Wednesday, September 16.

Communications by the following authors were presented and discussed: R. H. Atkinson and A. R. Raper; Professor A. Portevin and P. Bastien; Professor D. Hanson and E. J. Sandford; and L. Northcott. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

VOTES OF THANKS.

The PRESIDENT: You will all realize that such a meeting as this would not be possible without considerable personal effort on the part of someone. Those of us who have some inside knowledge and who had an opportunity to discuss the details of this visit to Paris, the first that the Institute has made to France, are fully aware that an immense amount of such personal service has been put into making it a success, and has been rendered in the most cheerful spirit and with an extraordinary willingness to meet the idiosyncrasies of the visitors. I am referring, as you all know, to the wonderful work of M. Douchement, whom we are delighted to have had the pleasure of meeting. The members of the Council who are visiting Paris join with me in asking M. Douchement to accept a small souvenir of this visit as a tangible expression of our appreciation. I have, therefore, much pleasure in handing to M. Douchement, and asking him to accept, this cigarette case in gold and wood, while assuring him that the smallness of the gift is no measure of the warmth of our thanks.

The presentation was made amid applause.

M. J. S. DOUCHEMENT: I thank you for this gift and for the very kind words you have used in presenting it. It has been a great pleasure to me to be entrusted with the organization of this meeting, and I am very happy that our arrangements have been to your satisfaction.

The PRESIDENT: We now come to the last item of our more formal business, but I would plead that we do not regard it as a mere formality. We are accustomed at the end of our London meetings to pass omnibus votes of thanks, but we wish on this occasion in no formal spirit to pass a resolution of thanks to those to whom our gratitude is due. The motion which I have to propose is:

That the best thanks of the Institute of Metals be given to

(1) The Bureau International des Applications de l'Aluminium and to the Chambre Syndicale des Métaux à Paris for their cordial welcome to Paris and for their hospitality;

(2) The Municipal Council of Paris for the reception of members and their ladies at the Hôtel de Ville;

(3) The industrial firms in Paris and district who have granted permission to members and their ladies to visit their works, and for their hospitality;

(4) M. Dalmais, the President of the Local Reception Committee, M. Douchement, the Honorary Local Secretary, and to all the members of the Local Reception Committee for all the services that they have rendered to the Institute in this most carefully planned and generously organized visit to Paris.

Dr. A. G. C. Gwyer, Vice-President: It gives me the very greatest pleasure to second this proposal, and I think that it is right that on this occasion the vote of thanks should be expressed in more cordial and less formal terms than we are in the habit of using in London. This meeting has been a most successful one in every way. The great interest shown in it is evinced by its international character. The papers have been of a high order and have aroused great interest. We are greatly indebted to our hosts for the trouble they have taken. We have been able to hold our meetings in this beautiful building, and last night in another part of the building we were entertained in the most bounteous fashion. I should like to refer in that connection to the beautiful concert at the end of the dinner. The exhibition of instruments by itself could not fail to interest those who have any interest in music whatever, and although the hour was late many stayed behind last night to talk with the musicians themselves. I notice that the formal resolution contains no reference to the care which has been taken of the ladies, and we are under a great debt of gratitude not only to M. Douchement—an old friend of mine—under whose guidance the arrangements were bound to be successful, but to Mlle. Sigwalt, for the assistance that she has given to M. Douchement in the organization of this meeting and for looking after the ladies so well.

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

M. J. Dalmais (*speaking in French*): I can only repeat what I said yesterday, that it has given us the greatest pleasure to receive you here in Paris. We were extremely happy when you accepted our invitation, because we know that you go abroad but rarely and we are glad to benefit from your doing so on this occasion.

The business meeting then terminated.

During the morning the ladies visited Notre-Dame and the Saint-Chapelle.

Afternoon.

Members visited by invitation the works of the Société H. et M. Farman à Billancourt, the Fonderie de Précision à Nanterre, and the Imprimerie de l'Illustration à Bobigny. The ladies visited the Château de Malmaison.

At 5.30 p.m. members and their ladies attended a Civic Reception by the Municipal Council of Paris at the Hôtel de Ville.

Evening.

Members and the ladies were the guests of the Local Reception Committee at a dance held at Pavillon Dauphine in the Bois de Bologne.

Thursday, September 17.

There was an all-day excursion to Versailles. Visits were made to the Château and the Trianons.

Friday, September 18.

Members and their ladies took part in a whole-day excursion to Rouen and Havre. Arriving at Rouen at 9.45 a.m., the party visited various places of interest in the city. After lunch, the party divided into two parts—one taking part in a motor visit to the Abbey of Jumièges, Caudebec-en-Caux, and the Abbey of St. Wandrelle, while the other visited the works of the Tréfileries et Laminoirs du Havre.

The party returned in the evening to Paris, where the meeting terminated.

AUTUMN LECTURE, 1936.

THE SCIENTIFIC ORGANIZATION OF WORKS.

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FIFTEENTH AUTUMN LECTURE TO THE INSTITUTE OF METALS, DELIVERED SEPTEMBER 14, 1936.

By Professor PIERRE CHEVENARD,* Corresponding Member to the Council for France.

" Scientists," wrote that celebrated clock-maker, Henri Robert, " are very clever men, for, after a long series of calculations, they arrive at exactly the same results as those which the genius of technicians had discovered. They are also the kindest of men for they also prove that these results are the best."

These ironical words were addressed to the theorists of the chronometer and directed against their work on the regulating spiral, since the " final bends " they obtained by calculation agreed exactly with those obtained by clever clockmakers, by the method of trial and error, one hundred years previously. Had similar words been used twenty years ago with reference to metallographists would they have seemed excessively unjust?

Certainly metallography had achieved some important successes, such as the classification of alloys according to their equilibrium diagrams and the interpretation of their properties according to their constitution, structure, and polymorphic transformations. Although the spontaneous hardening of light alloys was still an enigma, scientists were explaining, simplifying, and codifying the long since discovered processes of the quenching and tempering of steel, and were also reducing to a coherent theory the surprising properties of nickel steels; but as yet they had invented no completely new alloy or any really novel process of manufacture.

The discovery of high-speed tool steel by Taylor just prior to 1900 was, indeed, rather the triumph of the methodical organization of research than a true metallographical success. A lucky chance, judiciously exploited by Ch.-Ed. Guillaume, led to the discovery of Invar. Thus, before the War it could be said that metallurgy had scarcely left the *explanatory stage*.

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* Formerly Professor of Metallurgy at the St. Etienne School of Mines; Scientific Director of the works of the Société de Commentry, Fourchambault et Decazeville.

This is no longer true to-day. If Taylor were attacking the problem of tool steels at the present time the knowledge that has been accumulated on ternary, quaternary, and still more complex alloys, and on the processes of annealing, quenching, tempering, and structural hardening would appreciably hasten the solution of the problem. Elinvar is not a chance find like Invar, but a true discovery; with Guillaume's theory of the ferro–nickels as a basis, the composition of this alloy could be predicted almost exactly, and produced, as it were, practically without a procedure of trial and error.

Such new products as the non-rusting steels, heat-resisting alloys, austenitic alloys amenable to structural hardening, ferro–nickels of high magnetic permeability, the latest magnet steels, and tools made of sintered carbides of tungsten or tantalum, and such new processes as nitride case-hardening, &c., prove that metallurgy is now in the midst of its *constructive stage*, and the famous alliance of Science and Industry, now realized, is bearing fruit. How can we make this union yet more intimate and productive?

"In every enterprise," wrote H. Fayol, "simple or complex, big or little, there are six groups of *essential functions :* the technical function, the financial function, the commercial function, the accounting function, the security function, and the administrative function." Now, in view of the present complexity and difficulty of manufacture, at least with work of a delicate technical nature, as, for example, that of factories making special alloys, a seventh function, which is to some extent an offshoot of the first, should be taken into consideration; this is the *scientific function.*

The first objective of science in a factory is the *maintenance* of results already acquired; this is the purpose of *control* which prevents deviations in the normal processes of manufacture, and also of *expert investigations,* which determine the cause of the inevitable failures. The second objective of science is the *improvement* of manufacturing technique either by amplifying or remodelling the processes of manufacture or by creating new products; this is the purpose of *laboratory research* and *tests in the works* for the application of research results to practice.

For 25 years, both in my industrial life and in my teaching, my thoughts have revolved around this double problem of *maintenance* and *improvement*, and, since this year you have done a ferrous metallurgist the honour of inviting him to deliver the Autumn Lecture, the moment seemed opportune to talk to you about *scientific organization.* Moreover, our President, Mr. Barclay, was kind enough to invite me to do so, and I wish to express to him my thanks for such an honour.

This subject is certainly not a new one. Numerous authors since Taylor, Le Chatelier, and Charpy have discussed it in general terms. My ambition is, however, more modest; I wish simply to explain to you how we have conceived and endeavoured to realize the impregnation of science into manufacture in the works of the Société de Commentry, Fourchambault et Decazeville. Obviously I shall refer especially to the works at Imphy, the most important and the most advanced of the metallurgical establishments of this Company. These works are 300 years old, and for a long time have been specializing in fine steels and precision alloys.

The personal character of these notes is but a mark of prudence, since it is always rash to extrapolate in matters of organization, yet I hope that certain general ideas will be apparent, for the conceptions I am about to explain are an attempt to reflect those of the masters who have guided me by their teaching, their writings, and their advice: G. Friedel, H. Fayol, A. Pourcel, Ch.-Ed. Guillaume, and H. Le Chatelier.[1] I am happy to express to them here my gratitude. I would also like to thank the directors of the Société de Commentry, Fourchambault et Decazeville, the managers of the various works, and all my colleagues for their confidence and devotion.

The equipment of the research and control laboratories at Imphy has already been described on several occasions.[2, 3] I do not propose to return to this subject, but simply to recall the principles that have governed the material organization of these laboratories. In order to lessen the dryness of this account, however, a section in the chapter on "Control" will be devoted to new measuring apparatus.

ON THE FUNCTION OF SCIENCE IN WORKS.

"To administer," wrote H. Fayol,[4] "is to foresee, to organize, to direct, to co-ordinate, and to control." This eminent originator of the theory of administration defines the task of the general manager in control of the whole enterprise as follows: to organize the plan of campaign, to unite individual efforts, and to harmonize the work; but again he said "Administration is not a prerogative of the managing director of the firm." The man in charge of the scientific side, to whom I shall refer briefly as the scientific director, has also a complex and delicate administrative task. To describe this it is convenient, therefore, to examine the five functions enumerated by H. Fayol: foresight, organization, direction, co-ordination, and control.

I.—Foresight.

Industry is in a state of perpetual evolution. The discovery of a new mineral deposit, a new process, or a new product sometimes upsets situations which appear to be the most stable. Bessemer's invention abolished puddling furnaces, the open-hearth furnace supplanted the converter for the manufacture of good-quality steels, and now the electric furnace, in its turn, has become a victorious rival of the open-hearth furnace, especially for the manufacture of special steels for motor-cars and aeroplanes.

Invar has modified the technique of measuring apparatus and Elinvar has revolutionized the manufacture of chronometers. By the discovery of nickel–aluminium magnet steels, with their enormous coercivity, the magneto, the galvanometer, and the relay have been simplified and their shape considerably modified. Alloys of the Permalloy type have made possible long-distance telephony by subterranean and submarine cable, and finally the popularity of wireless has incited the advances made in ferro–nickels with very low hysteresis.

The manager of an enterprise must, therefore, scan the horizon so as to prepare the factories to utilize new ideas at the opportune moment, to satisfy the future needs of customers, and to frustrate all possible competition. To do this he will need *commercial feelers,* so to speak, and a *scientific foundation.*

Since it is his duty to build up this foundation, the scientific director should in his turn prepare himself by acquiring a knowledge of the four principal operations that come under the heading of foresight, namely :

(1) The creation of scientific equipment.
(2) The formulation of a scientific theory of manufacture to be a basis of the technical progress of the enterprise.
(3) The preparation and direction of the evolution of the industrial technique.
(4) The formation of the staff of the laboratories and imbueing the manufacturing staff with the scientific outlook.

§ 1. *The Creation of the Scientific Equipment.*

However numerous and perfect the devices used in commerce for measurement and observation may be, they cannot fulfil all requirements. In a factory such as that at Imphy, where very special alloys are made, new problems of measurement often arise, and, more frequently still, the classical problems present new aspects. The discovery of Elinvar 20 years ago involved the thermoelastic study of numerous ternary ferro–nickels, previously an unusual procedure in industrial laboratories. The apparatus used for classifying the varieties of Invar according to their thermal expansion properties is quite different from the dilatometer used in thermal analysis. Again, a special thermomagnetometer had to be constructed for studying the heterogeneity of austenitic solid solutions. We have made it our practice, therefore, to construct most of our own research and testing apparatus and a precision workshop for this purpose forms an annexe to the research laboratory at Imphy. This has supplied practically all the testing equipment, except the most delicate optical instruments, the classical mechanical testing machines, and certain other cheap apparatus in common use. From this workshop have come the differential dilatometer, the thermal analyzer, the galvano-pyrometer, the thermomagnetometer, the dilatometric pyrometer, and the micro-machine for the testing of metals. All these instruments have been described previously,[2, 3, 5] and I do not intend to discuss them again. The moment seems opportune, however, to recall the principles which directed the study, construction, installation, and employment of these devices.

A special apparatus is used for each type of measurement. Thus there are separate dilatometers for determining the transformation points of alloys, for studying refractory products, for testing Invar, &c. This method, contrary to appearances, is quicker and less expensive than the employment of a single apparatus adapted to many different uses; above all it is far more reliable, since for each special use there is a principle, a mechanism, a scale of measurement, a sensitivity, &c., more adequate than any other for the particular purpose in view.

The one essential quality of a measuring apparatus is constancy; the principle is therefore chosen to reduce as much as possible the action of disturbing factors which are so numerous and intense in a factory, namely shocks and vibrations, changes of temperature, variations in the magnetic field, stray currents, &c. Thus the dilatometric pyrometer so extensively used at Imphy is far less sensitive to disturbing factors than the thermoelectric pyrometer. The pieces of apparatus are simply constructed, and only materials of great stability are employed. Automatic recording, used in nearly all the apparatus, reduces the personal equation to the absolute minimum and at the same time reduces the cost of the tests.

Not less important is the sensitivity of the apparatus, or more accurately stated, the resolving power comparable to the resolving power of the optical worker. For example, certain phenomena of great metallographic importance are accompanied by changes of only very small amplitude; this is the case with the dilatometric anomalies observed in the transformations which occur in light alloys.

The sensitivity of the instruments may be increased by the differential method which isolates the phenomenon studied from the effects of secondary phenomena; thus the differential dilatometer, which eliminates the greater part of the normal expansion of the specimen due to temperature, throws into sharp relief even the very smallest anomalies in the expansion due to structural or other changes.

As for the precision of the instrument, which is a complex function of all the elementary qualities (correction of the principle, sensitivity, constancy, &c.), this should be adequate for the purpose in view. "In metallurgical studies," said H. Le Chatelier, "an accuracy of 1 per cent. is nearly always sufficient; an accuracy of 0·1 per cent. is often useless and unnecessarily costly," but there are exceptions to this statement. According to Ch.-Ed. Guillaume, "nothing is more definitely fruitful in pure science than the gain of a decimal place," and this is also frequently true in industrial research. Are not all the industries which use the inert gases based on a secondary phenomenon observed by Ramsay; namely, that the densities of atmospheric and chemically prepared nitrogen differ by a very small fraction?

Apparatus once constructed is installed permanently in spacious and well-lighted rooms on robust tables with anti-vibratory supports to prevent movement and damage, the mountings are simplified as much as possible to obtain a neat, workmanlike assembly, and careful attention and periodic control are given to keep the instruments always ready for instant use.

Order and cleanliness reign everywhere in the laboratory to ensure an atmosphere of unhurried activity so favourable to scientific work.

§ 2. *Collection of Information. Research Work.*

To make progress in an industry it is first necessary to elucidate the nature and the laws of the phenomena which govern the processes employed; it is in guiding the research work that Science, in the words of Montaigne, reveals itself as "a tool of marvellous service."

Subjects for research are numerous, but can be grouped under five headings:

(a) *The works encounter difficulties.*—Various incidents repeatedly occur and experiments reveal a new fact or more frequently a known fact, the cause of which has not previously been established; the research laboratory then takes the matter in hand and sometimes discovers the cause of the trouble and a remedy.

The formation of quenching cracks in steel, studied by Portevin, is evidently due to internal stresses produced by different parts of the metal undergoing at different times the volume changes caused by contraction during allotropic transformations. Research on the efficacy of quenching liquids, on the thermal conductivity and tensile strength of steels at high temperatures, on the common deformations, on the dilatometric phenomena associated with the transformations, on the critical rate of quenching, &c., has elucidated, at least in principle, the mechanism of cracking and furnished means for eliminating it; among these the two-stage quench is one of the most efficacious.

Is it necessary to recall the researches of Houdremont on the origin of flakes in massive sections of self-hardening special steels? An analysis of the conditions which caused these faults to appear indicated that hydrogen played a determining rôle in their formation; this gas dissolves in liquid steel, is liberated again on cooling, and can exercise sufficient pressure to break the solid metal, but it can also diffuse through the hot solid metal if given sufficient time and, therefore, it suffices to cool the metal slowly after crushing or forging to prevent the hydrogen pressure from reaching a dangerous value. This simple precaution which has now been universally adopted has practically completely eliminated these flakes.

(b) *Other subjects for research are suggested by customers.*—Warned and informed by the commercial service, the research service includes in its programme the study of difficulties and failures for which it tries to find a remedy; it notes the tendencies of the consuming industries, the evolution of which demands new materials.

The intercrystalline corrosion of welded tanks of 18 : 8 austenitic stainless steel incited the well-known work of Strauss, Monypenny and others who discovered that the cause of the trouble was the precipitation of chromium-rich carbides under the action of the heat of welding, and that it could be overcome by reducing the carbon content to a low value, by addition of titanium to prevent carbide precipitation, or by addition of molybdenum to produce an austenite–ferrite structure.

The laboratory at Imphy has carried out prolonged research into the cause of corrosion-cracking of ferro–nickels in steam. This arose from an accident which occurred before the War to a turbine fitted with blades of ferro–nickel containing nickel 24 and chromium 2 per cent. The result of the research from the practical point of view was the development of a resistant alloy for the blades, consisting of ferro–nickel with nickel 35 and chromium 11 per cent., which is now manufactured under the name "ATV." From the scientific point of view the researches resulted in a satisfactory theory of corrosion-cracking which explained all the problems of the chemical resistance of the alloys in corrosive atmospheres.

(c) *Inventions* furnish many subjects for research. Thus, to put into practice his idea of making a refining slag react very rapidly with a bath of molten metal, Perrin not only worked out a technical method of carrying out these reactions but also determined by accurate researches the chemical activity of the refining slags, their fluidity and their electrical conductivity.

I have previously explained how, through a request from G. Claude who wished to improve the Haber process of ammonia synthesis by increasing the working pressure from 200 to 1000 atmospheres, the Imphy laboratories started in 1918 to study the deformation of alloys at high temperatures, and how this work resulted in the development of the first alloys with a high strength at high temperatures suitable for making the synthesis vessels.

(d) *The observation of an unexpected fact in the laboratory or workshop* is often the beginning of a fruitful research. In studying the expansion of iron–nickel alloys, Ch.-Ed. Guillaume found that one alloy had an expansion coefficient one and a half times as great as that of either of the constituent metals, whereas another alloy had a coefficient of expansion only half as great. This anomaly, discovered by chance, led to a systematic study of the whole system, as a result of which Invar was discovered.

Tests made at the Imphy laboratory showed that ferro–nickels containing chromium and carbon give thermomagnetic curves of peculiar shape; the disappearance of strong magnetism as the Curie point is approached does not follow the theoretical law of Langevin and Weiss but extends over a temperature range. Once this unforeseen result was confirmed, it was connected with the heterogeneous nature of the complex austenite. Researches undertaken to confirm this theory led to the measurement of the amplitude and extent of the heterogeneity, to the elucidation of the conditions governing the appearance and disappearance of the phenomenon, to an exact determination of the part it plays in the structural hardening and corrosion-cracking of the alloys, and, finally, to the development of heat-treatment procedures which assured their chemical resistance.

(e) *Researches carried out as part of a comprehensive programme of exploration.*—On starting the research laboratory at Imphy in 1911, H. Fayol set himself the task of "investigating special ferrous alloys with the object of discovering and exploiting their peculiar properties." Since 1911 this programme has been followed in co-operation with Ch.-Ed. Guillaume. It has furnished a mine of information which has been condensed into binary and ternary diagrams relative to the properties of reversible ferro–nickels: expansion and specific volume, modulus and coefficient of thermoelasticity, magnetization and resistivity, thermo-resistivity and thermo-electric power, mechanical properties and internal friction of plain ferro–nickels and ferro–nickels containing chromium, manganese, molybdenum, &c. All this work resulted in the development of Elinvar and a whole series of alloys derived from precision metallurgy.

Conduct of researches. Industrial researches should be carried out according to the methods of pure science.—If, with the object of saving time, the rule of changing only one variable at a time is broken, there is a great risk of missing the result, and if, under the pretext of undertaking only useful tests, the scientific director restricts his outlook, there is every chance that the most interesting results will be overlooked. It is necessary to allow for a certain breadth in the research plan, for only in this way will "Science treat us as masters and possessors of Nature," in the words of Descartes.

It is not sufficient to collect exact results; a catalogue of figures and an album of diagrams are useful sources of information but not of new ideas. It is necessary to interpret these results, to make them speak and to develop from them a *theory*. Buffon was fond of saying "Let us assemble facts to get ideas," and E. Picard adds "With these ideas let us build theories which will allow us to foresee new facts."

In a works laboratory, however, the utilitarian objective of research should never be lost sight of. Repetition of work already done should be avoided unless some new element of success can be introduced; hence the need for an extensive and up-to-date bibliography of information.

To sum up, the scientific director, assisted by his reading of papers on the progress of metallurgy and metallographic discoveries and kept informed by the commercial service of the progress and evolution of the consuming industries, should direct his researches in such a way as to build up in the shortest time and at the least cost a scientific theory of manufacture capable of ensuring the security of the work and the technical progress of the enterprise.

§ 3. *Evolution of Industrial Technique. Putting Research into Practice.*

The creation of new products and the improvement of processes and apparatus of manufacture are based on scientific information obtained by researches. From these it is known how each of the properties investigated in an alloy depends on its composition and on its thermal and mechanical treatment; the influence of the principal factors of a process are known at least qualitatively, &c., and in one word the result can be predicted; between a predicted alloy and an alloy ready for sale, a projected apparatus and an apparatus in operation, and the process devised and the process in operation, there is, however, often a long and rough road to traverse. Let us take as an example the creation of a new alloy: here are the steps necessary for putting it into commercial production:

Each of the required properties of the alloy occur to the desired extent only within a certain range of composition and all the points common to these different ranges are possible solutions of the problem. If there are no common points then the nearest points must be chosen, taking into account the relative importance of the various properties. Having selected a suitable theoretical composition, alloys are prepared and their properties determined until a suitable one is found.

In order to reduce costs, the test ingots are made as small as possible, especially if any of the constituents are very costly. At Imphy a complete equipment has been installed for studying the physical, chemical, thermal, and mechanical properties of a steel ingot weighing only 300 grm. For simplicity and to avoid the chance of being led astray, pure materials are used and melted in highly refractory crucibles *in vacuo* or in an inert gas.

Once the predictions have been verified and the best composition and most favourable treatment determined, the commercial manufacture of the alloy is taken in hand and then many new problems arise.

The first problem concerns the inevitable impurities: can they be tolerated?; if not, can purer but more costly raw materials be used?; or again, is it possible to eliminate the impurities from the bath of molten metal? The great revolution in steel manufacture brought about by dephosphorization with basic slags is well-known, as well as the extraordinary precautions necessary in the preparation of non-rusting austenitic chromium–nickel steels with a very low carbon content.

In an industrial furnace the molten alloy reacts with the refractories, takes up nitrogen and oxygen from the atmosphere, and absorbs carbon from the electrodes or fumes. The transition from the small test-ingot to the large ingot of the forge or rolling-mill results in the appearance of many difficulties; the increase in weight favours segregation and results in growth of the primary dendrites. The crystallization of a large ingot also depends on the temperature and rate of pouring, on the shape and thickness of the mould, on the presence of inclusions introduced by the deoxidants, &c., &c. All these phenomena must be studied in such a way as to discover the most favourable factors.

Whether these tests are true researches or simply putting research into practice and whether they are made in the laboratory or workshop they should be carried out on scientific principles, *viz.* systematic variation of the factors, and with measurements sufficiently simple to be rapid and inexpensive but sufficiently precise to lead to the desired result.

Once the works has completed its tests to apply the results of research to practice, that is to say once the most perfect, most certain, and least expensive conditions of manufacture have been established, it is essential that the results acquired with so much trouble be stabilized, that is to say, the technique which is to be used must be codified; this is the purpose of manufacturing standards. These standards specify dogmatically the sequence of operations, the most suitable magnitudes of all the factors susceptible of measurement, and the precautions necessary for maintaining a correct manufacture.

§ 4. *Formation of a Personnel. Education.*

The American author Spooner has enumerated the qualities which he requires in engineers and in the technical personnel of the laboratory and the factory. Quite rightly he attaches great importance to *character:* a sound professional conscience, tact, a pleasant manner, diligence, enthusiasm, initiative, and confidence in himself are essential requisites in a technical man; he should also have the following *mental qualities:* good sense and sound judgment, a spirit of invention and ingenuity, facility of expression and explanation, precision, and aptitude for rapid work. Finally, he must have an *excellent technical foundation:* professional and encyclopædic knowledge, aptitude for acquiring new ideas, and manual dexterity for experimenting and designing.

These qualities are so numerous that only very rarely can candidates be found capable of satisfying Mr. Spooner. Fortunately, however, a beginner has not attained his full moral and intellectual development; this is susceptible of formation, and every chief has the duty of moulding his subordinates, not only in the interests of the firm but also as a social duty.

A humorist has said " Quelqu'un a plus d'esprit que M. de Voltaire, c'est M. Tout-le-Monde." In the same way it is possible to accumulate in an enterprise more science and talent than can be contained in the brains of the engineers: it suffices to utilize the grey matter of the greatest possible number of workers in all degrees of the hierarchy. This is particularly necessary in such an establishment as the Imphy works. This little community with a small population has only small resources in personnel: the manufacture of products of precision is so delicate and so sensitive to deviations that it is essential to obtain from all the staff not only complete obedience to all orders given but also a clear understanding of the usefulness and importance of these orders. It is not sufficient to teach the delicate nature of the work only to the laboratory staff and to accustom them to scientific discipline, but all the manufacturing staff must be taught likewise. The objective should definitely be that the whole works' staff should have the scientific outlook; this is attained by education.

The technical education given at Imphy is of three types: continuation classes for apprentices, courses of improvement for the development of the employees and technical staff, and conferences for the higher technical staff (engineers and heads of the manufacturing departments).

(1) *Continuation classes.*—These are designed to improve and extend the general education of apprentices, to explain their professional status, to teach them the technical principles of their work, and to develop their manual dexterity.

(2) *Courses of improvement.*—These are given to young men and women nominated for positions in the works and selected by their superiors as likely candidates for advancement; the choice is based on moral value, intelligence, and diligence. The selected pupils undergo a training, take notes, write accounts of their work, do practical exercises, and take examinations. In addition young foremen follow these courses with profit, attending simply as listeners without being under the necessity of doing written exercises or taking examinations, or even of attending regularly, which may be difficult in view of their duties in the works.

The course of study is spread over three years, at the end of which a new cycle is commenced, but the scholastic year extends only over the autumn and winter months so as to avoid all danger of overwork and not to interfere in any way with sports and gardening. There are 50 lessons per annum given on two days a week from 5.30 to 7 p.m. Conscious of the service which is thus given to them, the pupils and other listeners voluntarily make an effort to attend regularly.

The first two years are devoted to general courses, including mathematics, physics, chemistry, secretarial work and accountancy, while the third year is confined to specialized courses in which the pupils and other listeners are divided into three groups: employees, physical chemists, and mechanics.

Future employees in the commercial, library, and accountancy services are given lectures on the rudiments of the theory of administration, technical and commercial literature, secretarial work and accountancy.

The education given to the physical chemistry group aims at the development of operatives for the steelworks, casting, and heat-treatment shops, and senior workers in the research and control laboratories; it includes courses on metallurgy, metallography, assaying, and industrial measurement.

The mechanics who are the future designers and overseers of the forge, rolling mills, wire-drawing mills, tube-drawing mills, electrical plant, and maintenance services, are given instruction on the resistance of materials, hot- and cold-working of metals, electrotechnology, and the construction and operation of the machines.

The teachers are recruited from among the young engineers of the works; their aim is to attempt to imbue the employees with the scientific spirit without losing sight of the essentially practical nature of the education they give. On every possible occasion they instil into their students the principles of the scientific organization of manufacture, discrimination and measurement of factors, systematic study of their effects, determination of the most favourable arrangement of these factors, and maintenance of the normal course of manufacture by efficient control.

(3) *Conferences among the senior technical staff.*—Since they are fully occupied by the administration of their own departments, the engineers and senior staff have little leisure to complete their own scientific education. In view of the very large amount of technical work, and literature packed with review articles and patents, how can they find time to discern really original ideas and learn new essential facts? The problem would be quite insoluble without the spirit of collaboration. Under the direction of the scientific director, the engineers assume responsibility for collecting complete information on a subject useful to all, based on their own personal experience and on the literature; they then explain to their colleagues the results of their labours and the conclusions they reach. This mutual aid in the intellectual and scientific plan is one of the most efficacious applications of the motto " Each for all and all for each."

This work of imbueing all grades of the works' staff with the scientific outlook has evident advantages which have been confirmed by our own experience at Imphy.

Not only do the workmen and the supervisors acquire a consciousness of an immediate benefit, but, above all, *they learn to learn*; becoming capable of interpreting and assimilating the innumerable facts which come under their observation every day, they acquire more rapidly that reasoning experience which develops in them initiative. Certain of seeing their orders well understood, the engineers can leave their secondary duties to their assistants and reserve their activity for the more difficult duties. Above all, education creates unity of theory, harmonizes the different techniques, and, eventually, improves the output of the enterprise. The advantages in the moral and social order are just as great. The working population cannot fail to recognize the efforts made to allow them to educate themselves. Education creates team mentality and a house patriotism, that is to say a sporting spirit directed towards the better running of the works. It establishes and maintains contact between the students and the teachers and thus results in a better mutual understanding and the possibility of dissipating certain misconceptions.

"The flame of a solitary lamp," said J. B. Dumas, "can light a thousand others without losing any of its own brightness." More favoured still, the engineer who trains his own assistants and contributes to the erudition of his colleagues is the first to benefit from his efforts. Teaching obliges him to classify and clarify his ideas and to fill up the hitherto unsuspected lacunæ in his own knowledge; above all it ennobles him by giving him the opportunity to exercise the highest and most acceptable form of fellowship.

II.—Organization.

"To organize an enterprise," wrote Fayol, "is to supply it with all that is necessary for its functioning." This chapter will, therefore, be devoted to the staff, laboratories, apparatus, and technique necessary to all the operations which compose the scientific function.

§ 1. *Scientific Direction and Direction of the Work.*

In an enterprise in which the technique is simple and the evolution slow, a Thomas steelworks for example, the scientific function merges easily into the technical function, a single chief in charge of this function (called, according to the works, chief engineer, technical director, or the like) holding in his own hands all the organism of study, manufacture and control, and defining the programme of tests, specifying the task of the laboratories, regulating the conduct of the workshops, and co-ordinating the activity of all the technical services; but this simple solution is scarcely admissible in a works making special steels and alloys the very delicate manufacture of which is in a state of perpetual evolution.

Absorbed in his daily task, the technical director has scarcely the time to follow in detail the progress of metallurgical science; the outlining of the programmes of manufacture, the decisions necessary for harmonizing the conduct of the works and of surmounting unexpected difficulties, the care of the working costs and delivery, the delicate problems of workmanship, &c., occupy the first place in his thoughts. Engrossed by the present, how can he have the leisure in which to reflect at length on the metallurgy of the future?; and again, if he could find the time, has he the qualities, the preparation, and the training requisite for the scientific function? It is very difficult to find a man who is at the same time a scientist and a good technician; a talented composer is not necessarily a very good conductor of an orchestra.

"As an enterprise grows," wrote Fayol, "new agencies arise destined to replace that at first in charge of all the functions." In the same way as the technique becomes more advanced, more delicate, more complex, and susceptible to more rapid evolution it becomes more and more necessary to duplicate the technical function, which should be divided into two chief branches, the scientific function and the technical function proper, the appanages respectively of a scientific director and a works manager.

Unity of direction is assured by the managing director. This new organization appears at first sight to deviate from the principle of unity of direction, the other postulate of the theory of administration; however, as I will show later, this unity is not compromised. The difficulties which the duplication of the technical function might tend to create are easily surmounted thanks to the willingness of all. Besides, it cannot be gainsaid that this duplication is a necessity in an important establishment with numerous complex and precise techniques; the creed of the hierarchy should give place to the creed of competency.

§ 2. *Scheme of Scientific Organization of an Enterprise.*

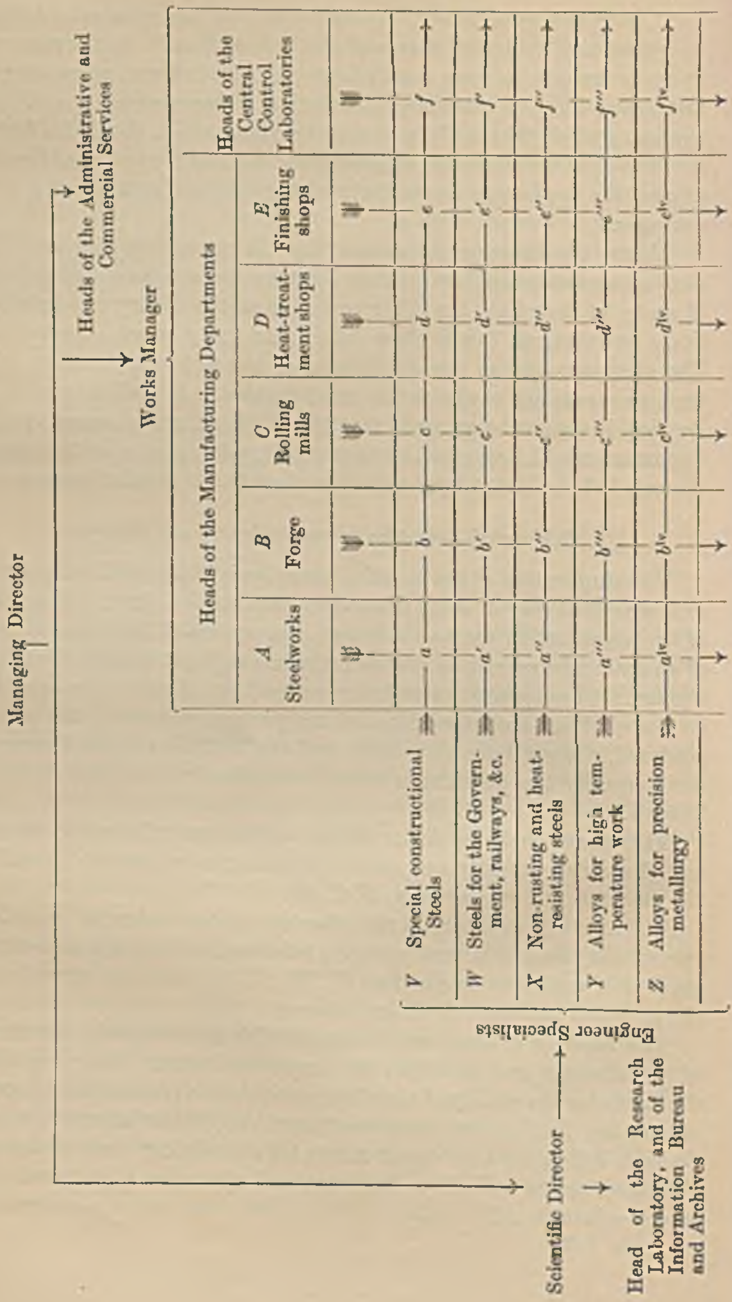
This duplication of the technical function is in fact realized in a more or less explicit way in many important metallurgical firms. The details of the organization vary a little since the powers of the high personnel of an enterprise cannot be confined within a rigid set of rules established *a priori*. These powers extend more or less beyond these rules according to the qualities and capabilities of the persons concerned, the services rendered, the positions they hold, and the traditions of the Company; but generally the problem is solved somewhat on the lines shown in Table I.

The works manager is in charge of the manufacturing services, and the various testing and control laboratories which are directed by the departmental managers *A*, *B*, *C*, &c.

The scientific director, on the other hand, has under his immediate control the research laboratories, the information bureau, and a certain number of engineers or chemists, *V*, *W*, *X*, &c., who are specialists in the principal productions of the factory.

The function of these men is to establish and maintain the theory of manufacture and to advise the executive branch; they lay down standards for the quality of the alloy, point out the precautions necessary in melting, forging and heat-treatment, &c., direct attention to the probable difficulties and suggest means for overcoming them in the case of all new orders and all works tests, and whenever a new product or process is introduced.

TABLE I.


Managing Director
Heads of the Administrative and Commercial Services
Works Manager
Heads of the Manufacturing Departments
A Steelworks
B Forge
C Rolling mills
D Heat-treatment shops
E Finishing shops
Heads of the Central Control Laboratories
V Special constructional Steels
W Steels for the Government, railways, &c.
X Non-rusting and heat-resisting steels
Y Alloys for high temperature work
Z Alloys for precision metallurgy
a
b
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bᴵᵛ
cᴵᵛ
dᴵᵛ
eᴵᵛ
fᴵᵛ
Engineer Specialists
Scientific Director
Head of the Research Laboratory, and of the Information Bureau and Archives

These *instructions* are transmitted to the foremen in charge of the work, *a*, *b*, *c* . . . *a′*, *b′*, *c′*, &c., either through the head of their department or directly, as shown by the horizontal arrows in the table, according to the "passerelle" (lit. footbridge) principle advocated by H. Fayol to speed up the transmission of orders. The foremen, however, receive their *orders* only from the works manager through the heads of their respective departments, as shown by the vertical arrows, just as the artistes in a concert actually obey only the conductor of the orchestra.

Thus the scientific director is responsible for the accuracy and practical value of the theory of manufacture, while the works manager is alone responsible for putting it into practice; he alone, decides, as final arbiter, the proper measures to be taken to reconcile technical perfection with regular production, the best utilization of men and material, a low cost of production and a correct time of delivery.

The organization adopted obviously cannot give good results unless there is a perfect understanding between the scientific director and the works manager; such an understanding is easy if it is based on mutual esteem, confidence, and friendship, and if it inspires pride in the prosperity of the enterprise.

§ 3. *Research and Works Laboratories.*

As has already been said, the scientific work of the factory is divided into research proper, development tests, works tests to apply the results of research, and control tests. The development work is carried out in the shops, but the other tests are divided between the research and works laboratories, the pure research work being kept entirely separate from any kind of works test, since the former is concerned in preparing for the future whereas the latter deals with the present. Research explores the unknown step by step, carefully and conscientiously; it requires very detailed preparation, a calm atmosphere, continuity of application, and concentration of thought. Works and control tests, on the other hand, are based on known facts; if they are to be sufficiently precise to yield certain results they must have the essential qualities of reproducibility, simplicity, rapidity, and cheapness. Frequently they are only simple identification tests. Thus, it is necessary to separate the two groups of laboratories, since their preoccupations, methods, and outlook are entirely different.

The works laboratories comprise one or more central laboratories and the departmental or shop laboratories. The former undertake the control of raw materials, intermediate products, auxiliary products, and manufactured goods. Whether the work is for the verification of an internal specification or for a customer's specification, determinations are made of the composition, the mechanical properties, and certain chemical or physical properties on which the use of the alloy depends: the constitution, structure, and homogeneity by micro- and macrography; the quenching conditions for a steel by dilatometry; the behaviour of the alloy in corrosive conditions; the magnetic and electrical properties, the modulus of elasticity and internal friction, the coefficient of expansion, &c. The central laboratories also carry out tests which do not relate to difficulties of a new character and which do not require a very delicate technique; these are left to the research laboratory, as also are certain control tests which are particularly difficult and require great precision.

The managers of the works departments are responsible for their own technique (and, therefore, for deviations therefrom), and must consequently be provided with means for ensuring smooth operation of their departments; in most cases, this is best effected by attaching to the workshops a departmental laboratory in which the necessary work can be carried out more rapidly and efficaciously than in the central laboratory. For example, at Imphy there is a small laboratory attached to the steelworks in which the course of the refining operations in making special steels is followed so as to determine the exact time of casting, and there is also a special equipment at the service of the heat-treating department to check pyrometers and control the hardness of the alloys, &c. Thus, the departmental laboratory with the simplest organization and under the direct control of the head of the department contributes to the smooth progress of the work, and, being so close to the actual manufacturing work it assists in detecting minor deviations without delay; thus it plays the part of a "feeler" for the scientific director.

§ 4. *Staff Connections and the Organization of the Work of the Laboratory.*

Grouped in sections according to their special type of work, the operatives obey their foremen, who are themselves directed by the engineers in charge of the laboratories. These latter outline broadly the work according to the general plan of research or control and according to the difficulties which have given rise to the tests, they study the application of new methods of investigation, superintend the installation and putting into operation of new apparatus, codify the manipulative technique, and collate the experimental results, elaborating, discussing, and correlating them with information in the literature and reaching the necessary conclusions which enable them to modify the scientific theory, accept or reject a product, give advice to the workshops, or reply to suppliers or customers, &c.

The foremen, on their part, prescribe the details of the tests, fix the task of each operative, and supervise the work; they check the calculations, see that the results are coherent, if necessary transfer them to diagrams, and collaborate in the interpretation of the observed facts.

In the installation of the laboratories, the apparatus and mountings and the methods of working have been so designed as to obtain the greatest possible number of accurate results in the shortest time with the minimum of cost and fatigue. The apparatus is specialized and always arranged in the order of use, the manipulations are standardized on Taylor's principle, and the hours of working are designed to obtain the best out of the operatives. Thus, in the physico-thermal laboratory at Imphy two women operatives look after four recorders, preparing the specimens, mounting them, carrying out the tests, developing the films, calculating the results, and keeping notes, but to attain this result everything is run automatically so far as possible. To give only one example, annealing and tempering operations follow a predetermined "temperature-time law" with the aid of a thermal cycle regulator which not only suppresses every large source of error and assures a precision quite unrealizable by hand-controlled heating, but also relieves the personnel from a tedious and monotonous task.

III.—Direction and Co-ordination.

From all that has been said it will be seen that the scientific director occupies a position as it were at the centre of a double pyramid; towards him converge the various problems—present and future needs of customers pointed out by the commercial service, perspectives opened out by the researches, bibliographical information, and incidents and difficulties of the manufacturing operations, and from him emerge suggestions for solving these difficulties, improving the processes, or developing new products, these suggestions being prompted by the results of laboratory work and tests in the workshops.

The scientific director is in direct charge of the personnel of the research laboratory and he exercises a less direct, but none the less important, control over the personnel of the works laboratories, and the men in charge of putting works-scale tests into operation, who are really under the authority of the works manager. Actually he it is who outlines the general plan of control, dividing up the work according to the difficulties of manufacture, and he develops methods and, when necessary, the simplest but most efficacious type of apparatus for the tests in view. He is also responsible for drawing up the programme for putting the research results into practical operation, and he sees to the judicious division of the work between the laboratories and the workshops, the synchronization of their progress, and the coherent character of the tests; in a word he co-ordinates the activity of all the organs which make up the scientific function.

§ 1. *Direction of the Personnel of the Laboratories.*

Chosen with care and trained to delicate work and scientific discipline, the foremen and their assistants are very easy to direct; they work in hygienic and comfortable surroundings, and in an admirable and ordered routine, and their work is interesting and not too hard, the material organization (automatic apparatus) of the laboratories having suppressed the tiring and tedious jobs.

It is not sufficient, however, to give them a professional training only; they should also be made to understand the utility of their work and the importance of their mission; in other words they must be imbued with a kind of scientific mysticism. The most potent factor to this end is the example of their superiors. If they are worthy of their position, they (*i.e.* the engineers of the laboratories) have not to be stimulated but only directed, and this is a delicate task for the scientific director; he must guide them without curbing their initiative and without decreasing their personality, *i.e.* he should follow the advice of an industrial magnate and "suggest rather than impose." He will respect their legitimate ambitions and seize opportunities of allowing them to be fulfilled; in other words he will act in such a way that his collaborators, in the words of Descartes, "will be grateful to him, not only for the things he has explained but also for the things he has voluntarily omitted, to allow them the pleasure of inventing them themselves."

§ 2. *Co-ordination of the Scientific Work.*

In a factory making special alloys there are always a large number of problems. Are they to be approached all together, at the risk of sterilizing the work by excessive dispersion, or is the whole activity to be concentrated on two or three important problems, thus putting the workshops and commercial service in an embarrassing position as regards the others? Between these two extremes, equally prejudicial, there is a happy mean.

The works manager and the scientific director should meet, with their principal colleagues, in periodic conferences at which a plan of campaign is elaborated for the approval of the managing director. For certain problems a provisional but rapid solution will be found by simple tests in the laboratory or workshops, but other more important and more difficult problems will give rise to lengthy researches.

The plan of action once decided upon, it remains to divide the work between the various executants. In particular, the research laboratory and the control and testing laboratories, although they are under different heads and their objectives are different, must come to a mutual agreement. The division of the experimental work is made with care to use the best personnel, to make the best use of the available installations and to avoid all unnecessary expense and a double use of any apparatus. At Imphy, for example, a large number of analyses necessary for the research work are carried out by the central chemical control laboratory and conversely the research laboratory makes certain very delicate control tests. This mutual exchange is subject merely to the formalities which regulate the execution by one department of work for another; it is made easy by the spirit of collaboration which animates all the personnel of the enterprise.

Having divided the work, the tests are commenced and the scientific director surveys their execution and verifies the correct application of the methods and the accuracy of the manipulations. With the aid of his assistants he centralizes the results, completes and, if necessary, verifies, and elaborates them, and from them finally reaches conclusions of a scientific nature. As for decisions of a practical nature, these are made during conferences of the type already mentioned; for problems which are not solved a new programme of tests is laid down, and for those for which a solution has been found the practical application of this is discussed, including ways and means for putting a new process into operation or for the commercial launching of a new product.

IV.—CONTROL.

The scientific director has a twofold task of control—to organize the technical control of the manufactures and to control, in its entirety, the scientific function.

§ 1. *Technical Control of the Manufactures.*

The hero of a witty comedy, Dr. Knock, desirous of extending his patients, attempted to attract healthy people by telling them that " health is an unstable and transitory condition which never portends anything good." This humorous definition is scarcely an exaggeration when applied to a badly controlled manufacture, since its course is subject to deviation for many reasons.

Inevitable changes occur in the composition and physical state of the raw materials, the fuel, and the refractories; who can guarantee a constant quality for the scrap used by a steelworks? Atmospheric conditions affect not only the operation of the blast furnace and reverberatories, but also that of electric furnaces. A fatal consequence of the law of minimum effort is that oral traditions always have a tendency to vary, vigilance becomes deadened, and strict prescriptions become weakened. Sometimes these small disturbing factors compensate one another and no ill-effects are observed for a more or less long time; then, suddenly, they all work in one direction, the work is thrown into confusion, and it is difficult to find a remedy since, owing to the large number of factors which are concerned, it is almost impossible to know in which direction to look for the cause of the trouble. The only way to maintain a smooth course of manufacture it to enclose it in the armour of a rigid control.

The armour should be close-knit; in principle every measurable factor should be taken into account, and, without careful consideration, nothing should be excluded even if its influence appears negligible at first sight. When Houdremont stated that the humidity of the air should be noted during the melting of steel much scepticism was aroused, but, from the data subsequently collected, a valuable theory of the rôle of hydrogen in the formation of flakes was established.

The armour should also be rigid; in other words the control tests should be significant and of sufficient accuracy. The only difficulty consists in reconciling these conditions precisely with the necessity for avoiding a slowing down of the manufacturing processes and an increase in the cost of production.

§ 2. *General Plan of Control.*

Since the quality of a metallurgical product depends on its whole history, control must start with the raw materials and extend over the auxiliary materials, the steps in the manufacture, the intermediate products and, finally, the finished product.

(a) *For the primary and auxiliary materials* such as moulding sands, refractories, &c., chemical analysis is universally employed, but is rarely sufficient. The grain of a cast iron reacts by heredity on the properties of pieces cast from a second fusion. For foundry sands it is the practice to make a screen analysis, to measure the coherence, plasticity, &c., and to determine the melting point, resistance to crushing at high temperature, expansion, and rate of corrosion by slags; all these tests are made in the works control laboratories.

(b) *Control of the process of manufacture* is delicate to organize; the armour should prevent deviations without paralyzing movement and should cost no more than it saves. Among the numerous factors involved it is necessary to select those which have the greatest repercussions on the quality of the product. The temperature of furnaces is always controlled, but the atmosphere in the melting furnaces and in the heat-treatment processes must not be neglected.

In the same way it is important to ascertain the steps in the manufacture where it is most useful to standardize the quality of the product. After casting an alloy it is the rule to make tests on a cast specimen by chemical analysis and determination of the physical and mechanical properties. It is often of advantage, however, to split one of the principal ingots below the casting head in order to reveal the macrostructure and to verify the soundness. The control of a lot of bars of constructional steel is effected by examining the surface after rolling, by measuring the hardness, by determining the superficial decarburization after a prolonged anneal, and by measuring the mechanical properties and examining the microstructure after heat-treatment. The cold-rolling of magnetic ferro-nickel sheets is controlled by measurements of the permeability at convenient stages in the rolling and heat-treatment operations, &c.

Part of this experimental work is in charge of the central laboratories, and the remainder is done in the laboratories attached to the various shops under the direct supervision of the overseers, who thus acquire a greater knowledge of their work.

(c) *The control of the finished products*, which precedes delivery of the goods, is divided into two parts: checking the identity, appearance, and dimensions, which is carried out by the despatch services, and control of the qualities defining the uses of the goods—tenacity, elastic limit, and resilience for metal required for mechanical service, expansion of Invar standards of length, thermo-elastic coefficient of Elinvar tuning forks, &c.—which is conducted at the central laboratories, except for a few delicate tests which are confided to the research laboratory.

Often the final tests result in the destruction of the test-piece, *e.g.* the firing of a shell. The piece thus sacrificed is regarded as representing the mean of the lot to be delivered. Mechanical tests as ordinarily carried out on standard test-pieces also involve an apparent sacrifice; if, to avoid this, recourse is had to separately cast or forged test-pieces the results are very uncertain. "*A priori*," says Portevin, "the relation between the properties of the test-pieces and the material which they purport to represent is unknown and there is every chance that one or the other will be different."

The solution of this problem is to use testing apparatus which requires only small specimens, such as the micro-machine recently developed in the Imphy laboratory. The tensile specimens, having a diameter of

1·5 mm. and an effective length of only 7 mm., are sufficiently small to be taken without damage to the majority of pieces by making a hole for a bolt or a groove for a cotter pin.

§ 3. *Properties Submitted to Control.*

In working out their ideas constructional engineers apply the theories of physicists but often prove their insufficiency. The theories relate to simple mechanisms and to ideals such as the perfect gas or the perfectly elastic solid. Again, the functioning of real machines is more complex than that of theoretical, and the true properties of bodies have not the beautiful simplicity of those of ideal bodies.

(*a*) Sometimes an approximation is sufficient. Works of art, the members of a framework, and machines which work slowly, when constructed on the formulæ of the resistance of materials, have a solidity which is attested by experience; for such applications steel approaches sufficiently closely to a perfectly elastic body. In the same way it is possible to calculate very closely for an electrical apparatus. Under these conditions, where theory agrees closely with practice, the study of solids is reduced to a measurement of certain elementary properties such as the modulus of elasticity, elastic limit, density, resistivity, magnetic permeability, specific inductive power, &c.

(*b*) More often it is impossible to neglect the phenomena of which the profound nature is still obscure, the mechanism imperfectly understood, or the factors too numerous to allow for the quantitative elucidation of their action. Thus, the fracture of a piece of metal by vibration is evidently dependent on the elastic hysteresis, but the internal friction is not sufficient by itself to characterize the tendency to fatigue failure; the crystallization of the metal, the distribution of inclusions and surface imperfections are also factors in fatigue failure and their quantitative action is still uncertain.

The resistance of a glassworks mould to reticular fissuration is a function of numerous factors such as expansion, capacity for deformation, specific heat, thermal diffusibility of the metal, thickness of the walls, rhythm of the operation, relative mass and dimensions of the mould and the moulding, &c. In similar cases the control of the product is based only on a complex property. Such a property aims to characterize broadly the value of a product for a definite purpose or process, such as resistance to alternate bending, castability, weldability, forgeability, corrodibility, &c.

(c) Finally, control is exercised sometimes not on properties on which the use of the material depends, but on other properties allied with these and easier to control. Thus, except in unusual cases, a consignment of vehicle springs is not tested by alternate bending; the tests are confined to chemical analysis and determinations of the elastic limit, hardness, resilience, and flexibility, since long practical experience has shown the perfect fitness of springs having values for these properties within certain limits. Identification tests are of a similar nature; they prove simply that the piece examined is sufficiently close to the standard which experience has dictated.

Short-time mechanical tests at high temperatures are simple identification tests, since only very prolonged tests at very low rates of creep can lead to values of the limiting charge which can be used in practice.

§ 4. *Quality of the Methods of Control.*

(*a*) The methods used for the control of the elementary properties are those of the physicist and chemist adapted to the needs of industry by being made simple, rapid, certain and, so far as possible, automatic.

(*b*) For a complex property characteristic of the aptitude of a product to undergo an industrial operation or to support a certain fatigue in service, the method of testing aims to reproduce this operation or method of fatigue.

Everyone knows the spiral method for determining the castability of an alloy. At Imphy the weldability of an alloy is determined as follows:[6] Two sheets 12 mm. wide are butt-welded, using coated electrodes of the same or different composition and the arc or oxy-acetylene torch under standard conditions as regards rate of welding, amount of metal deposited, and power or gas consumption. A small bar 1·5 mm. in diameter and 40 mm. long is then machined perpendicular to the line of weld and this is cut by the micro-machine into sections 1·5 mm. long with automatic recording of the strain–depth of cut curves; from these curves diagrams of the resistance, elastic limit, and elongation in shear fracture along a line perpendicular to the weld are constructed. These diagrams are characteristic of weldability.

(*c*) Before instituting an identification test it is necessary to be quite certain that the property tested bears a definite relation to the property representing the value of the material in use. The method of determining the resistance of an austenitic non-rusting steel to corrosion-cracking in steam by the use of the Strauss reagent gives results which appear to be of practical value, but the value of a corrosion test in dilute sulphuric acid for determining the resistance of a steel to rusting in atmospheric exposure is extremely doubtful. "An identification test," says Portevin, "should be significant, unaffected by the personal factor, quantitative, and appropriate to the purpose in view."

In instituting a control technique for routine operations, use is made of Taylor's rational methods of organization. For example, for the determination of the density of a specimen taken from a cast or welded article in order to test its soundness, the hydrostatic balance is employed using, instead of water, carbon tetrachloride, which is 1·6 times as dense and which wets metal inadequately degreased. The cylindrical test-pieces are machined to standard sizes so as to be of approximately equal weight, and the weighings in air and in the tetrachloride are made in series; under these conditions one operator can make a dozen accurate determinations in an hour.

Even if sometimes the methods used in the tests are the same for the research as for the works tests, it is often preferable to keep the tests separate, reserving for the research laboratory the more delicate technique and more precise apparatus and for the works laboratory the more rapid methods and more robust instruments. Table II shows how this is accomplished at Imphy.

§ 5. *Some Control Apparatus.*

To illustrate the considerations just discussed three types of apparatus recently developed at Imphy will be described.

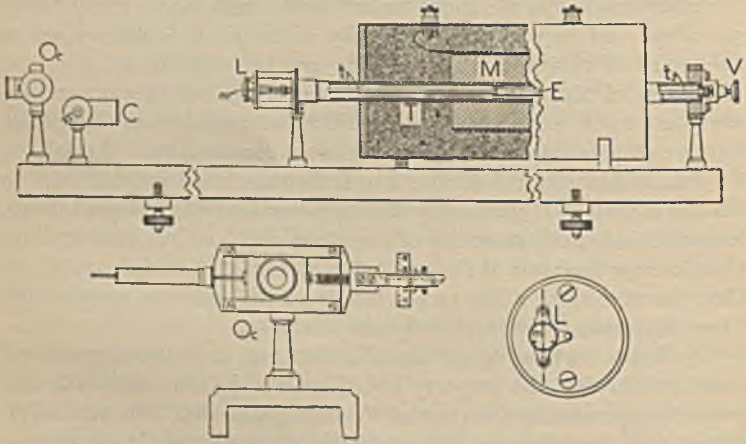

FIG. 1.—Dilatometer of High Sensitivity for the Control of Invar.

Dilatometer for the control of Invar rods (Fig. 1).—The coefficient of expansion of Invar varies from 0 to $1{\cdot}5 \times 10^{-6}$ per ° C. according to the composition and heat-treatment. The commercial value of the alloy is based on the magnitude of this coefficient, so that a sensitive and accurate apparatus must be used for its control.

The specimen, E, used is a rod 50 cm. long which is centred by collars

TABLE II.

Metallurgical Product.	Properties Characteristic of its Value in Use.	Research Apparatus.	Control Apparatus.
Alloys of definite expansion Invar Bimetals	Coefficient of expansion	Differential dilatometer (photographic recorder)	Differential dilatometer with photographic or mechanical recorder Special dilatometer * Special recorder *
Alloys for electrical resistances	Resistivity Temperature coefficient of resistivity	Wheatstone bridge Galvanopyrometer	Wheatstone bridge Galvanopyrometer
Base metal thermocouples	Thermo-electric power	Galvanopyrometer	Galvanopyrometer
Elinvar	Thermo-elastic coefficient	Coulomb pendulum	Coulomb pendulum Stroboscopic apparatus for the control of diapasors
Magnetic ferro-nickel Mumetal	Initial permeability Rayleigh coefficient	Maxwell bridge (measurement of the self-induction of a toroidal coil) Magnetometer	Simplified bridge for testing toroidal cores. Magnetometer
Ferro-nickels for thermal compensators for magnets (NMHG)	Thermomagnetic coefficient	Ballistic galvanometer (Rowland's method applied to different temperatures)	Thermomagnetometer with special recorder *

* Described in Section 5.

in the fused silica tube, T, and rests on the silica rod, t_2, which in turn rests on the adjusting device, V, while a second silica tube, t_1, transmits the expansion to a lever rod, L, of the optical device. The deviation of the mirror attached to the lever is measured accurately by the displacement of the micrometer eye-piece, O_c, which is moved in such a way as to keep on the cross-wires the image of a thin wire stretched in front of the collimator opening, C. Readings are made to 0·02 mm., the amplifying power of the lever is 200, and thus the expansion is measured to 0·1 μ approximately.

The rod is heated by an electric resistance furnace, and the temperature is kept uniform by a thin aluminium sleeve, M, and controlled by three nickel–chromium/nickel–copper thermocouples, the hot-junctions of which are inserted in small cavities in the middle and at both ends of the rod. The couples are standardized against a precision mercury thermometer checked at the International Bureau of Weights and Measures, and reading to 0·05° C. In calculating the mean temperature of the rod a parabolic distribution along the length is assumed.

The amplification factor is determined geometrically and the expansion of the silica, the remaining constant of the apparatus, is deduced from a series of measurements made by Ch.-Ed. Guillaume at the Pavillon de Breteuil. The micrometer is read at 20°, 30°, and 40° C., and the value of the true coefficient of expansion at 20° C. (α_{20}) is calculated from the results, with a probable error of less than $0{\cdot}02 \times 10^{-6}$ per ° C.

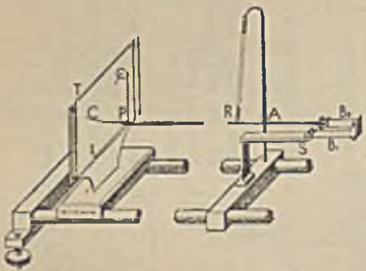

Fig. 2.—Recording Apparatus for Testing Bimetals by Determining the Villarceau Coefficient.

Apparatus for the control of bimetal strips (Fig. 2).—With the discovery of the reversible ferro–nickels, Guillaume suggested that their very different expansion properties and good mechanical properties should make them valuable for the manufacture of precision bimetal strips. Such strips are now made regularly at Imphy. In association the ferro–nickels produce bimetals having a more or less wide temperature range of usefulness and sensitivity according to the composition of the other metal. This sensitivity is expressed by the ratio $\frac{d\frac{1}{\rho}}{d\theta}$, where $\frac{1}{\rho}$ is the curvature at temperature θ, and thus varies in inverse proportion with the total thickness e of the strip and directly with Villarceau's coefficient V, *i.e.* $\frac{d\frac{1}{\rho}}{d\theta} = \frac{V}{e}$.

The parameter, V, is of the nature of a coefficient of expansion; it has its maximum value when the thickness of the two sheets is in inverse ratio to the square root of the moduli of elasticity of the two metals, therefore $V = 1{\cdot}5(\alpha_2 - \alpha_1)$, *i.e.* V is one and a half times the difference in the coefficients of expansion of the two metals. A high value of V therefore indicates a correct ratio of the thicknesses of the two components as well as a judicious choice of alloys.

The very simple apparatus shown in Fig. 2 serves to measure V for a bimetal plate which can be rolled to strip of any desired thickness. The apparatus combines in a diagram the deviations of two bimetals, B_1 and B_2, carried by a support S and heated to the same temperature by an electric furnace; B_1, a standard bimetal made of two ferro-nickels, rigid at high temperature, serves to indicate the temperature in the test, while B_2 is the test-piece having a length of 25 mm., a width of 7 mm., and a total thickness of 1 mm. On heating the bimetals curl in two directions perpendicular to one another, thus forcing the pen, P, to describe the curve, C, which represents the deviation, δ, of the bimetal B_2, as a function of the temperature θ.

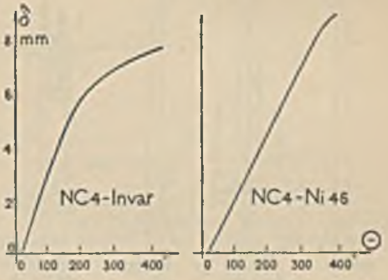

Fig. 3.—Deviation-Temperature Curves Relative to the Two Formulæ of Bimetals, and Traced by the Apparatus of Fig. 2.

This curve is inscribed point by point on the plate T, by means of an alternating movement which eliminates friction of the pen on the paper. Fig. 3 shows two curves obtained in this way; they are sufficiently clear for calculating the value of V, which is seen to be about $0{\cdot}5 \times 10^{-6}$ per ° C. in this case.

Thermomagnetometer for the control of the alloy NMHG (Fig. 4).—A ferro-nickel containing about 30 per cent. of nickel has a Curie point a little higher than room temperature; its magnetic permeability therefore decreases rapidly as it approaches this point, and this change is almost exactly reversible. Meylan has found an ingenious use for this alloy of high thermomagnetic coefficient, which has been made for nearly thirty years at Imphy under the name of "NMHG"; it is used for the thermal compensation of apparatus having a permanent magnet, such as meters, galvanometers, tachymeters, &c.

The flux of a magnet decreases with increase in the surrounding temperature, but if it is shunted by a rod of "NMHG" alloy the derived flux decreases at the same time and if the dimensions are suitable the principal flux can be kept at a constant value. Hence the value of the alloy in use depends on the thermomagnetic coefficient at room temperature.

Like all ferrous alloys, ferro-nickel "NMHG" contains carbon, silicon, and manganese, and these additions have an additive effect in lowering the Curie point. This displacement is so rapid that the manufacture of the alloy would be a very delicate process if the Curie point could not also be displaced by quenching or annealing; fortunately, however, heat-treatment will change this point by as much as 20° C. and this fact is utilized in adjusting the point to the desired temperature. On the other hand it is essential to supervise with the greatest care all the thermal operations to which the alloy is subjected in order to avoid irregular results; hence the necessity for a severe control not only during manufacture but also after the last treatment.

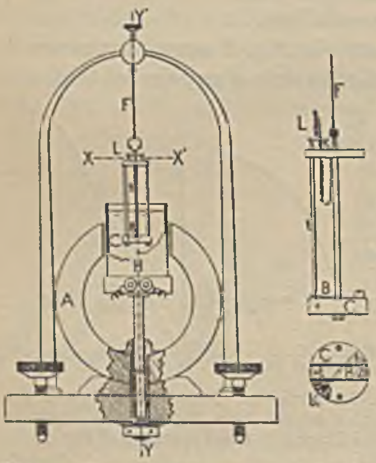

Fig. 4.—Thermomagnetometer for Testing the Alloy "NMHG" with a High Thermomagnetic Coefficient.

This control is easy thanks to the thermomagnetometer shown in Fig. 4, which utilizes the method of P. Weiss. The specimen, a rod, b_1b_2, 20 mm. long and 1 mm. in diameter, is carried by a block of copper, *C*, suspended by the torsion wire, *F*, in the field of the permanent magnet, *A*, which can be turned around the vertical axis, *YY'*. *A* is turned until the couple exerted on the rod is a maximum, at which point it is fixed; in this position the axis of the rod is at an angle of 45° to the lines of force of the magnetic field, and the couple measured by the angle of deviation of the instrument is proportional to the square of the magnetization, $\mathfrak{J}^2$. Temperature variations are obtained by using the oil-bath, *H*, the oil in which is first cooled to $-$ 30° C. and then slowly heated to 110° C. by a small electric radiator, the temperature being controlled by the bimetal strip, *B*, made of two non-magnetic metals and fixed to the copper block. The deviations of the bimetal are transmitted to the optical lever, L, by a small silica rod, t.

It can be seen that the optical lever can turn both about the horizontal axis, XX', according to changes in the temperature, θ, and about the vertical axis, YY', according to variations in the magnetic couple, and therefore the curve of $(\mathfrak{J}^2, \theta)$ is traced photographically on the sensitive paper by the movement of the lever during the test. Two such curves are shown in Fig. 5; their perfect sharpness is apparent.

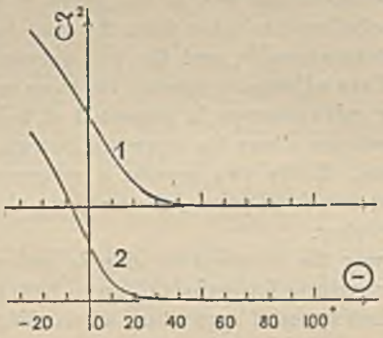

FIG. 5.—Magnetization-Temperature Curves Recorded by the Thermomagnetometer shown in Fig. 4. "NMHG" alloy with 29·8 Per Cent. Nickel. (1) Alloy Air-Quenched from 850° C. and Reheated at 450° C. for 7 Hrs.; (2) Alloy Air-Quenched from 850° C. but not Reheated.

The operator in charge of the test has standard curves (corresponding to the different applications of the alloy) on sheets of tracing paper, and by simply placing one of these sheets over the curve obtained in the test he can judge the quality of the metal immediately. Two curves can be obtained in one day of eight hours, but, since the apparatus is automatic, only one hour's effective labour is required.

§ 6. *General Control of the Scientific Function.*

Once the laboratories have been supplied with adequate material and with a competent staff, the research programme and works tests mapped out, the work divided among the various executants and the necessary co-ordination measures taken, it rests with the scientific director to control, in its entirety, the scientific function. There is first the problem of command or direction, which will not be insisted upon now, and secondly there is the technical problem.

It is particularly essential to avoid slow changes or "drift" in the processes and apparatus which will inevitably occur unless care is taken to prevent them. The scientific director and his colleagues have no time to follow all the day's tests on the same day, but must allow the results relative to each problem to accumulate for a longer or shorter period before considering them in series. The perfectly coherent character of all these results, however, cannot be obtained except at the price of "an anxious vigilance" at all times.

Among the means used to prevent drift should be mentioned the checking of one apparatus against another of the same type and the simultaneous employment of independent methods of measurement. At Imphy the 18 thermocouples used in the group of apparatus for the thermal analysis of alloys are taken from the same batch of wires and are, therefore, interchangeable, and the wall galvanometers to which they are attached are adjusted to exactly the same sensitivity. If one of the couples or galvanometers is suspected of being unreliable the arrangement of switches allows the suspected instrument to be changed in a few moments. Every two months a systematic check on the couples is made at two fixed points, the melting point of gold and the boiling point of sulphur.

In the same way the temperature of rods undergoing mechanical tests at high temperatures for periods of up to 1000 hrs. is checked by two entirely distinct types of apparatus—a recording expansion pyrometer and a thermoelectric couple. Since the causes of error of these two instruments are entirely different, agreement in the temperatures recorded is a guarantee of their accuracy.

CONCLUSIONS.

If two words will suffice to characterize the rôle of science in a works, namely, *maintain* and *improve,* the scientific function comprises a whole series of complex and delicate operations. I have attempted to describe these, to show their mechanism, and to explain their importance for the security of the routine and the progress of the enterprise.

In order to classify these operations I have naturally referred them to the five fundamental operations of Fayol's administrative doctrine : foresight, organization, direction, co-ordination, and control, and this affords me another opportunity to acknowledge my indebtedness to the eminent founder of this doctrine, the creator of the Imphy research laboratory, and the leader of men who has "catalyzed" my career.

The task of a scientific director is manifold, difficult, and sometimes painful; to produce good work it is necessary for him to love his profession, and to have an invincible faith in the fertility of methodica research, an obstinate tenacity, and the spirit of continuity. Unlike the student in the educational laboratory, he cannot choose his own subjects for research; in attacking less novel problems he has less chance of making an important discovery. He should not aim at making discoveries, according to the advice of Le Chatelier, because the chance of so doing is very small and the practical results often deceiving. More modest than his ambition, he will endeavour to make " small improvements which are additive and eventually lead to advantages the importance of which grows without limitation."

Although thus confined, this task is intensive. In the moral sense he has the satisfaction of doing useful work, and in the scientific sense his efforts sometimes find happy compensations. If he frequently knows that " sadness of not knowing," on which E. Picard wished to write a chapter, sometimes, for the price of his " long patience," he finds that " joy of knowing " celebrated by Termier in a whole beautiful book. And of this I cannot find a better witness than the illustrious physicist " that man of thought and man of action, equally ready to manage the firm of White and Thomson as to speculate on the degradation of energy, that savant whose life," said E. Picard, " is a model, perhaps unique, for those who will not separate theory from practice " ; I mean, Lord Kelvin. " In the pursuit of truth work is its own reward, and allows the scientist to accomplish with joy his daily task."

REFERENCES.

[1] H. Le Chatelier, "De la méthode dans les sciences expérimentales," Paris: **1936.** (Dunod.)

[2] P. Chevenard, " Méthodes de recherches et de contrôle dans la métallurgie de précision," *Bull. Soc. Ing. civils France*, 1923, **76**, 932.

[3] P. Chevenard, " L'installation et l'organisation d'un laboratoire sidérurgique moderne," *Bull. Soc. Ing. civils France*, 1932, **85**, 1109.

[4] H. Fayol, " Administration industrielle et générale," Paris: **1917.** (Dunod et Pinat.)

[5] P. Chevenard, " Micromachine à enregistrement photographique pour l'essai mécanique des métaux," *Bull. Soc. d'Encour. Ind. nat.*, 1935, **59**, 134.

[6] P. Chevenard and A. Portevin, " Micromechanical Study of Welds," *Iron Steel Inst., Symposium on Welding*, 1935, **2**, 333.

FLUXES FOR USE IN SOFT-SOLDERING.* 732

By J. W. WILLSTROP,† B.Sc., MEMBER, A. J. SIDERY,† Assoc.Met. (Sheff.),
MEMBER, and H. SUTTON,‡ D.Sc., MEMBER.

SYNOPSIS.

An examination was made of the soft-soldering of materials that are not very easily soldered with the aid of the usual fluxes, particular attention being devoted to the soldering of corrosion-resisting steel and to the corrosive effects of flux residues. The features of ortho-phosphoric acid as a flux and the properties of fluxes containing organic phosphates as the active agent were investigated. Fluxes based on organic phosphates permit easy soldering of many materials without residues of the fluxes causing corrosion. The fluxes may be used satisfactorily on corrosion-resisting steels and other materials not readily soldered with the use of fluxes containing zinc chloride as the active constituent.

It is well known that the production of soft-soldered joints in certain materials, *e.g.* corrosion-resisting steels, zinc, aluminium–bronze, &c., with the fluxes usually employed in ordinary soft-soldering operations is a matter of some difficulty. In some cases soldering is much facilitated by the use of a zinc chloride flux to which some free hydrochloric acid has been added, but residues of such fluxes, which must almost inevitably remain in complicated or re-entrant joints, are liable to cause serious corrosion. For some purposes the use of chloride fluxes, even without added free acid, is so liable to result in corrosion by flux residues that the use of such fluxes is undesirable. A well-known method for reducing appreciably the tendency of the flux residues to cause corrosion is to use fluxes in the form of pastes made up with mineral jelly and other similar substances, but the success of this method is at the best only partial.

The object of the experiments described in this paper was to evolve a flux which would be free from undesirable corrosive effects, but which at the same time would be capable of exerting a satisfactory effect in soft-soldering operations on a wide range of engineering materials.

The first experiments were made with a number of substances including dibasic ammonium phosphate, ammonium benzoate, borax

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and boric acid as flux. Corrosion-resisting steels of the 18 per cent. chromium : 8 per cent. nickel, 18 per cent. chromium : 2 per cent. nickel, and 13 per cent. chromium types, cleaned with emery cloth or by pickling anodically in a bath containing one-third by volume of concentrated sulphuric acid and 1·5 per cent. of potassium dichromate, were used in the tests, the solder being ordinary tinman's solder (tin 65, lead 35 per cent.). Of these fluxes, dibasic ammonium phosphate was found to be the only one of practical value. In this case it was observed that the solder began to unite with the steel after the soldering-bit had been applied long enough to heat the ammonium phosphate above its temperature of decomposition. It was concluded that the fluxing action was due to the product of decomposition—meta-phosphoric acid.

PHOSPHORIC ACID.

As meta-phosphoric acid is, at ordinary temperatures, a hygroscopic solid and, therefore, not convenient to use in practice, it was decided to try ortho-phosphoric acid, which, in its commercial form, is a somewhat syrupy liquid having a purity of about 89 per cent. Joints were made successfully with all the corrosion-resisting steels mentioned above with the tin 65 : lead 35 per cent. solder and also with another solder containing tin 50, lead 47·5, antimony 2·5 per cent. The ease of "tinning" the steels with this flux appeared comparable with that of "tinning" brass with the use of a zinc chloride flux. Phosphoric acid could be used equally well for soldering ordinary steels, brass, copper, &c., whilst for soldering aluminium–bronze, zinc, and cadmium- or zinc-plated steel it appeared to be much superior to zinc chloride fluxes.

The effect of diluting phosphoric acid on its action as a flux was investigated. Samples of commercial acid (89 per cent.) were diluted so as to contain, respectively, 61, 48, and 37 per cent. of phosphoric acid. Although soldering was possible with all these solutions, their efficiency noticeably decreased as the phosphoric acid content became less, and it appeared necessary to use a larger quantity of the diluted acid. It would, therefore, seem that phosphoric acid may be used most economically in concentrated form.

CORROSION EXPERIMENTS WITH JOINTS MADE WITH PHOSPHORIC ACID OR ZINC CHLORIDE.

Three corrosion-resisting steels were used in sheet or strip form representing the main types : (*a*) straight 12–13 per cent. chromium steel (D.T.D. 46A); (*b*) 16–20 per cent. chromium, 1–2 per cent. nickel (D.T.D. 60A); (*c*) 14–20 per cent. chromium, 6–12 per cent. nickel

(D.T.D. 57A). Lapped joints were made of small sheet or strip samples cut from pieces which had been cleaned anodically in sulphuric acid containing potassium dichromate. In the case of the austenitic steel (*c*) joints were also made in the bright-rolled, "as received" material.

The solders used were: (1) B.S.I. Grade A—tin 64–66, antimony ≯ 1·0 per cent.; (2) B.S.I. Grade B—tin 49–51, antimony 2·5–3 per cent.; (3) pure tin; and the fluxes were ortho-phosphoric acid and zinc chloride flux to Specification D.T.D. 81.*

The samples were exposed in the laboratory, in the open air, or to the sea-water spray test for 6–14 months.

The tests showed that the corrosion-resisting steels when cleaned anodically could be soldered readily with either ortho-phosphoric acid or acid zinc chloride solution as flux, and, provided the joints are thoroughly washed, no corrosive effects need be anticipated under conditions such as prevailed in the tests employed. Residues of flux, however, resulted in corrosion near the joint, and this effect was much more serious with zinc chloride than with phosphoric acid. With the latter, corrosion appears to stop at some stage when metal has dissolved to form a protective coating of phosphate.

In the bright-rolled condition the austenitic corrosion-resisting steel could be soldered or "tinned" satisfactorily without preliminary pickling or etching treatment, provided that phosphoric acid was used as flux. With the zinc chloride solution as flux the same steel could not be soldered readily with lead–tin solder, but soldering was somewhat more easy when pure tin was employed.

The general effect of intermittent sea-water spray on the soldered joints is to cause a certain amount of corrosion at the surface of the exposed solder, but not of serious extent. Appreciable rusting only occurred with chromium steels containing little or no nickel. No material difference in corrodibility of the solders was noticed in superficial examination of the samples subjected to the test.

ORGANIC PHOSPHATE FLUXES.

Phosphoric acid dissolves many metals, and for many purposes the danger of residues of the acid in soldered articles would be very objectionable. It was considered that by combining phosphoric acid with a volatile base weaker than ammonia the resulting phosphate might be

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* D.T.D. 81.

Zinc chloride	5 lb.	Made up to 1 gall. with water.
Ammonium chloride . . .	½ lb.	
Hydrochloric acid, sp. gr. 1·16, up to	4 fl. oz.	

superior to ammonium phosphate as a flux for soft-soldering operations while not possessing the objectionable features of phosphoric acid. A number of organic nitrogen compounds were selected and their respective phosphates prepared. The behaviour of these phosphates as fluxes was examined, and the results obtained in soft-soldering operations on corrosion-resisting steels are given in Table I. The soft solders employed were Grade A and Grade B, and it was found necessary to clean the steels chemically by etching or pickling, for easy soldering.

TABLE I.—*Behaviour of Organic Phosphates as Fluxes in Soft Soldering Operations.*

Base.	Behaviour of Phosphate as Soldering Flux.
Pyridine . .	Satisfactory as flux, but odour highly objectionable
Aniline . .	Satisfactory; no objectionable odour
Toluidine (ortho)	Satisfactory, but no better than aniline phosphate
Quinoline . .	Scarcely satisfactory, and odour rather objectionable
Urea . .	Unsatisfactory; charring of base occurred on soldering bit.
Hexamine .	Ditto ditto
Triethanolamine	Ditto ditto

The most satisfactory results were obtained with the phosphates of aniline and toluidine. From considerations of cost aniline is to be preferred.

The three possible phosphates of aniline were made, and it was found that a preparation consisting approximately of the monobasic phosphate ($C_6H_5{\cdot}NH_2{\cdot}H_3PO_4$) gave the best results. For convenience it was found desirable to embody the phosphate in a paste, by intimately mixing the powdered phosphate with an approximately equal weight of heavy mineral oil or ethylene glycol.* Tests of such fluxes on copper, brass, and ordinary steel free from heat-treatment scale indicated that the fluxes behaved satisfactorily in soft-soldering operations on these materials in the absence of preliminary cleaning or pickling operations.

CORROSION TESTS—ORGANIC PHOSPHATE FLUXES.

Tests were made to examine the corrosive effects of proprietary fluxes containing zinc chloride as the active constituent, zinc chloride flux to Specification D.T.D. 81, ortho-phosphoric acid, and two experimental organic phosphate fluxes consisting of a suspension of aniline phosphate (approximately monobasic aniline phosphate) in ethylene glycol and mineral oil, respectively. Two of the proprietary fluxes were of the zinc chloride–mineral jelly type.

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* British Patent No. 400,609.

Lapped joints were made in brass (B.S.I.S. 3B5), mild steel (B.S.I.S. S3), and austenitic corrosion-resisting steel (D.T.D. 166) using tinman's solder (B.S.I. Grade A). Flux residues were allowed to remain on the samples after the soldering operation. The samples were allowed to stand in an unheated building for 6 months, during which time they were kept under observation for corrosive effects of the flux residues, the results being summarized in Table II.

TABLE II.—*Corrosive Effects of Flux Residues.*

Flux.	On Brass (B.S.I.S. 3B5).	On Mild Steel (B.S.I.S. S3).	On Austenitic Corrosion-Resisting Steel (D.T.D. 166).
Proprietary 1	(E) Extensive	(E) Extensive	(I) ...
" 2	(E) Moderate	(E) Moderate	(I) ...
" 3	(E) Very Slight	(F.D.) Moderate	(I) ...
D.T.D. 81 *	(E) Moderate	(E) Extensive	(F.D.) Moderate. Solder blackened.
Phosphoric Acid	(E) Moderate	(E) Moderate	(E) Slight. Solder bright
Exp. Flux A †	(E) Uncorroded	(E) Uncorroded, apart from slight independent rusting	(E) Uncorroded. Solder bright
Exp. Flux B ‡	(E) Uncorroded	(F.D.) ditto	(F.D.) ditto

* D.T.D. 81 flux contains zinc chloride 5 lb., ammonium chloride ½ lb., hydrochloric acid (sp. gr. 1·16) up to 4 fl. oz., made up to 1 gall. with water.

† Flux A—Aniline (commercial) 51 c.c., phosphoric acid (sp. gr. 1·75) 34 c.c., ethylene glycol (commercial) 40 c.c. approx.

‡ Flux B.—Aniline (commercial) 51 c.c., phosphoric acid (sp. gr., 1·75) 34 c.c., mineral oil 60 c.c. (approx.).

The letters in brackets indicate the relative ease or difficulty of soldering the metal with each particular flux: E = easy, F.D. = fairly difficult, I = impossible.

The results obtained indicate that the useful properties of phosphoric acid as a flux for soft-soldering may be obtained in a substantial degree without the various disadvantages by using it in more or less complete combination with volatile organic bases, aniline in particular, and in a convenient vehicle. When such fluxes are heated in soft-soldering operations the organic phosphates undergo partial decomposition. It is evident that the hot phosphoric acid thus liberated can exert satisfactory etching or cleaning effect on the material being soldered, provided that it is initially free from heavy films of oxide or foreign matter, so far as many of the common metals and alloys are concerned. The results of corrosion tests suggest that the small amount of phosphoric acid and the organic phosphate remaining in flux residues on soldered work are free from objectionable corrosive effects on long standing in contact with the metals and alloys investigated. Experiments with phosphoric acid alone indicate that residues of the acid cause the formation of protective films on the materials examined, and it would appear that similar films are produced in samples soldered with fluxes containing organic phosphates as the active constituent.

In addition to the advantages of freedom from corrosive effect of residues, the phosphate fluxes are more effective than fluxes containing zinc chloride in soft-soldering many common types of material, such as corrosion-resisting steels, aluminium–bronze, zinc, and cadmium.

NOTE ON PICKLING OR ETCHING BATHS FOR DURALUMIN.* 736

By H. SUTTON,† D.Sc. (Member), and T. J. PEAKE,‡ B.Sc.

Synopsis.

In view of the dangers involved in handling and transporting hydrofluoric acid, a search was made for pickling baths free from such objection. Various treatments were examined. Treatment in a bath prepared by adding 1 per cent. by weight of sodium fluoride to 10 per cent. (vol.) sulphuric acid followed by dipping in 50 per cent. nitric acid (pickling treatment D) gave satisfactory etching. The Wöhler fatigue range (10 million cycles) of Duralumin specimens was reduced from ±10·85 to ±10·1 tons/in.^{2}, a decrease of 6·9 per cent., by the pickling treatment. The resulting decrease in fatigue range is nearly as small as that observed after pickling treatment C which gave the least that was observed in a previous investigation § and less than any observed in the present investigation. From the points of view of absence of danger in the preparation of the bath and also of the quality of the etch the new treatment appears to be superior to any other yet investigated.

Experiments on the influence of pickling or etching treatments on the fatigue-strength of Duralumin have already been described,§ all the treatments investigated resulting in a reduction of the Wöhler fatigue range. The observed reduction of stress range for 10 million cycles endurance was in one case as great as 31·4 per cent., but that resulting from pickling in a solution containing 4 parts of 10 per cent. sulphuric acid and 1 part hydrofluoric acid followed by dipping in 50 per cent. nitric acid (treatment C) was only about 6 per cent., while the etching effect of the treatment appeared to be satisfactory.

The use of hydrofluoric acid in preparing the bath for treatment C necessitates special precautions, owing to the extremely irritating effects of the acid on the skin. Operators must wear rubber gloves when handling hydrofluoric acid, and special gutta percha containers are required for its storage. A further disadvantage is the high cost of the acid. The purpose of the present investigation was to discover

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§ H. Sutton and W. J. Taylor, *J. Inst. Metals*, 1934, 55, 149.

a pickling treatment for Duralumin satisfactory from the point of view of etching yet avoiding the use of hydrofluoric acid as such.

ETCHING EXPERIMENTS.

A large number of small pieces of Duralumin (¾ in. long, ¾ in. diameter) were prepared for pickling and etching experiments. The specimens had approximately the same surface area, and therefore, by subjecting them to different pickling treatments and in each case noting the loss in weight after immersion some measure of the degree of attack could be obtained. This, in conjunction with the quality of the resulting etched surface, was taken into account in judging the relative merits of different pickling treatments.

An attempt was made to replace the hydrofluoric acid in the main bath of pickling treatment C by hydrochloric acid, but this was unsuccessful; once the reaction had commenced it was practically uncontrollable and the resulting etch was very poor.

A 10 per cent. solution of sodium carbonate at increased temperatures was found to be more promising, the etch being satisfactory but the action was very sluggish.

Unsuccessful attempts were made to employ acid solutions containing chromic acid, acetic acid, and other substances, but satisfactory etching was not obtained.

A bath was prepared containing 10 per cent. of sulphuric acid and 1 per cent. of commercial hydrofluoric acid by volume. Although this bath contains only a very small amount of hydrofluoric acid, compared with the main etching bath of treatment C, with a period of immersion of 10 minutes at 20° C. the macro-etching effect obtained was superior to that of treatment C. The degree of attack was comparable with that of treatment C. Final cleaning of the specimens was effected by dipping in 50 per cent. nitric acid. This treatment also rendered fine cracks in Duralumin readily visible. These and earlier experiments indicated the very considerable advantages of etching baths containing hydrofluoric acid.

PICKLING TREATMENT D.

In order to obviate the use of hydrofluoric acid as such it was decided to try the effect of substituting an equivalent amount of sodium fluoride. In powdered form, sodium fluoride may be stored in glass containers and is fairly safe to handle. When sodium fluoride is introduced into an aqueous solution of sulphuric acid free hydrofluoric acid is produced. A bath was prepared containing 10 per cent. by volume of sulphuric acid and 1 per cent. by weight of sodium fluoride.* Since the hydrofluoric acid used in the previous bath was 50–60 per cent., this is about the equivalent amount of sodium fluoride. Immersion of the pieces in this bath initially at 20° C. for a period of 10 minutes, without previous heating, followed by a rinse in water and immersion in 50 per cent. nitric acid for 1 minute (pickling treatment D) gave a satisfactory etch on samples having machined surfaces and an improved etch on samples polished down with " 0 " grade emery paper. Figs. 1 and 2 (Plate I) of the same area of a Duralumin forging as received and after etching show the manner in which a fine fatigue crack is made easily visible by application of the " 0 " emery polish and etching treatment.

PICKLING TREATMENT E.

Another treatment (pickling treatment E) had been suggested by a light alloy manufacturer, and was investigated. The specimen is immersed, usually for 5 minutes, in a bath consisting of a 20 per cent. solution of orthophosphoric acid (sp. gr. 1·5) in water, to which 0·5 per cent. by volume of hydrofluoric acid is added. The bath is used at room temperature. After immersion in the bath, the pieces are rinsed and transferred to a bath of cold 50 per cent. nitric acid. If the pickling solution shows signs of weakening a further 0·5 per cent. of hydrofluoric acid may be added.

Pickling experiments were made on Duralumin bar the composition and properties of which are given in Table I.

TABLE I.—*Composition and Properties of the Duralumin Bar Material.*

Composition.	Per Cent.		Mark.	
			71.	723.
Copper . .	4·25	Diameter, in. . . .	0·565	0·565
Magnesium .	0·93	Limit of proportionality, tons/in.^{2} . . .	12·1	14·3
Manganese .	0·57	0·1% Proof stress, tons/in.^{2} .	19·3	20·7
Iron . .	0·50	0·5% Proof stress, tons/in.^{2} .	21·3	21·8
Silicon . .	0·32	Maximum stress, tons/in.^{2} .	29·9	31·4
		Elongation on $4\sqrt{A}$., per cent.	20·0	19·5

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* This bath was mentioned by Mr. E. Wood in discussing the earlier paper, see *J. Inst. Metals*, 1934, **55**, 161.

ETCHING QUALITIES OF THE VARIOUS TREATMENTS.

Etching tests were first carried out on short lengths of bar machined all over to determine the loss of metal and the general quality of the etch. Pickling treatment E as originally proposed gave a very faint etch and only about 35 per cent. of the loss of metal resulting with treatment D. The period of immersion was increased to 15 minutes, whereupon a uniform etch was obtained and the loss of metal was of the same order as that accompanying pickling treatment D. The results are given in Table II. In the case of pickling treatment C the samples were immersed in boiling water before being introduced into the pickling bath, but this was not done with treatments D and E.

TABLE II.—*Loss of Metal in Different Pickling Treatments Applied to Duralumin Specimens.*

	Pickling Treatment.		
	C.	D.	E.
Time of immersion, minutes	3	10	15
Temperature of bath, ° C.	20	21	26
Loss in weight, grm.	0·0517	0·0407	0·0380
Thickness of metal removed, in.	0·00030	0·00029	0·00027

Fig. 3 (Plate II) shows samples which were machined from a piece of extruded light alloy tube and then subjected to different pickling treatments, in order to reveal the macro-structure of the material. It will be seen that pickling treatment D reveals the macrostructure quite plainly when applied to the " as machined " surface.

Some samples of 20-S.W.G. Duralumin sheet were subjected to pickling treatments A, C, and D for examination of the effect of the attack in the pickling treatments. Pickling treatment A (2·5 minutes in 10 per cent. sodium hydroxide solution at 60°–70° C., rinse, 1 minute in cold 10 per cent. nitric acid, 10 per cent. (vol.) sulphuric acid solution, rinse, and dry) * was the most drastic of any investigated, both with reference to the amount of metal removed and to the reduction of the fatigue strength (31·4 per cent.).

Transverse sections were cut from the pickled samples and also from a sample of the untreated material. These sections were polished, great care being exercised to prevent rounding of the edges during polishing, and then lightly etched, for the same period in each case, Figs. 4–7 (Plate III). The thickness of metal removed by treatment

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* H. Sutton and W. J. Taylor, *loc. cit.*

A had previously been found to be nearly 0·001 in.; on comparison with Table II it will be seen that this is approximately three times the thickness of metal removed by treatments C and D. Consideration of Figs. 4–7 discloses the fact that the degree of serration produced upon the surface of the material by pickling is greater with treatment A (Fig. 5) than with treatments C and D (Figs. 6 and 7).

FATIGUE TESTS.

Wöhler type fatigue tests were carried out on material in the following conditions:

(*a*) As received.

(*b*) Pickled—Treatment D (10 minutes in 10 per cent. H_2SO_4, 1 per cent. NaF at 20° C.; 1 minute in 50 per cent. HNO_3).

(*c*) Pickled—Treatment E (15 minutes in 20 per cent. H_3PO_4, 0·5 per cent. HF at 20° C.; 1 minute in 50 per cent. HNO_3).

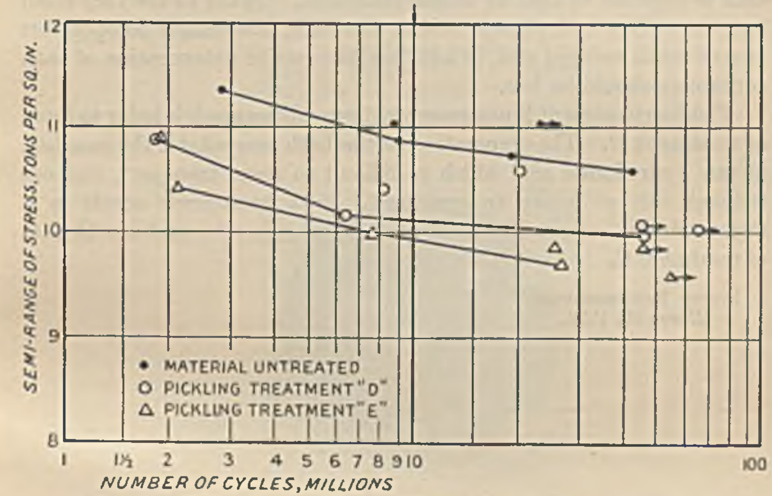

FIG. 8.—Wöhler Fatigue Tests of Treated and Untreated Samples.

The fatigue tests were commenced within 1 hr. of completion of the pickling treatment. The results are given in Fig. 8 and are summarized in Table III, from which it is seen that the reduction in fatigue limit (at 10 million cycles) of the Duralumin bar was slight in the case of both pickling treatments, that after treatment D being apparently somewhat less than that after treatment E and of the same order as that observed after pickling treatment C.*

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* H. Sutton and W. J. Taylor, *loc. cit.*

TABLE III.—*Fatigue Limits Based on* 10 *Million Cycles Endurance.*

Pickling Treatment.	Untreated.	Pickled.	
	Fatigue Limit, Tons/in.².	Fatigue Limit, Tons/in.².	Decrease in Stress, Per Cent.
Control	±10·85	...	...
"D"	...	±10·1	6·9
"E"	...	± 9·9	8·7

CONCLUSIONS AND DISCUSSION OF RESULTS.

Pickling treatment D is an improvement on pickling treatment C from the practical point of view. The preparation of the bath does not necessitate the handling of raw hydrofluoric acid, and the quality of the etch is superior to that of others examined. Owing to the very small amount of free hydrofluoric acid in the bath, the danger to operators is very much reduced and, in addition, the rate of deterioration of bath containers should be less.

Pickling treatment E possesses etching qualities much inferior to those of treatment D. The preparation of the bath necessitates the handling of raw hydrofluoric acid which is difficult to store, transport, and use without risk of injury to personnel. Both treatments result in a slight reduction of the Wöhler limit of Duralumin comparable with that of treatment C.

SOUTH FARNBOROUGH,
March 10, 1936.

FIG. 1.—Duralumin Specimen Containing Fatigue Crack: Before Polishing and Pickling. × 8.

FIG. 2.—Duralumin Specimen Containing Fatigue Crack: After Polishing and Pickling Treatment D. × 8.

PLATE II.

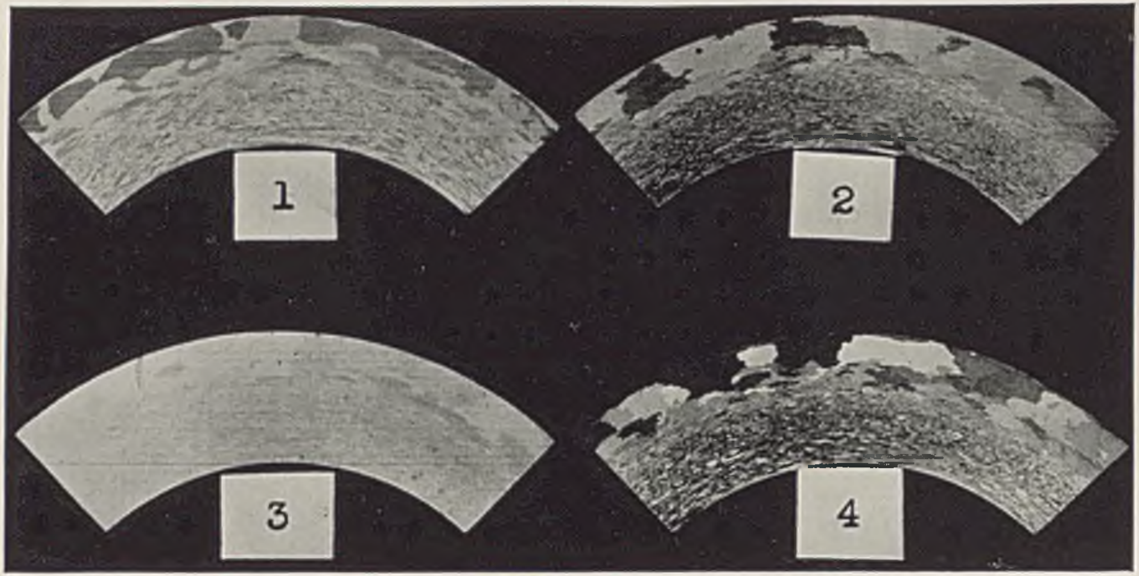

FIG. 3.—Samples of Extruded Tube Etched by Different Treatments to Show the Macrostructure. × 1½.

(1) As machined—pickling treatment C; (2) As machined—pickling treatment D; (3) As machined—pickling treatment E; (4) Polished—pickling treatment D.

PLATE III.

FIG. 4.—Untreated.

FIG. 5.—Treatment A.

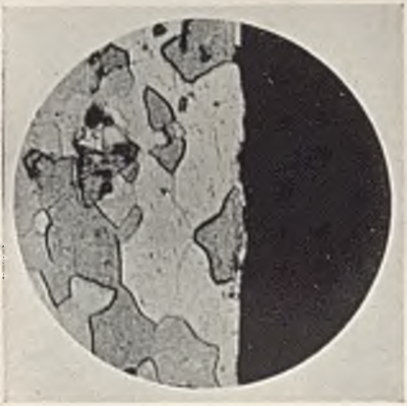

FIG. 6.—Treatment C.

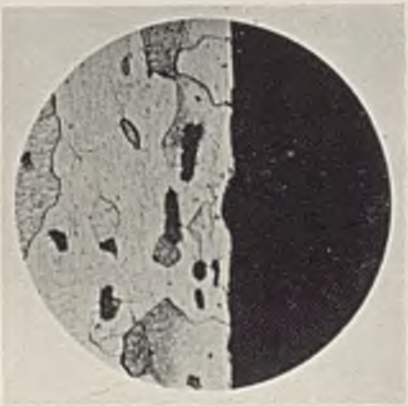

FIG. 7.—Treatment D.

Sections Cut from Samples of 20-S.W.G. Duralumin Sheet, Pickled by Different Treatments, Showing the Degree of Attack upon the Surface of the Material Produced by Pickling. × 500.

A NOTE ON THE INFLUENCE OF SALT-BATH HEAT-TREATMENT ON THE CORROSION-RESISTANCE OF DURALUMIN SHEET.* 737

By A. J. SIDERY,† Assoc.Met. (Sheff.), MEMBER, and B. EVANS,‡ B.Sc.

SYNOPSIS.

Some experiments were carried out to provide information as to whether the use of a nitrate salt-bath as the medium in the final heat-treatment of Duralumin has any deleterious effect on the corrosion-resistance of the material as compared with that of material which has been heat-treated in an electric furnace. Further, the influence of salt residues on the surface of the sheet during prolonged storage was investigated.

It was found that the use of nitrate salt-baths in the heat-treatment operation has no deleterious effect on the corrosion-resistance of Duralumin, but that salt residues are liable to foster local surface pitting of the material during storage.

IN view of the extensive use of salt-baths in the commercial heat-treatment of Duralumin, it was considered desirable to investigate the influence of this method of heat-treatment on the corrosion-resistance of the material as compared with that of heat-treatment in air at the same temperature. Two series of tests were made.

For the first series a supply of Duralumin that had not been in contact with salt at any stage of its manufacture was procured. Samples were heat-treated at 490° C. in pure sodium nitrate, in salt mixtures, and in salts supplied and as used by four aircraft contractors, *viz.* Messrs. James Booth & Co. (1915) Ltd., Fairey Aviation Co., Ltd., Hawker Aircraft, Ltd., and Supermarine Aviation Works (Vickers), Ltd. The heat-treatment was followed by quenching in cold water, or in some cases, in cold dilute solutions of the salts employed in heat-treatment. These variously heat-treated samples were then subjected to immersion tests and to intermittent sea-water spray tests for appropriate periods. The corrosion-resistance was investigated by visual and microscopical observations and also by mechanical tests.

In the second series of tests an attempt was made to examine the

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corroding effect of adhering salt from the heat-treatment bath during subsequent storage of the material.

DESCRIPTION OF EXPERIMENTS.

SERIES I.

The materials used in the experiments consisted of 20- and 15-S.W.G. Duralumin sheets, the analyses of which are given in Table I.

TABLE I.

	20-S.W.G.	15-S.W.G.
Copper, per cent.. . .	4·46	4·47
Silicon, ,, . . .	0·28	0·24
Manganese, ,, . . .	0·62	0·63
Iron, ,, . . .	0·47	0·56
Magnesium, ,, . . .	0·55	0·44
Aluminium, ,, . . .	remainder	remainder

Samples measuring 10 × 2·5 cm. were cut in the direction of rolling and subjected to heat-treatment for 15 minutes at 490° C. as follows:

(*a*) Heated in pure sodium nitrate and quenched in cold water.
(*b*) Heated in pure sodium nitrate and quenched in a 1 per cent. aqueous solution of the salt.
(*c*) Heated in eutectic mixture of sodium and potassium nitrates and quenched in cold water.
(*d*) Heated in eutectic mixture of sodium and potassium nitrates and quenched in a 1 per cent. aqueous solution of the salt mixture.
(*e*) Heated in salt supplied and as used by aircraft contractor " A " and quenched in cold water.
(*f*) Heated in salt supplied and as used by aircraft contractor " B " and quenched in cold water.
(*g*) Heated in salt supplied and as used by aircraft contractor " C " and quenched in cold water.
(*h*) Heated in salt supplied and as used by aircraft contractor " D " and quenched in cold water.
(*j*) Heated in an electric furnace and quenched in cold water.

After being allowed to age for 7 days the specimens were subjected to the following corrosion tests:

(i) Water-line immersion test for 28 days in normal sodium chloride solution acidified with 1 per cent. by weight of hydrogen chloride, equivalent to 29·4 c.c. of hydrochloric acid of sp. gr. 1·15, or 27·4 c.c. of hydrochloric acid of sp. gr. 1·16, per litre.*

(ii) Water-line immersion test in sea-water for 28 days.

(iii) Sea-water spray test for 6 months.

In the sea-water spray test the samples were exposed to the open air, but protected from rain, and were sprayed with sea-water from the English Channel three times during each working day at intervals of approximately 3 hrs. The sea-water was directed at the specimens in the form of a fine mist by means of compressed air.

Sufficient samples were heat-treated to provide duplicates in all conditions.

"Water-Line" Immersion Tests.

Superficial observations: All the samples immersed in the acidified sodium chloride reagent behaved similarly, slight effervescence being observed soon after immersion. This activity increased to a maximum intensity after 2 days and then slowly subsided. A loose dark-brown coating accumulated on the immersed surfaces and surface pitting occurred. The samples immersed in sea-water were apparently all corroded to the same extent. The degree of attack, however, was not comparable with that obtaining in the acid sodium chloride solution. A white gelatinous deposit appeared at the water-line in increasing quantities as the test proceeded and small centres of surface attack became perceptible.

Microscopical observations: Sections across the water-line were prepared from the various samples and examined microscopically. It was found that most of the corrosion took the form of surface pitting. The sections from the specimens immersed in the acidified sodium chloride solution were irregularly and deeply pitted, but no intercrystalline channels had developed except in two cases, where minute traces of this form of penetration were observed. One case was on a section taken from a sample that had been heat-treated in an electric furnace and quenched in cold water, while the other case was on a section taken from a sample that had been heat-treated in a sodium nitrate salt-bath and quenched in water, any adhering salt being completely removed by washing. It is considered that the extent of these intercrystalline channels would not justify any importance being attached to their occurrence. Examination of the sections from the various samples immersed in sea-water did not reveal any appreciable variation in the degree of attack. Some irregular surface pitting was observed,

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* This reagent has proved of service in producing intercrystalline corrosion consistently in samples of Duralumin susceptible to this type of corrosion, see Sidery, Lewis, and Sutton, *J. Inst. Metals*, 1932, **48**, 168.

TABLE II.—*Mechanical Test Results on Samples Exposed to Sea-Water Spray Test for 6 Months.*

Treatment.	Uncorroded.		Corroded.															
	Heated in Electric Furnace, Quenched in Cold Water.		Heated in Electric Furnace, Quenched in Cold Water.		Heated in NaNO$_3$ Bath, Quenched in Cold Water.		Heated in NaNO$_3$ Bath, Quenched in 1% Soln. of Salt.		Heated in K/NaNO$_3$ Bath, Quenched in Cold Water.		Heated in K/NaNO$_3$ Bath, Quenched in 1% Soln. of Salt Mix.		Heated in Salt from Mnfr. "A," Quenched in Cold Water.		Heated in Salt from Mnfr. "B," Quenched in Cold Water.		Heated in Salt from Mnfr. "C," Quenched in Cold Water.		Heated in Salt from Mnfr. "D," Quenched in Cold Water.	
	20 S.W.G.	15 S.W.G.	20 S.W.G.	15 S.W.G.	20 S.W.G.	15 S.W.G.	20 S.W.G.	15 S.W.G.	20 S.W.G.	15 S.W.G.	20 S.W.G.	15 S.W.G.	20 S.W.G.	15 S.W.G.	20 S.W.G.	15 S.W.G.	20 S.W.G.	15 S.W.G.	20 S.W.G.	15 S.W.G.
Limit of proportionality, tons/in.^{2} .	10·9	8·7	10·2	9·4	11·0	10·3	8·9	9·6	9·2	11·7	10·6	11·9	11·8	9·2	9·9	10·2	10·0	11·5	10·5	11·6
0·1% Proof Stress, tons/in.^{2} . .	15·9	15·1	16·5	15·5	16·0	16·1	16·5	15·3	16·2	16·3	16·3	15·9	16·4	15·5	17·0	15·4	17·1	15·5	16·6	15·5
0·5% Proof Stress, tons/in.^{2} . .	18·2	17·0	18·4	17·4	18·1	17·9	18·1	17·3	17·8	17·9	18·2	17·4	18·3	17·2	18·6	17·2	18·9	17·2	18·4	17·2
Ultimate Stress, tons/in.^{2} . .	28·0	27·0	26·3	26·4	26·8	26·6	25·5	26·5	26·2	26·9	26·9	26·0	25·5	26·6	26·8	26·5	27·3	26·0	25·9	26·4
Elongation, per cent. on 1 in. . .	10·0	19·0	13·0	17·0	14·0	14·5	10·0	16·0	11·5	16·0	14·0	14·0	9·0	16·0	12·0	15·0	11·5	14·0	11·5	14·0
"E" × 10^{-6}, lb./in.^{2}	10·2	10·9	10·6	10·5	10·1	10·1	10·6	10·5	10·5	9·6	10·3	10·3	10·2	10·3	10·7	10·2	10·5	9·9	9·8	9·7

but no trace of intercrystalline corrosion was detected in any of the samples.

Sea-Water Spray Tests.

It was considered that the determination of the tensile strength after six months' exposure to the sea-water spray test would afford a convenient means of measuring the relative corrodibility of the variously treated samples.

The dimensions of the individual samples were determined prior to the test and the stress values after exposure calculated accordingly. The mean results of duplicate tests, together with the values for the uncorroded material, are given in Table II.

The tensile values obtained did not indicate that heat-treatment in nitrate salt-baths was deleterious, nor did there seem to be any disadvantage, from the point of view of corrosion-resistance, in the use of such media in comparison with heating in an electric furnace. In fact, there was no marked margin of variation in the values as a whole.

SERIES II.

Ordinary commercial British Duralumin in three thicknesses, 16, 18, and 24 S.W.G., was obtained for this part of the work. The results of chemical analysis of samples of each gauge of material are given in Table III.

TABLE III.

	16-S.W.G.	18-S.W.G.	24-S.W.G.
Copper, per cent.	3·82	4·11	4·17
Silicon, ,,	0·55	0·36	0·23
Manganese, ,,	0·51	0·58	0·60
Magnesium, ,,	0·79	0·59	0·66
Iron, ,,	0·38	0·57	0·45
Aluminium (by difference), per cent.	93·95	93·79	93·89

Strips measuring 2 ft. long by 2 in. wide were cut from the respective sheets. Five lengths of each thickness were taken and assembled to form three coils having an outside diameter of 5 in. Each coil consisted of about eight turns or laminations and the clearance between successive laminations varied to a maximum of 0·006 in. In addition to these coils, strips measuring 1 ft. long by 2 in. wide were prepared from each of the three sheets.

The coils and strips were then heat-treated in a commercial salt mixture having a melting point of about 180° C. The mixture consisted essentially of sodium and potassium nitrates and solidified from the liquid state to form a hard, dense mass which did not dissolve very rapidly in still cold water. A qualitative analysis indicated the presence of considerable amounts of nitrites, while chlorides were also present in small quantity.

The heat-treatment temperature employed was again 490° C. The coils were held in the bath for 30 minutes and the strip samples for 20 minutes before they were quenched in cold water. The water was allowed to drain away from the samples, which were then dried off normally without any other treatment. The amount of salt entrapped at the interfaces of the laminations in the coils was, of course, much greater than that which remained on those samples heated and quenched as single strips.

The treated coils and strips were then stored in an unheated building for a total period of twelve months. Superficial observations were made at intervals, while at the end of the test period a thorough superficial and microscopical examination was made.

Results of Tests.

Superficial observations : Examination of the coiled material showed that considerable quantities of salt still remained on the sheet surfaces corresponding with the interfaces of successive laminations. Where the salt had been entrapped there was a large amount of greenish-grey deposit, which was fairly adherent, on the surface of the sheet. When this deposit was removed pronounced pitting as well as more general surface etching was in evidence. In the case of the single strip specimens, isolated spots of white deposit were fairly general over the surfaces. Very small surface corrosion pits were observed on all the strip samples and there was no appreciable difference in the appearance of the sheets in the three gauges.

Microscopical observations : Sections were prepared from the lower edges of the inner, middle, and outer lengths of strips in the coils. There was a tendency for the entrapped salt to be more plentiful in the regions chosen than on the other portions of these strips.

Numerous corrosion pits were observed on all the sections examined. The actual depth of these pits, however, was surprisingly small and none more than 0·005 in. deep were detected.

There was no trace of intercrystalline corrosion on any of the sections examined. The complete absence of this type of corrosion from the sections taken from the middle strip in the different coils was also surprising, inasmuch as it would be expected that these would have had a higher susceptibility towards intercrystalline penetration, by virtue of the lower rate of cooling on quenching from the salt-bath during heat-treatment, than the more exposed strips on the outside or inside of the coils.

It appears possible that heat-treatment in a nitrate salt may have a slight tendency to inhibit the development of intercrystalline corrosion.

GENERAL DISCUSSION OF RESULTS.

The water-line immersion tests indicated that the mode of heat-treatment and/or the quenching medium employed had not introduced any variation in either the nature or degree of attack. Negligible traces of intercrystalline corrosion were observed on a few samples immersed in the acidified sodium chloride reagent. No attack of this nature occurred on immersion in sea-water. A considerable amount of superficial pitting developed on all the test-pieces. This was, of course, very much more severe in the acidified sodium chloride solution than in normal sea-water.

The mechanical test results obtained on the series subjected to the sea-water spray test did not reveal any marked margin of variation and there was no evidence of any unfavourable influence arising from the use of any one salt or salt mixture as compared with material heat-treated in an electric furnace in air.

Incomplete removal of nitrate heat-treatment salt from Duralumin sheets after quenching resulted in the development of surface pitting when the latter material was subsequently stored. There was, however, no tendency towards intercrystalline corrosion of the material under these conditions. Apart from the tendency of salt residues present as a result of inadequate washing to cause superficial corrosion on subsequent storage, such residues are objectionable on surfaces to be enamelled or varnished without prior anodic treatment.

These observations are in agreement with the conclusion reached by Rawdon,* namely, that, from the point of view of causing intercrystalline corrosion in Duralumin, nitrates are not as dangerous as chlorides.

ACKNOWLEDGMENTS.

The work described in the paper was carried out for the Air Ministry and under the direction of the Aeronautical Research Committee.

The authors desire to express their thanks to the Director of Scientific Research, Air Ministry, for permission to publish the paper and also to the Aircraft Contractors who co-operated by supplying samples of the salt mixtures employed at their works.

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* (*U.S.*) *Nat. Advis. Cttee. Aeronautics, Tech. Note* No. 283, 1928, p. 34.

741

SHRINKAGE DURING THE SOLIDIFICATION OF ALUMINIUM ALLOYS.*

By VAUGHAN H. STOTT,† M.Sc.

Synopsis.

If a molten pure metal or a eutectic alloy be solidified upwards in a bottle-shaped vessel with a long narrow neck, it is possible to obtain an ingot free from cavities and to measure the shrinkage during solidification by direct observation of the descent of the liquid in the neck of the vessel. Measurements made in this way for aluminium and its eutectic with silicon are in close agreement with those of Edwards (*Chem. and Met. Eng.*, 1921, **24**, 61; 1923, **28**, 165) who used a different method. Calculations based on the data of Edwards and others, show that the shrinkage of the commercial aluminium-rich alloys not containing silicon, is usually between 6·5 and 8 per cent. The presence of silicon results in a marked lowering of the shrinkage.

It is pointed out that although these results have a bearing on the formation of pipes in castings, it must not be supposed that the size of a pipe in given circumstances is proportional to the shrinkage of the metal during solidification. For a detailed discussion of this matter the reader is referred to a paper by Edwards and Gammon (*Chem. and Met. Eng.*, 1921, **24**, 338).

Introduction.

The programme of general research of the Department of Metallurgy of the National Physical Laboratory has included a study of the factors which influence the production of castings from fluid metal. Among these factors is the change of volume which a metal or alloy undergoes during solidification. In the course of a research undertaken for the British Non-Ferrous Metals Research Association at Sheffield University, a differential gas dilatometer was devised [1] which allowed such determinations to be made under conditions which ensured equilibrium, and with an improved form of this apparatus a series of determinations was made for metals and alloys of low melting point.[2] It was desired to extend this work to aluminium and its light alloys, but the original method could not be adopted, owing to the action of molten aluminium on the silica vessels which might have been used as containers. An apparatus was constructed in which the gas-tight parts were of metal,

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* Manuscript received November 7, 1935.

† Department of Metallurgy, National Physical Laboratory.

but experimental difficulties were encountered in its use, and recourse was had to a simple form of dilatometer by means of which measurements could be made directly.

EXPERIMENTAL METHOD.

A clay-alumina pot, of the shape shown in Fig. 1, and containing molten metal, was cooled from the bottom. The shrinkage of the metal as it solidified caused a gradual descent of the still molten metal in the neck, which was observed until solidification was complete. Temperature measurements were made at the bottom of the pot, and the first discontinuity in the curve obtained by plotting liquid levels against temperature, indicates the beginning of solidification.

In order to ensure that solidification of the metal proceeded always upwards, a Nichrome heating coil wound on a silica tube was slipped over the neck of the pot. The pot of metal stood on the bottom of an outer thin-walled cylindrical pot some 30 cm. in height, and about 7 cm. in external diameter. The space between the two pots was filled to the height of the inner pot with calcined alumina. The outer pot was placed in a vertical Nichrome resistance furnace of which the tube was 60 cm. in length, and 7·5 cm. in bore. When in position, the point *A* (Fig. 1) of the inner pot was half-way up the furnace. With this arrangement a difference of temperature of some 15° C. was observed between thermocouples tied to the outside of the pot of metal at the points *B* and *C* of Fig. 1.

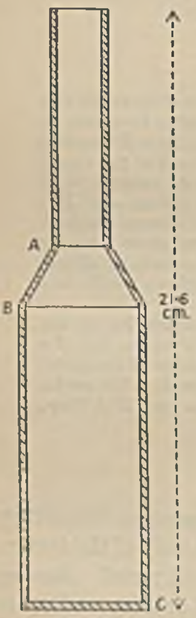

FIG. 1.

The volume of the inner pot at various levels with respect to the mean level of four points equally spaced round the top of the neck, was determined by filling with mercury to levels measured by making an electrical contact between the centre of the meniscus and a wire mounted on a micrometer.

At the high temperatures, two methods were used for the determination of the level of the liquid metal. The first method was the same as that used in calibration, except that tungsten instead of nickel wire made the contact. With pure aluminium on which the first experiments were conducted, this method was successful in spite of a certain amount of difficulty occasioned by the gradual accumulation of dross.

Very great accuracy in the measurement of the level of the liquid was fortunately not required, since a change in level of about 1 cm. was produced by a shrinkage of 1 per cent. of the volume of the metal. At the same time it was realized that the difficulties resulting from the formation of dross would be greater with alloys than with pure aluminium. A simpler, and very satisfactory method of measurement was then used. A Nichrome wire of 14 S.W.G. was bent into a hook at its upper end and was hung on the lowest point of a curved knife edge mounted on a vertical micrometer. The molten metal was so strongly illuminated as to appear quite cold, and visual inspection sufficed to determine when the lower end of the wire was in contact with the metal. For this purpose a slight swing was given to the wire while it was being lowered, and the swinging would stop immediately when the wire reached the film of oxide on the surface of the metal. The wire was then moved about, while just in contact with the scum, in such a way as to cause the meniscus to assume a position of equilibrium. In all the experiments the falling meniscus was almost flat, and concave upwards, the normal form of meniscus being observed only during an earlier stage of the experiment while the temperature of the metal was increasing. The position of the centre of the meniscus was finally determined by lowering the wire very cautiously until slight lateral movement produced a bright streak on the molten surface, showing that the film of oxide had been penetrated. The measurements were relative to the positions of four points equally spaced round the top of the neck of the pot. The mean height of the top of the pot was always measured before the beginning of the solidification and after its close, and the measurements agreed to within about 0·05 mm. It was not necessary to make corrections for changes of dimensions of *any* part of the apparatus during the solidification of the metal. In particular, it will be realized that the ratios of volumes determined by calibration with mercury at room temperature remain unchanged at all temperatures.

In order to fill the pot with metal, a number of rods of ½ in. diameter (a loose fit in the neck of the pot) were placed in the cold pot, and reached the height *B* shown in Fig. 1. A central rod reached nearly to the top of the neck, which was temporarily closed with a rubber stopper to prevent ingress of alumina during packing. The pot was placed in the furnace in the afternoon, and the heating adjusted so that by the next morning a temperature of about 400° C. would be attained. The heating currents were then increased, and when all the metal was molten additional rods were dropped through the neck of the pot with the aid of tongs. These rods had been preheated to a temperature a little below the melting point in order not to risk cracking the pot. At the end of this process the pot was almost filled to the top of the neck, and it was then stirred as thoroughly as possible with a Nichrome wire to remove bubbles and scum, which were liable to be produced owing to the tenacity of the oxide films on the surfaces of the rods. The stirrer was bent so that it could reach the periphery of the bottom of the pot, since preliminary experiments showed that bubbles were liable to be formed in this position. After some experience, ingots were obtained having densities as high as 2·695 at 17° C. The density of pure aluminium has been found by the use of X-rays to be 2·699. The metal used in the experiments now described contained 0·1 per cent. iron and 0·05 per cent. silicon, which would increase its density to 2·701. Sawing through the axis disclosed no visible cavities in these castings. In the preliminary experiments stirring was less thorough, as it was feared, needlessly, that the Nichrome wire might be attacked by the metal. In these experiments small cavities were found on the surfaces of the castings, and in one case in the interior. These cavities had apparently been present in the liquid state, the measured shrinkage of the metal during solidification being unaffected by their presence. In all the experiments the liquid from which the metal rods were prepared had been freed from gas as far as possible by passing through it a current of nitrogen mixed with the vapour of carbon tetrachloride.

In calculating the results, a correction was made for the adherence of metal to the inner surface of the neck of the pot. This correction was obtained by subtracting the weight of the ingot after breaking away the pot, from the total weight of metal originally in the pot. It was assumed that no metal adhered to the pot below the neck. This was substantially exact for aluminium and the aluminium–silicon alloy of eutectic composition, but was not accurate in the case of two other alloys. The correction for aluminium was only about 1 part in 500 of the total volume. A small correction was also made for the temperature gradient in the liquid at the beginning of solidification. It was assumed that this gradient was roughly indicated by the readings of the two thermocouples. This is probably far from exact, but the correction was only about 1 part in 1000 of the total volume.

The duration of freezing was usually 2 or 3 hrs., although in one case it was prolonged to 6½ hrs. The times of the various temperature measurements were noted, so that the time–temperature curves afforded a check on the volume–temperature curves. The indications of the beginning of solidification afforded by the two methods, were in agreement.

Fig. 2 shows typical curves obtained from an experiment on aluminium, an e.m.f. of 1 mv. in a thermocouple being roughly equivalent to 100° C.

Results and Comparison with Other Work.

The results given below were obtained for aluminium containing 0·1 per cent. iron and 0·05 per cent. silicon.

Shrinkage during Solidification,
Per cent.
6·9
6·7
6·7
6·6
mean 6·7

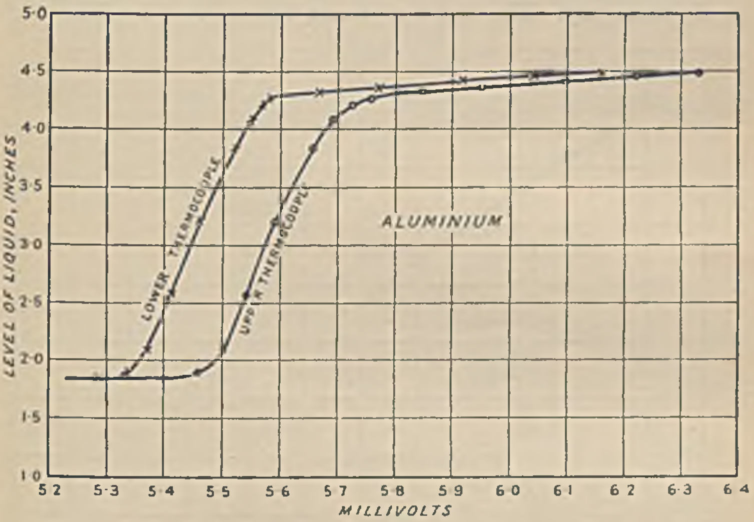

Fig. 2.

Edwards and Moorman [3] obtained the value 6·6 per cent. by calculation from the values of the densities of solid and liquid metal at the melting point. The density of the solid metal was calculated from its value at 20° C. and a formula representing its change with temperature. At the time of publication the authors were awaiting, from the Bureau of Standards (U.S.A.), the results of measurements of the thermal expansion of the particular aluminium used (99·75 per cent. aluminium). These results have since been published, and recalculation of the shrinkage yields the value 6·7 per cent. It is difficult to estimate the exactitude of the value, but the error from all sources is probably less than five units in the second significant figure. Direct measurements made earlier than those of Edwards and Moorman yielded lower values of the shrinkage, apparently owing to the formation of cavities in the solid metal.

After testing the method of measurement on aluminium, the present author determined the shrinkage of an aluminium–silicon alloy having a composition slightly on the silicon side of the eutectic. (The eutectic alloy contains 11·6 per cent. of silicon.) An alloy containing silicon 12·59, iron 0·46, and titanium 0·05 per cent., gave a shrinkage of 3·7 per cent. A duplicate determination on an alloy containing 12·75 per cent. silicon and impurities as before, gave a shrinkage of 3·4 per cent. The mean of these values has been marked with a cross on Fig. 3. The author's value for the shrinkage of pure aluminium is also indicated in the same way. The circles represent values given by Edwards,[4] and the line represents the results of calculations by the present author based on the data of Edwards.

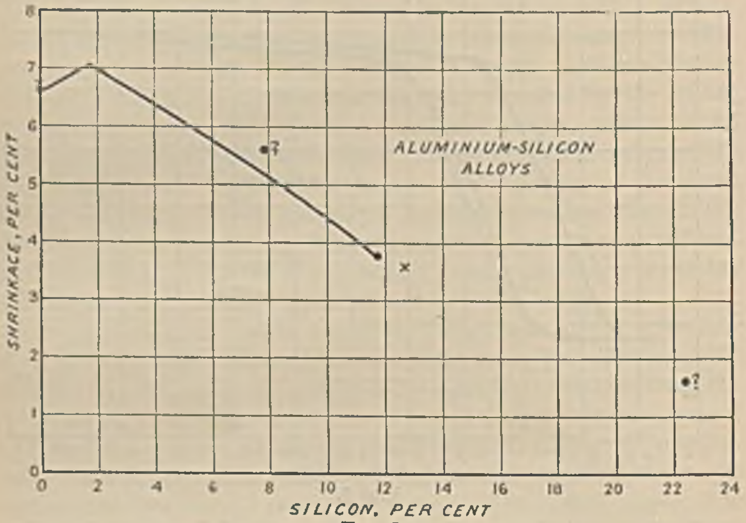

Fig. 3.

The value of the shrinkage given by Edwards corresponding with 7·81 per cent. silicon is inconsistent with both his numerical data and his graph. This discrepancy is probably due to the inadvertent substitution of the percentage expansion of the metal on melting for the corresponding shrinkage on solidification. The circle corresponding with 22·4 per cent. silicon represents a value quoted by Edwards as a good approximation based on fewer data then for his other values. The maximum of the shrinkage curve at 1·7 per cent. silicon corresponds with the maximum freezing range at this composition.

Shrinkage measurements on the two alloys known as " L5 " and " Y " were not satisfactory. Three experiments were made on the alloy " L5," and shrinkages were observed of 4·4, 4·8, and 4·4 per cent. On cutting open the first ingot, it was found that a pipe had formed, running from the centre of the bottom to the level *B* shown in Fig. 1. Similar pipes were formed in succeeding experiments. Their volumes were estimated by filling them with vacuum wax. On correcting the shrinkages in this way values of 6·1 and 5·6 per cent. were obtained. The bottom surface of each ingot, however, had a rough appearance suggestive of having been torn away from the bottom of the pot. On this assumption there would be an air space of unknown magnitude between the metal and the pot. From these considerations it is probable that the true shrinkage exceeds 6 per cent.

The apparent shrinkage of " Y "-alloy was 4·8 per cent., but the ingot was very porous, the cavities being closed, and distributed so that an estimate of their volume was not possible.

Estimates of the shrinkages of these alloys may be made by calculation.

ESTIMATES OF SHRINKAGE BY CALCULATION.

It will be assumed that the specific volume of a phase of an alloy of given composition is a continuous function of temperature for any range which does not involve the formation of a new phase. This assumption is not self-evident, for if there is any connection between the specific volume of an alloy and those of its components, the discontinuity in the specific volume of a component at a temperature at which it undergoes a change of phase may result in a discontinuity in the specific volume of the alloy at that temperature. Goodrich,[2] however, has published curves for certain alloys which verify the assumption for the liquid state for temperature ranges which include the freezing point of one of the components. Braesco [5] has published a similar verification for alloys which are solid solutions. Further evidence is afforded by the consideration that a discontinuity in volume is normally associated with an irregularity in a thermal curve, but such irregularity has probably never been observed unaccompanied by a change of phase.

Let there now be considered, at a temperature t, an alloy consisting of a single phase of specific volume v, formed from n parts by weight of a pure component of specific volume v_1, and $(1 - n)$ parts by weight of a pure component of specific volume v_2.

Since v is a function of n and t, and v_1 and v_2 are functions of t, it is *always* possible to write

$$v = nv_1 + (1 - n)v_2 + f(n, t) \quad . \quad . \quad . \quad . \quad (1)$$

the function f being defined by this equation.

Let it be supposed that the form of the function f has been established by experiment for a range of temperature within which v, v_1, and v_2 are continuous. Let it further be supposed that at some temperature or temperatures discontinuity occurs in one or both of the quantities v_1 and v_2. If v is continuous at such temperatures, the function f must be discontinuous in order to satisfy equation (1); but the continuity of v implies the possibility of extrapolating the right hand side of equation (1) term by term, using for the purpose the three functions of t, namely v_1, v_2, and f, in the forms in which they appear in equation (1) for the range of temperature within which all the functions are continuous.

Such empirical extrapolation is naturally subject to uncertainty. Fortunately, the coefficients of thermal expansion with which we shall be concerned are too small for this uncertainty to be important. Moreover, the extrapolations will be simplified by the circumstance that the value of $f(n, t)$ will always be zero, although this is not relevant to the validity of the principle which has been established.

Let there now be considered a binary alloy of aluminium containing 18 per cent. zinc. According to Hanson and Gayler [6] this alloy begins to freeze at 630° C., and is completely solid at 580° C. It is necessary, therefore, to calculate the specific volume of the liquid alloy at 630° C. and of the solid alloy at 580° C., in order to find the shrinkage on solidification.

From measurements made by Edwards and Moorman,[3] the specific volume (c.c./grm.) of molten aluminium is equal to

$$0{\cdot}4198/[1 - (0{\cdot}0001142)(t - 658)]$$

From the work of Hogness [7] the specific volume of molten zinc is equal to

$$0{\cdot}15175[1 + (0{\cdot}0001472)(t - 419)]$$

Bornemann and Sauerwald [8] have shown that the volumes of the aluminium–zinc alloys may be calculated by the mixture rule, both in the liquid state, and in the solid state at room temperatures. For the solid state at higher temperatures the validity of the rule will be assumed. By applying the mixture rule to this liquid alloy at 630° C., the specific volume is found to be 0·3713.

The corresponding calculation must now be made for the solid state at 580° C.

The specific volume of liquid aluminium at its freezing point is 0·4198. With the aid of the present author's mean value of 6·72 per cent. shrinkage on solidification, the specific volume of solid aluminium at 658° C. is found to be 0·3916. The above values are for aluminium containing about 1 part in 400 of impurities. For such metal it has been shown by Souder and Hidnert [9] that

$$L_t = L_0[1 + (21{\cdot}90\,t + 0{\cdot}0120\,t^2) \times 10^{-6}]$$

where L_t is the length of a specimen at t° C., and L_0 is the corresponding length at 0° C. From this formula the ratio of the specific volume of the solid metal at any temperature to its value at 658° C. may be calculated. The latter value being known, it is found that the specific volume of solid aluminium at 580° C. is 0·3883.

It is now necessary to find the specific volume of "solid" zinc extrapolated to 580° C.

Liquid zinc at 419° C. has a specific volume of 0·15175 c.c./grm. Goodrich [2] has shown the shrinkage on solidification to be 4·5 per cent. Hence, the specific volume of solid zinc at 419° C. is 0·1449. The value at 20° C. (from X-ray measurements) is 0·1399. If the variation with temperature be linear, the specific volume of solid zinc is

$$0{\cdot}1449[1 + (0{\cdot}0000865)(t - 419)]$$

Its extrapolated value at 580° C. is 0·1469. By the mixture rule the specific volume of the solid alloy at 580° C. is 0·3449. The shrinkage on solidification is, therefore, 7·1 per cent.

It is to be observed that this figure depends mainly on the temperatures at which the alloy begins and finishes freezing, and is little influenced by inaccuracies in the assumed values of other properties of zinc involved in the calculations. Thus, if the specific volume of liquid aluminium be extrapolated to 630° C. and the percentage decrease from this value to that of the solid at 580° C. be calculated, the value 7·2 is obtained. The small influence of the zinc is due partly to its small specific volume relatively to that of aluminium, and partly to the considerable shrinkage exhibited by the metal in the free state. (The case of silicon is markedly different. Edwards is of the opinion that pure silicon expands on solidification, but there is no certain information on this point.)

The specific volume and shrinkage on solidification of copper differ little from those of zinc, and the main effect of the presence of a little copper in an aluminium–zinc alloy is to alter the range of temperature within which solidification occurs. Thus, a shrinkage of about 7·8 per cent. would be expected for an alloy containing 5 per cent. copper and 15 per cent. zinc, with a freezing range from 611° to 480° C. There is some uncertainty concerning the theoretical freezing range of the alloy "L5" containing 3 per cent. copper and 15 per cent. zinc, but the calculated shrinkage must be within the limits of 7 and 8 per cent.

In the case of "Y"-alloy, which has a freezing range from 630°

to about 493° C., and contains 4 per cent. copper, 2 per cent. nickel, and 1·5 per cent. magnesium, a shrinkage of about 8 per cent. would be expected.

Edwards[10] has shown that the shrinkage of an aluminium alloy containing 8 per cent. copper, with no other metal, is about 7 per cent. For alloys with smaller amounts of copper, down to 5 per cent., the composition of the saturated solid solution at the eutectic temperature, the shrinkage would be almost the same. The shrinkages of alloys containing less than 5 per cent. copper lie between 7 per cent. and the value 6·7 per cent. found for pure aluminium.

CONCLUSIONS.

The above results are summarized in the statement that the shrinkage on solidification of aluminium and the commercial aluminium-rich alloys not containing silicon, is usually between 6·5 and 8 per cent., whilst the shrinkage of aluminium–silicon alloys containing from 11 to 13 per cent. silicon is about 3·5 per cent.

Although these results have a bearing on the formation of pipes in castings, it must not be supposed that the size of a pipe in given circumstances is proportional to the shrinkage of the metal during solidification. The theory of the formation of pipes is complex, and at present incomplete, but the general principles have been clearly stated by Edwards and Gammon[11] in a paper on the "Causes of Piping in Aluminium Ingots."

ACKNOWLEDGMENTS.

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REFERENCES.

[1] C. J. Smith, *Proc. Roy. Soc.*, 1927, [A], **115**, 554.
[2] W. E. Goodrich, *Trans. Faraday Soc.*, 1929, **25**, 531.
[3] J. D. Edwards and T. A. Moormann, *Chem. and Met. Eng.*, 1921, **24**, 61.
[4] J. D. Edwards, *Chem. and Met. Eng.*, 1923, **28**, 165.
[5] P. Bracsco, *Ann. Physique*, 1920, [ix], **14**, 5.
[6] D. Hanson and M. L. V. Gayler, *J. Inst. Metals*, 1922, **27**, 272.
[7] T. R. Hogness, *J. Amer. Chem. Soc.*, 1921, **43**, 1621.
[8] K. Bornemann and F. Sauerwald, *Z. Metallkunde*, 1922, **14**, 254.
[9] W. H. Souder and P. Hidnert, *Sci. Papers Bur. Stand.*, No. 426, 1922, 497.
[10] J. D. Edwards, *Chem. and Met. Eng.*, 1921, **24**, 217.
[11] J. D. Edwards and H. T. Gammon, *Chem. and Met. Eng.*, 1921 **24**, 338.

STUDY OF THE FORGEABILITY OF VARIOUS LIGHT AND ULTRA-LIGHT ALLOYS.* 745

By Professor ALBERT PORTEVIN,† Member, and Dr. PAUL G. BASTIEN,‡ Member.

Synopsis.

The authors have endeavoured to determine, by means of laboratory tests, the optimum conditions for hot-working light and ultra-light alloys. With this in view they have compared the results obtained from static bending and compression tests and dynamic bending and tensile tests. They have indicated the important part played by the rate of deformation, and have shown that the bending test appears to be the most convenient, speedy, and sensitive. The tests have been carried out on aluminium; on copper–aluminium alloys containing 6 and 12 per cent. of copper; on aluminium–magnesium alloys containing 5, 10, and 15 per cent. of magnesium; on magnesium; on magnesium–copper alloys containing 5, 10, and 15 per cent. of copper; and on magnesium–aluminium alloys containing 3, 6, and 9 per cent. of aluminium. The methods of testing employed have made it possible to define the capacity for hot-work of these various alloys.

Introduction.

The study of the mechanical properties of metallic materials at high temperatures is a subject which is very much in the foreground at the present moment, and which has given rise to a number of researches. It can be dealt with under two headings :

(1) Research on materials which are resistant at high temperature; in other words, determination of the temperature up to which deformations and speeds of deformation remain below certain values which are considered to be suitable in industry. The deformations and speeds of deformation must, therefore, remain excessively small. It is necessary on the one hand to carry out very prolonged tests in order to ascertain the law of deformation and on the other hand to make use of very sensitive methods to measure these deformations.

(2) Research on the possibilities and conditions of forming at high temperatures; in other words, the temperatures or ranges of temperature for which the amplitude of deformation and the value of the speed of deformation are large enough to be used industrially, that is to say,

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are above certain comparatively large values. The deformations studied, being large under these conditions, do not need to be amplified, and the temperatures are, for the same type of material, higher than those in the preceding case. The tests are very rapid, since industrial forming of materials must be rapid.

It will be seen, then, that in the two cases the ranges of temperature attained for the same metal will be very different and that the choice of tests and methods of measurement also will be very different.

This paper will only deal with the second problem, limiting it to light alloys, *i.e.* alloys rich in aluminium and ultra-light alloys which are rich in magnesium, and it is proposed to present here results of experiments carried out by mechanical means, ignoring for the moment the structural study of deformations and their consequences.

PART I.

(1) Objects and Methods of this Study.

The object of this study is to determine by accurate measurements the best conditions for forging two types of light and ultra-light alloys. Work carried out on steels * has shown that the methods of test which are most suited to the study of forgeability are: (*a*) tensile and compression tests; (*b*) static bending and shock tests; and (*c*) torsion tests. In this study torsion tests which give rise to deformations very different from those occurring in forging or rolling, have not been considered.

As it appears that the tendency to fracture at high temperatures is a function not only of the method of deformation but also of the speed of deformation, the authors have been led to study both static and dynamic tests. They have used (*a*) static tests in bending and in compression, the stress–strain diagram being registered at various temperatures; and (*b*) dynamic bending and tensile tests at various temperatures without recording a diagram.

The following metals and alloys have been studied:

(a) *Light Metals and Alloys:* aluminium, copper–aluminium alloys with 6 and 12 per cent. of copper, and magnesium–aluminium alloys with 5, 10, and 15 per cent. of magnesium.

(b) *Ultra-Light Metals and Alloys:* magnesium, copper–magnesium alloys with 5, 10, and 15 per cent. of copper, and aluminium–magnesium alloys with 3, 6, and 9 per cent. of aluminium.

The alloys were prepared from 99·6 per cent. pure aluminium,

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* A. Portevin, E. Prétet, and J. de Lacombe, *Congrès Internat. Min. Mét. Géol., Section de Métallurgie*, 1935, 1, 339.

99·5 per cent. pure magnesium, and electrolytic copper containing 99·9 per cent. of copper. They were chill-cast in the form of rolling slabs whose dimensions were 320 × 460 × 40 mm. and from which the test-pieces were cut out and machined.

(2) Description of the Experimental Methods Employed.

A. *Static Tests.*

(1) *Compression Tests.*—These were carried out on an Amsler machine whose maximum load could be varied between 100 kg. and 10 tons. The arrangements for heating and compressing the specimen *e* are shown in Fig. 2. The plungers *C* and *E* are thermally insulated from the machine by porcelain discs *b*, and the temperature is measured by the thermocouple *p*. The dimensions of the specimen are shown in Fig. 1(A). Compression tests for each test-piece were carried out until the specimen broke or until its height was reduced by 50 per cent.; to keep the compression of the specimen to this value it was surrounded by a guard ring *g* 10 mm. in height.

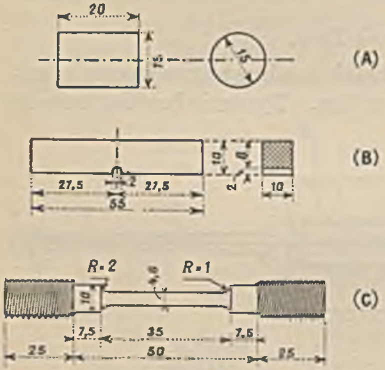

Fig. 1. (All dimensions in mm.)

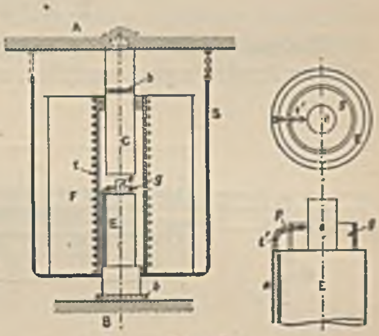

Fig. 2.

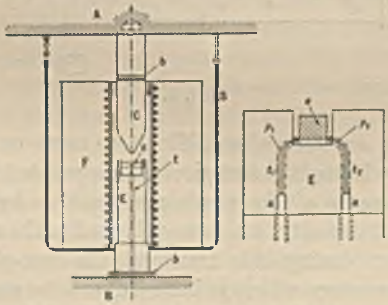

Fig. 3.

For each test the furnace was brought to a steady temperature, and the specimen was put into place by rapidly lowering and raising again the platform of the machine; it was then heated for 15 minutes and the compression test carried out.

(2) *Bending Tests.*—These were carried out in the same machine, the compressing plunger being replaced by a 45° knife edge, the edge having a radius of 5 mm. The arrangement is shown in Fig. 3, and the dimensions of the specimen in Fig. 1(B). The temperature was measured by two thermocouples one on each side of the specimen.

B. *Dynamic Tests.*

(1) *Dynamic Bending Tests.*—Dynamic bending tests were carried out with an Amsler impact pendulum machine. Dynamic bending tests at high temperature are somewhat difficult to carry out with precision: some authors have heated the test-pieces in a separate furnace and carried them to the supports of the pendulum machine by means of tongs having a high heat capacity, which were heated to the same temperature as the specimen; during this transport the test-piece undergoes a decrease of temperature which is both difficult to measure and varies with the temperature of heating and the skill of the operator. Other experimenters have heated the test-piece on the supports of the pendulum by means of an electric current. This method is inconvenient and, furthermore, uniformity of temperature is difficult to attain.

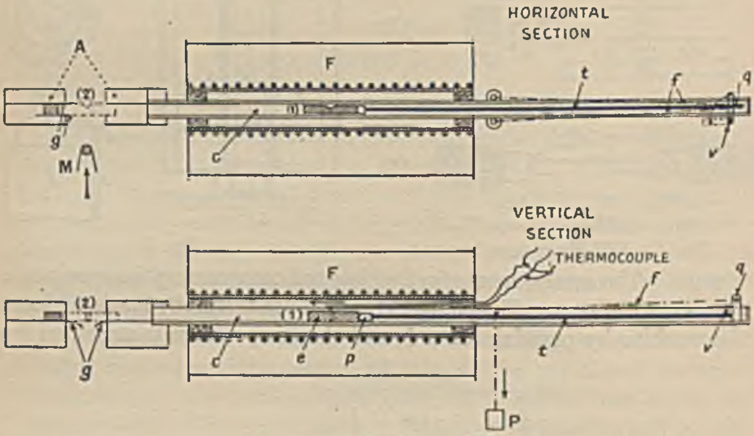

FIG. 4.

The present authors used the arrangement shown in Fig. 4. A Chevenard electric furnace *F*, whose temperature is automatically regulated, is placed perpendicular to the plane of movement of the pendulum *M* in such a way that its axis is in the prolongation of the straight line joining the centres of the small faces of a Mesnager test-piece placed on the supports of the apparatus. A channel *C* of mild steel, having a square cross-section, passes axially through the tube of the furnace, and rests on the support of the test-piece which it accurately prolongs. To heat the test-piece, it is placed in the channel in the centre of the furnace (position 1): after 15 minutes of heating the pusher *p*, which is given a uniformly accelerated movement by the weight *P*, makes it slide in the channel and puts it into place on the supports (position 2). The object of giving the pusher a uniformly accelerated motion is that the test-piece moves rapidly through the space in which it is out of the furnace. During heating a screw *V* holds the pusher in its initial position. This screw can be worked from a distance by a flexible joint; a second flexible joint operates on a screw holding the pendulum in its displaced position; the operator works the two flexible joints in succession. The time which elapses between the moment the test-piece leaves the furnace and that at which the hammer hits it is of the order of 0·5 second.

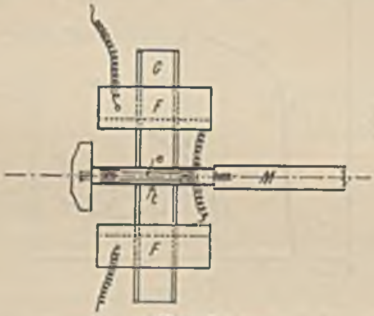

Fig. 5.

(2) *Dynamic Tensile Tests.*—Tensile tests in shock were carried out by a Charpy pendulum of 30 kgm.; the test-piece is shown in Fig. 1(c). After being fixed on the pendulum *M* (Fig. 5) it was heated in the displaced position of the pendulum in an electric resistance furnace *F*. After 15 minutes' heating at the required temperature, the furnace was opened rapidly by displacing the two parts of which it was formed along the rails *G*, and the pendulum was immediately released.

The first experiments showed that the test-pieces, owing to their small rigidity, bent by reason of inertia effects due to the fall of the pendulum. To overcome this the test-piece was placed inside a steel tube *t* (Fig. 5). This tube, in addition to supporting the specimen, ad the further advantage of making the temperature more uniform long the specimen.

MEASUREMENTS CARRIED OUT.

A. *Static Tests.*

(1) *Compression Tests.*—The following factors were noted for each st:

(*a*) The rate of compression; in general this was 4 cm. per minute.
(*b*) The temperature.
(*c*) Either the breaking load or the maximum load when any rupture took place. The types of curves obtained are shown in Fig. 6.

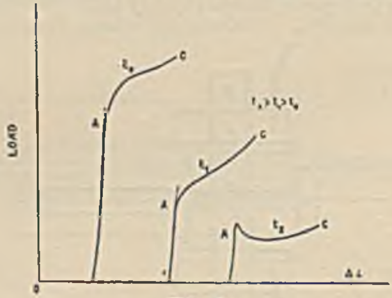

FIG. 6.

(*d*) The amount of flattening at the moment of fracture. When no fracture took place flattening was stopped when the specimen was reduced by 50 per cent.
(*e*) The appearance of the specimen.

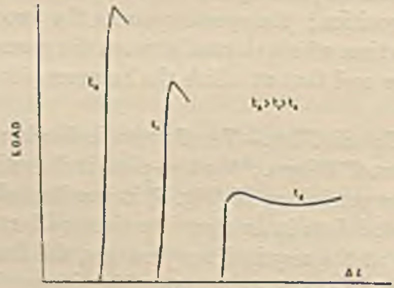

FIG. 7.

(2) *Bending Tests.*—The different types of curves obtained are hown in Fig. 7. The following were noted:

(*a*) The speed of displacement of the knife edge (generally 4 cm. per minute).

(*b*), (*c*), and (*e*) as above.

(*d*) The angle of fracture.

B. *Dynamic Tests.*

The speed of the pendulum, the temperature, and the work absorbed were noted in each case. In addition the angle of fracture or of bending (α) was noted in the case of bending tests and the elongation A on 30 mm. and the reduction in area Σ per cent. on tensile tests.

(3) THE INFLUENCE OF SPEED OF DEFORMATION.

Experience has shown that the speed of deformation plays an important part in the forgeability of light and ultra-light alloys. The authors have studied the influence of the speed factor on two types of alloys having a low capacity of deformation: magnesium + 15 per cent. aluminium and magnesium + 15 per cent. copper.

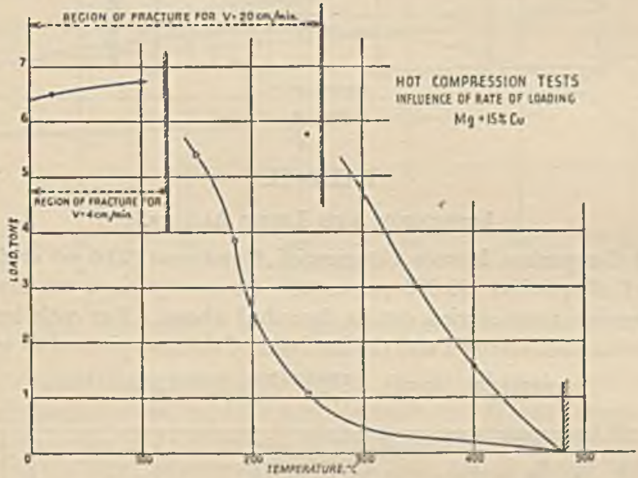

FIG. 8.

Static compression tests at various temperatures were carried out on these two alloys at rates of deformation of 4 and 20 cm. per minute, respectively. Figs. 8 and 9 show (i) the load necessary to cause the rupture of the specimen or its plastic deformation as the speed of deformation increases; (ii) that as the speed of deformation is increased the temperature over which fracture takes place is markedly displaced towards higher temperatures. This explains why in hot working light and ultra-light alloys, slow deformations are adopted (press forging for example).

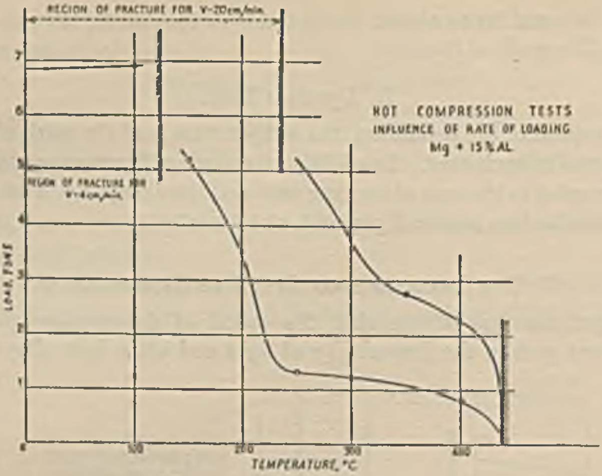

Fig. 9.

PART II.

Aluminium and Light Alloys.

(1) *Comparison between Commercial Aluminium* (99·6 *per cent.*) *and Refined Aluminium* (99·996 *per cent.*).—The comparison was made by compression tests carried out as described above. For each test the maximum load attained and the hardness of the test-piece after cooling

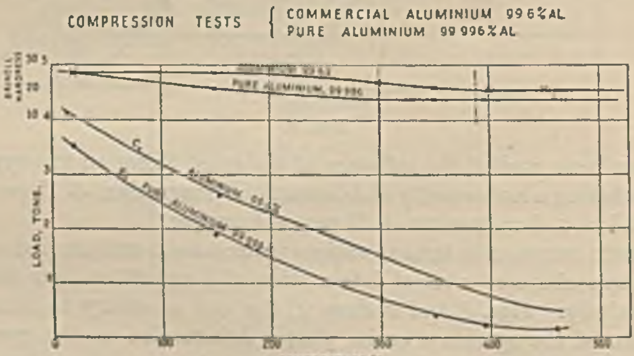

Fig. 10.

were noted. The results, which are given in Fig. 10, show that the loads are higher for commercial than for refined aluminium, and that the hardness after the test is the resultant of the increase in hardness due to working and its reduction by recrystallization. For pure aluminium the influence of the recrystallization comes into play earlier than for commercial aluminium which explains why the hardness of the pure metal remains constant above 300° C. while the same phenomenon does not take place with the commercial metal until 380°–400° C.

Owing to the plasticity of the metal, the compression tests on the aluminium test-pieces do not indicate clearly the existence of a zone of large deformability of fracture. To supplement the preceding results the authors have carried out dynamic tensile tests on commercial aluminium (Fig. 11)* which show the existence of a rapid increase of A per cent. and of Σ per cent. above 500° C. and a maximum of these variables at about 600° C.

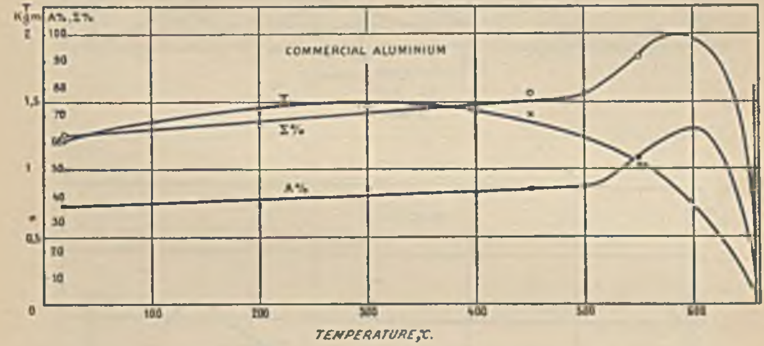

FIG. 11.

(2) *Copper–Aluminium Alloys.*—Figs. 12, 13, and 14 show the results of static bending tests, dynamic bending tests, and dynamic tensile tests on alloys containing 6 per cent. of copper, while Figs. 15 and 16 show the results of the first two tests on the 12 per cent. copper alloys. For this alloy, which is not readily deformed, the dynamic tensile tests do not give accurate results.

Attention is directed to the reduction of the range of high ductility under static bending, and of the maxima in the work and angle of bend curves under dynamic bending, in the 12 per cent. alloy compared with those of the 6 per cent. alloy.

---

* *Symbols used in the curves in Figs. 11–45* The meaning of the symbols used in the curves is given below:

R = maximum load in bending.
F = bend in mm. on a bend test.
ρ = work absorbed in an impact test.
a = angle of bend in an impact test.
T = maximum stress in a dynamic tensile test.
A = elongation, per cent., in a dynamic tensile test.
Σ = reduction of area, per cent.

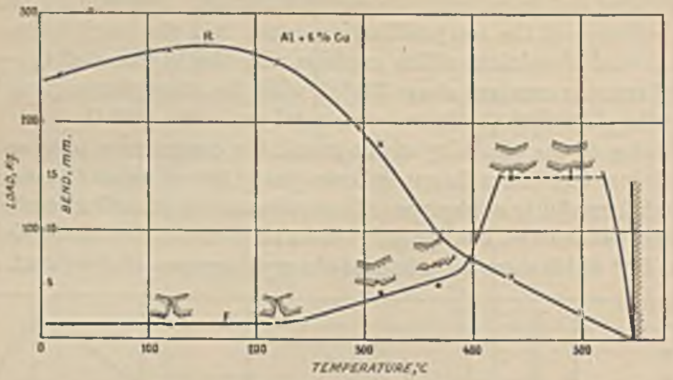

Fig. 12.

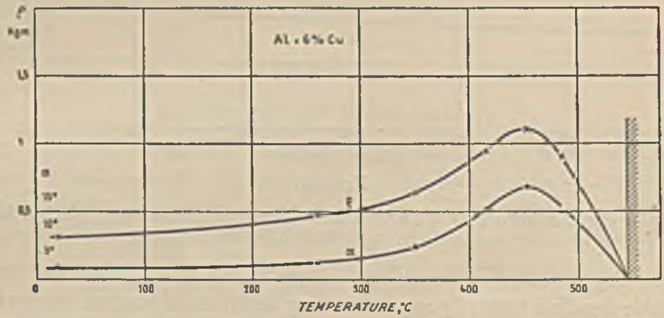

Fig. 13.

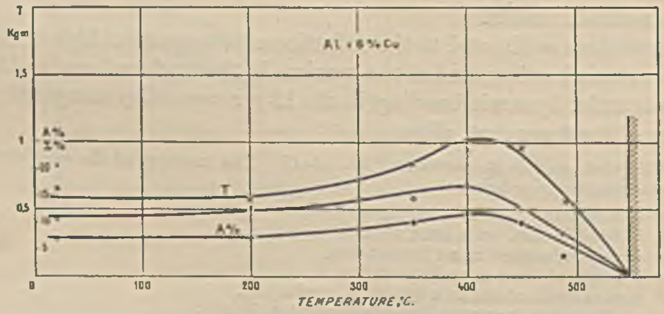

Fig. 14.

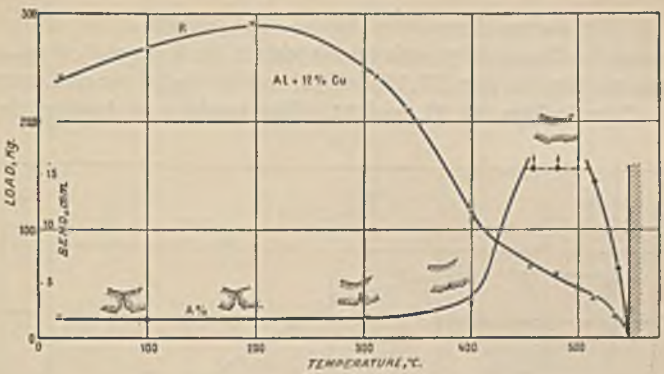

Fig. 15.

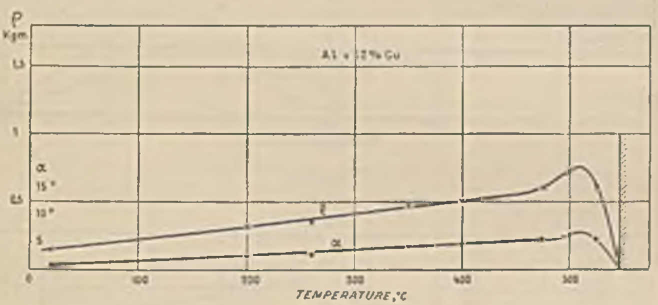

Fig. 16.

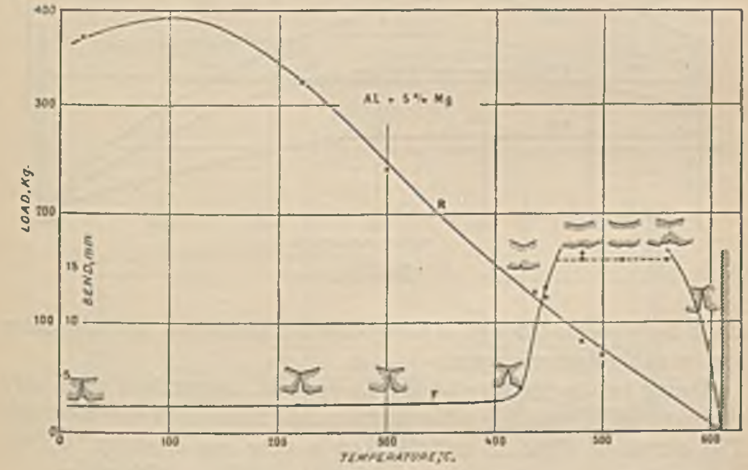

Fig. 17.

(3) *Magnesium–Aluminium Alloys.*—The results of the static and dynamic bending and dynamic tensile tests in the 5 per cent. magnesium alloys are given in Figs. 17, 18, and 19, and for the 10 per cent. magnesium alloys in Figs. 20, 21, and 22. The bending at fracture in the static tests passes through a poorly-marked maximum, and the same applies to the dynamic tests.

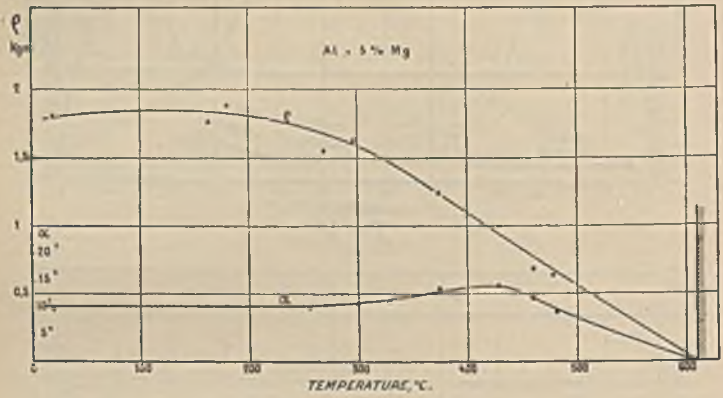

Fig. 18.

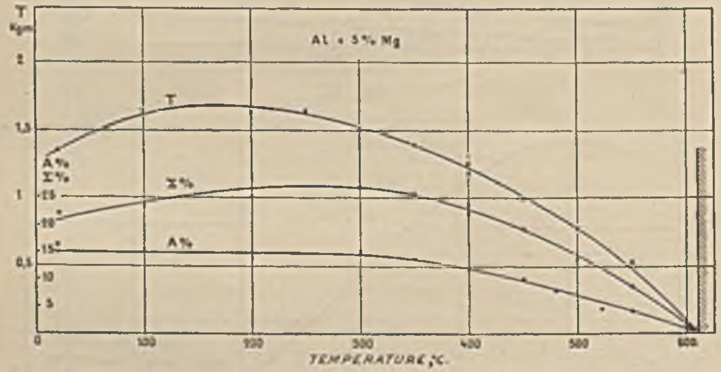

Fig. 19.

Owing to the fragility of the 15 per cent. magnesium alloy only the static and dynamic bending tests can be made with any accuracy. The curves of Figs. 23 and 24 show a very low capacity for hot deformation which gives rise to the non-forgeability of this alloy.

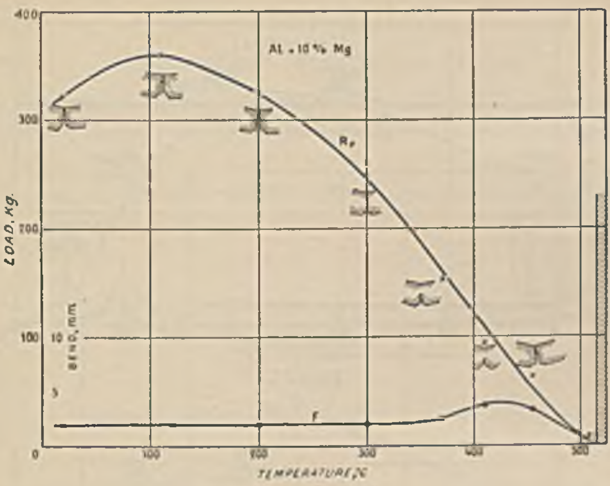

Fig. 20.

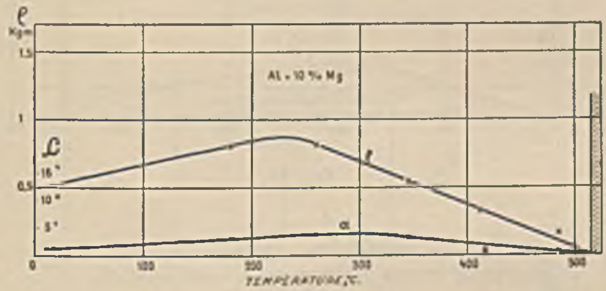

Fig. 21.

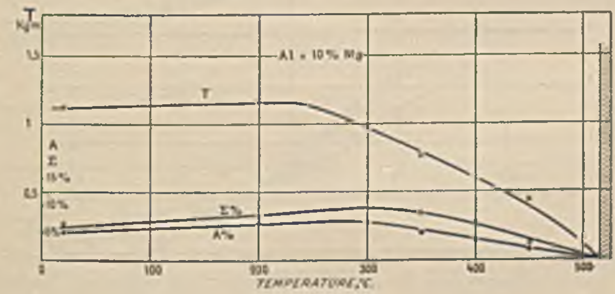

Fig. 22.

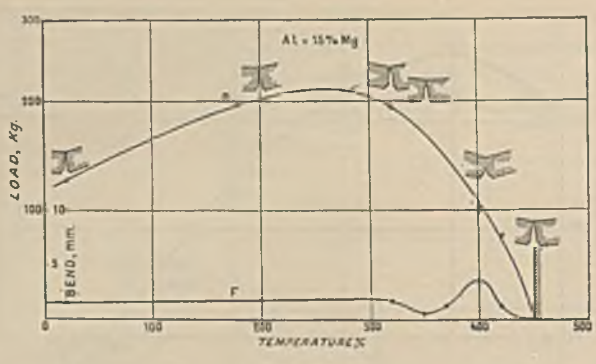

Fig. 23.

Fig. 24.

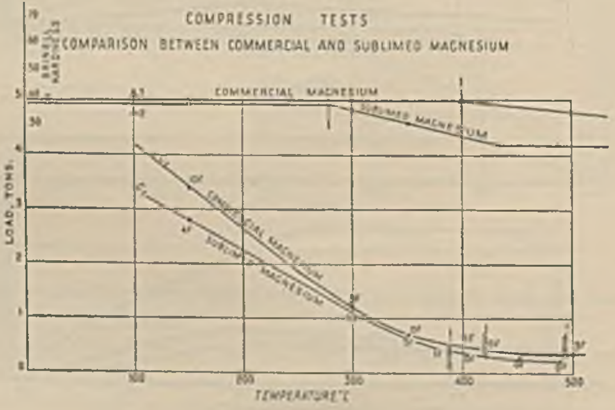

Fig. 25.

PART III.

MAGNESIUM AND ULTRA-LIGHT ALLOYS.

(1) *Comparison between Commercial Magnesium of* 99·4 *per cent. purity and Sublimed Metal of* 99·995 *per cent. purity.*—The sublimed magnesium used for these tests was obtained by the Chaudron–Hérenguel process, and the comparison was made by means of compression tests carried out at a rate of 4 cm./minute.

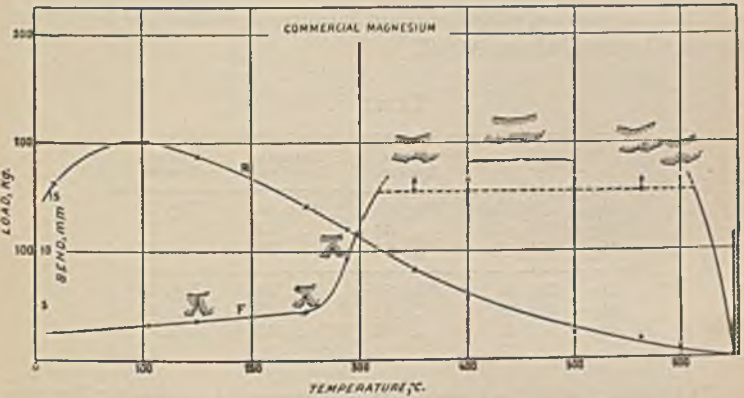

FIG. 26.

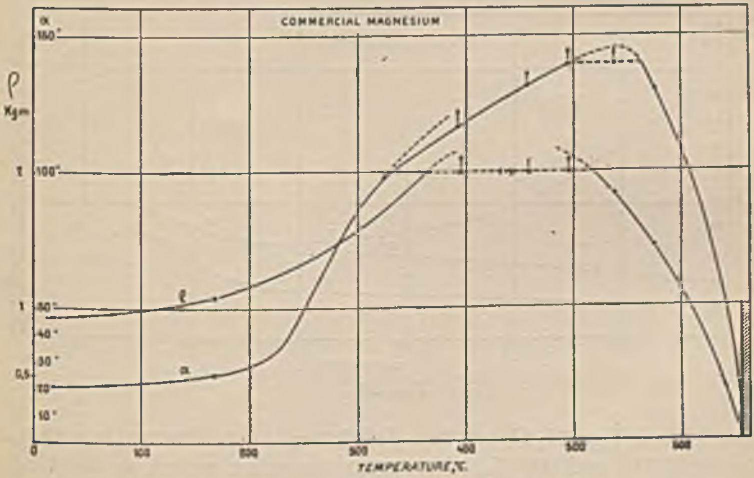

FIG. 27.

On each test the following were observed: the maximum load, the hardness of the test-piece on cooling, and the number of cracks visible on the "skin" of the metal ($1f =$ one crack, Fig. 25). It is deduced that the loads are slightly higher for commercial than for sublimed magnesium and that the influence of recrystallization is shown by the hardness curves, under the conditions of the test, from 285° C. in the case of sublimed magnesium, while the loss of hardness in commercial magnesium does not begin till about 400° C.

TABLE I.

Alloy.	Static Bending.	Dynamic Bending.	Dynamic Tensile.
Mg + 5% Cu	Fig. 29	Fig. 30	Fig. 31
Mg + 10% Cu	,, 32	,, 33	,, 34
Mg + 15% Cu	,, 35	,, 36	,, 37
Mg + 3% Al	Fig. 38	Fig. 39	Fig. 40
Mg + 6% Al	,, 41	,, 42	,, 43
Mg + 9% Al	,, 44	,, 45	...

Determination of the forgeability of commercial magnesium has also been carried out by means of static and dynamic bend tests and dynamic tensile tests (Figs. 26, 27, and 28). It is interesting to observe the region, between 300° and 600° C., where great elongation occurs, no cracking taking place between 400° and 550° C. (Fig. 26). In the shock tests the power available (2 kgm.) was insufficient to break the test-pieces (Fig. 27). The capacity for deformation under dynamic tensile tests reaches a maximum at about 550° C. for *A* per cent. and 600° C. for Σ per cent.,

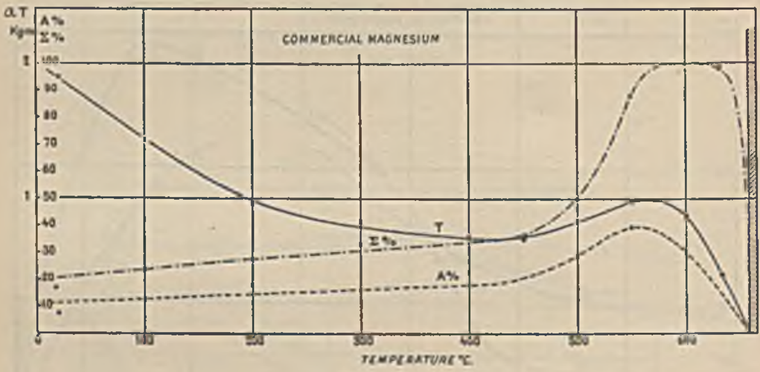

FIG. 28.

while the work T passes (Fig. 28) through a minimum and then a maximum at about 560° C.

(2) *Magnesium–Copper and Magnesium–Aluminium Alloys.*—Table I shows the composition of the alloys referred to in Figs. 29–45, and their properties dealt with as a function of temperature.

The following remarks may be made on these curves:

Magnesium–Copper Alloys.—A maximum exists on the curves showing capacity of deformation; it is more marked on the static tests than on the dynamic ones and on the low-copper alloys than on those of higher copper content. As already pointed out by one of the authors,* magnesium–copper alloys are forgeable up to 12 per cent. copper, whilst magnesium–aluminium alloys containing over 8 per cent. aluminium are forgeable with difficulty. The results now obtained show that up to about 15 per cent. copper these alloys are readily worked hot.

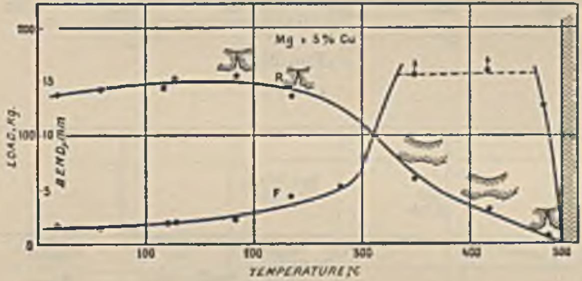

Fig. 29.

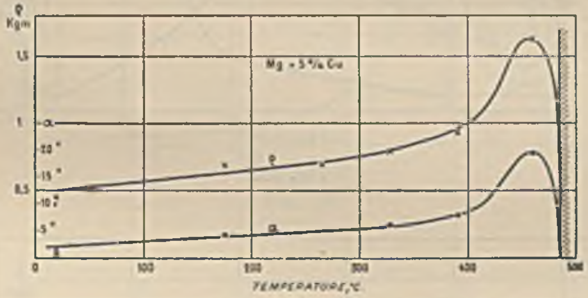

Fig. 30.

Magnesium–Aluminium Alloys.—Alloys containing 3 per cent. aluminium show a region of great elongation under dynamic bending

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* P. Bastien, "Study of Magnesium–Aluminium–Copper Alloys Rich in Magnesium," *Publ. sci. tech. Ministère de l'Air*, No. **20**, 1933, 1–9.

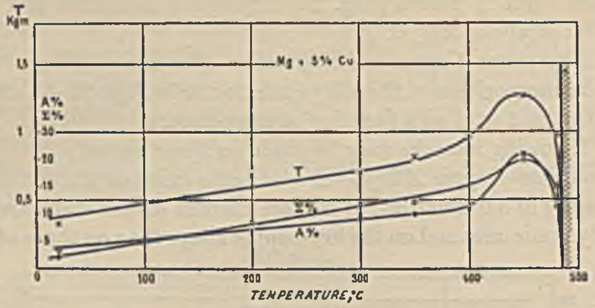

FIG. 31.

FIG. 32.

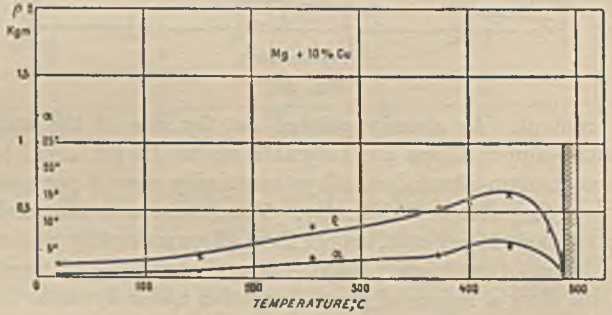

FIG. 33.

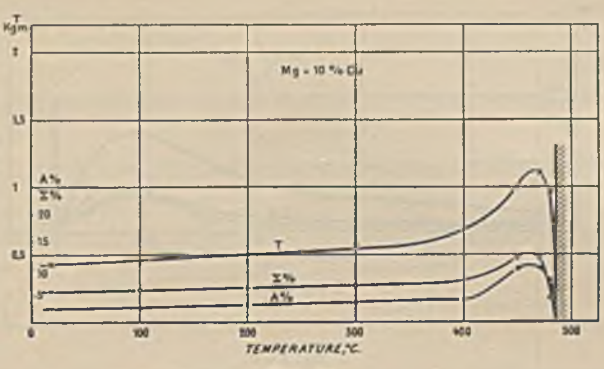

FIG. 34.

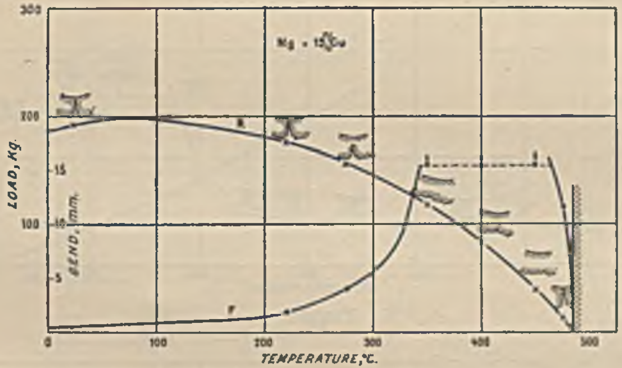

FIG. 35.

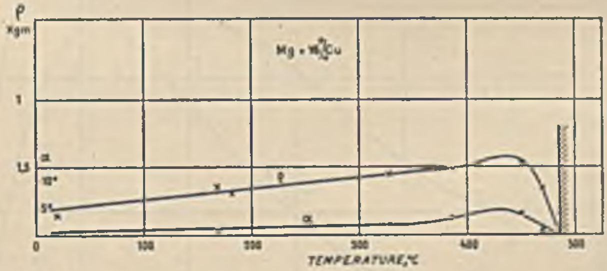

FIG. 36.

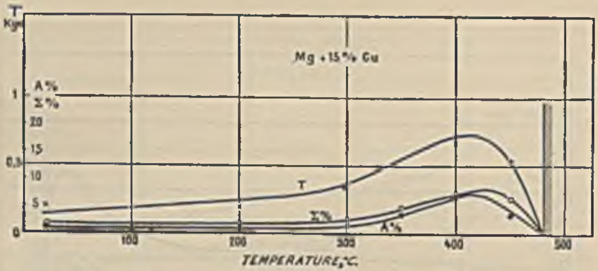

Fig. 37.

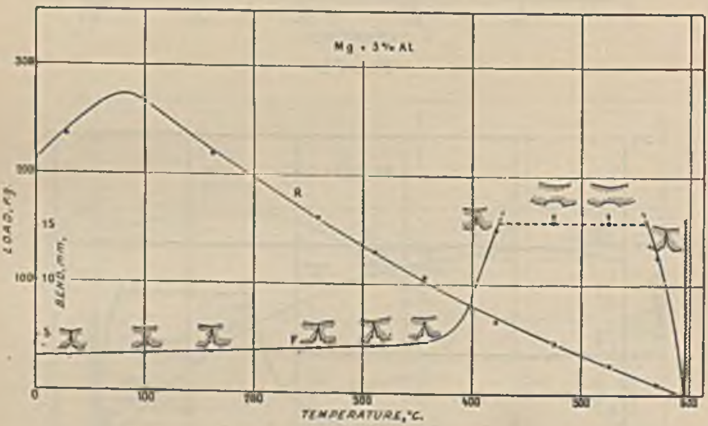

Fig. 38.

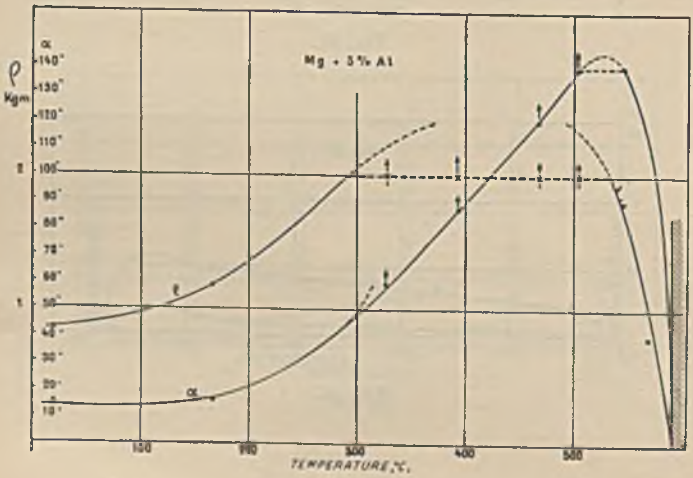

Fig. 39.

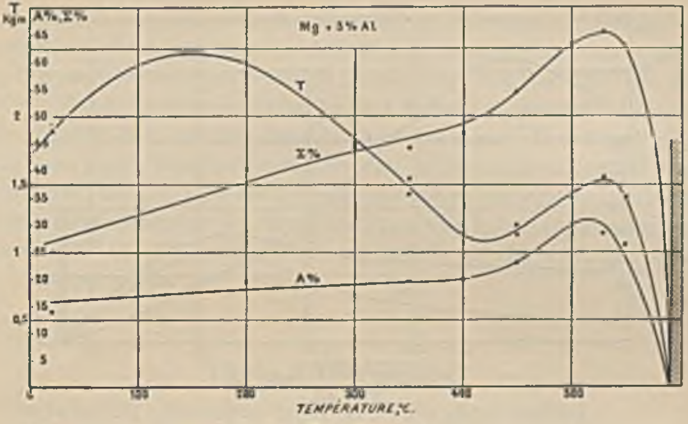

Fig. 40.

Fig. 41.

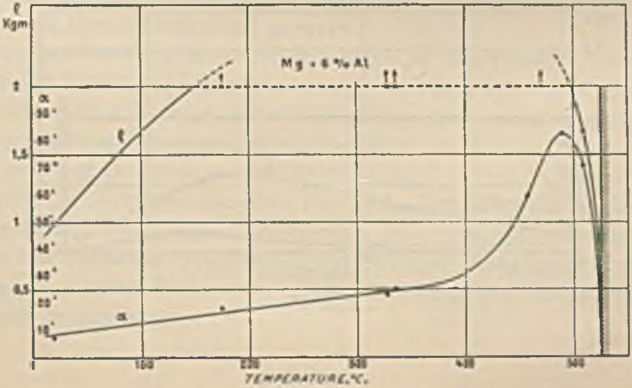

Fig. 42.

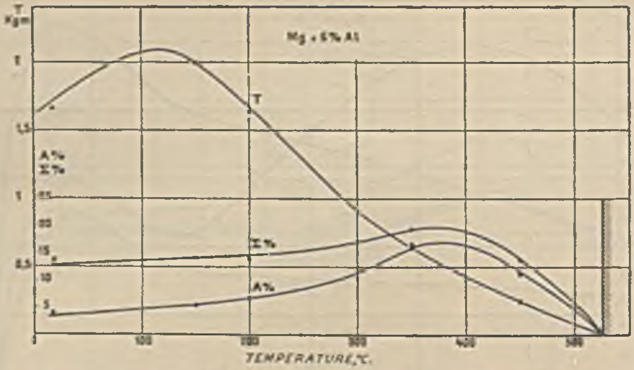

Fig. 43.

Fig. 44.

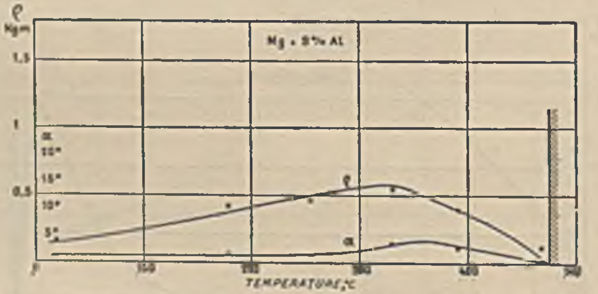

Fig. 45.

tests, as is the case in commercial magnesium; between 300° and 530° C. the work absorbed is greater than 2 kgm. and the test becomes a bending one, the angle of fracture reaching a maximum at about 530° C. The curve of shock fracture is similar to that found for commercial magnesium, having a minimum between two maxima. The 6 per cent. aluminium alloys behave in a similar way, the maxima in general being less marked, but the 9 per cent. aluminium alloys have little capacity for hot-deformation though the curves for F, ρ, and α have a slight maximum towards 350° C. The alloys were too brittle for the dynamic tensile test to be carried out.

GENERAL CONCLUSIONS.

The following conclusions apply to all the alloys studied :

(1) *Static Bending Tests.*—In every case, resistance to static bending passes through a more or less spread out maximum between 100° and 200° C. The bend at the moment of fracture, on the other hand, increases continually with temperature until a sudden decrease takes place at the melting point. Comparative curves follow the same course, the maximum being replaced, in the case of the more plastic alloys, by a fictitious flat, due to the passage of the test-piece between the supports. This flat ends, almost invariably, about 35° C. below the solidus.

(2) *Comparison between Static and Dynamic Bending.*—If capacity of deformation be defined by the bend in static bending and by the angle of fracture in dynamic bending, it is observed that the curves follow the same course and have a maximum, which is very much less marked for the angle α. The capacity for deformation by shock is, therefore, very much less, and sometimes the maximum disappears.

The positions of the maxima on the temperature scale do not agree on static and dynamic tests, being higher on the latter; this is connected with the influence of recrystallization after deformation, which is greater on slow deformation.

It appears that the absence of a maximum on the dynamic curves (or a very small maximum) indicates an alloy which is not practically forgeable, while even a narrow flat on the static curve indicates an alloy which can be forged at slow speeds or rolled.

The curve of variation of work absorbed on shock ρ is in general the same as that of the angle of fracture α and is unaffected by the maximum noted on that of the static load of fracture. In certain cases a maximum angle of fracture occurs without the occurrence of a maximum of work absorbed, at any rate in the same temperature range (*e.g.* aluminium + 5 per cent. magnesium).

(3) *Comparison of the Results obtained on the Different Dynamic Tests.*—This comparison only holds for alloys which are neither too brittle (aluminium + 12–15 per cent. magnesium) or too ductile (pure aluminium).

The curves representing capacity for deformation (those of the angle of fracture α, the elongation A per cent. or the reduction in area Σ per cent.) follow the same course without the maxima always occurring at the same temperature, those of tensile tests being generally lower (magnesium + 6 per cent. aluminium; aluminium + 5 per cent. magnesium or 6 per cent. copper); this is doubtless due to the influence of deformation by compression during bending.

The work absorbed in bending ρ, or in tension T, undergoes the same kind of variation, but T has sometimes a maximum at low temperatures (100°–200° C.), *e.g.* in magnesium + 3 per cent. aluminium and aluminium + 5 per cent. magnesium.

Under the experimental condition employed, the work absorbed on shock, ρ, gives the more sensitive and more economic evaluation; although the work absorbed in tensile shock gives, for the very ductile materials (unalloyed aluminium and magnesium), a value in accord with that of fracture in the region of deformability (which is not the case in bending); this is not of great practical interest, since in any case the thermal region for forging is clearly indicated by the constant value of the flats on the curves.

To sum up, static or dynamic bend tests appear to be the most suitable, convenient, and rapid for studying the forgeability of light and ultra-light alloys; where the metals are difficult to forge these tests make possible a determination of the best temperature range in which to carry out the work.

(4) *Comparison between the Different Alloys Investigated.*—From the results of these tests it would appear that magnesium alloys can be extruded up to about 15 per cent. of copper and about 9 per cent. of aluminium, and can with care be forged up to about 15 per cent. of copper and 7–8 per cent. of aluminium.

As for the aluminium alloys, that containing 12 per cent. copper should be able to be extruded and forged with care; while for those containing magnesium, the limit of forgeability must lie between 5 and 10 per cent. magnesium for metals of the purity employed.

BIBLIOGRAPHY.

[1] P. Ludwick, *Z.V.d.I.*, 1915, **59**, 657–664.

[2] W. Rosenhain, S. L. Archbutt, and D. Hanson, "Eleventh Report to the Alloys Research Committee on Some Alloys of Aluminium (Light Alloys)," *Inst. Mech. Eng.*, 1921, pp. 256.

[3] Martin Thomas, *J. Inst. Metals*, 1924, **31**, 121–152.

[4] P. Chevenard and A. Portevin, 5ème. Congrès de Chimie Industrielle, Paris, October 1925; *Chim. et Ind.*, 1926, **16**, 454.

[5] D. H. Ingall, *J. Inst. Metals*, 1925, **34**, 171–182.

[6] A. Portevin, *Rev. Mét.*, 1929, **26**, 435.

[7] J. Cournot, *Rev. Mét.*, 1929, **26**, 326.

[8] A. Portevin and F. Le Chatelier, *Compt. rend.*, 1929, **189**, 248.

[9] W. Schwinning and F. Fischer, *Z. Metallkunde*, 1930, **22**, 1.

[10] H. Sieglerschmidt, *Z. Metallkunde*, 1931, **23**, 26.

[11] R. L. Templin and D. A. Paul, *Symposium on Effect of Temperature on the Properties of Metals. Held at Joint Meeting of Amer. Soc. Mech. Eng. and Amer. Soc. Test. Mat.*, 1931, 290–313.

[12] D. Hanson and M. A. Wheeler, *J. Inst. Metals*, 1931, **45**, 229–257.

[13] T. Kobayashi, *Mem. Ryojun Coll. Eng.*, 1930, **3**, 145; *Brit. Chem. Abs.*, 1931, [B], 25.

[14] H. Bohner and R. Vogel, *Z. Metallkunde*, 1932, **24**, 169.

[15] L. Morell and J. Hanawalt, *Phys. Rev.*, 1932, [ii], **40**, 1035.

[16] S. I. Goubkin, *J. Rheology*, 1932, **3**, 501–548.

[17] E. Decherf, *Aciers spéciaux*, 1932, **7**, 329–344; 1933, **8**, 102–108, 315–327.

[18] A. E. van Arkel and M. van Bruggen, *Z. Physik*, 1933, **80**, 763–791.

[19] W. Schmidt (with H. Altwicker, A. Beck, H. Bothmann, E. Schmid, W. Schulze, and W. Spitaler), *Z. Metallkunde*, 1933, **25**, 229–236.

[20] R. Streeter, *Trans. Amer. Soc. Mech. Eng.*, 1933, **55**, IS, 55–57, 61–59.

[21] P. Bastien, *Rev. Mét.*, 1933, **30**, 528–542.

[22] A. von Zeerleder, R. Irmann, and E. von Burg, *Schweiz. Arch. angew. Wiss. Tech.*, 1935, **1**, 49–55.

[23] A. von Zeerleder and R. Irmann, *Z. Metallkunde*, 1935, **27**, 145–148.

[24] W. E. Prytherch, *J. Inst. Metals*, 1935, **56**, 133–154.

[25] J. Robinson, *Met. Ind.* (*Lond.*), 1936, **48**, 87–91.

[26] A. Portevin and P. Bastien, *Compt. rend.*, 1936, **202**, 2072–2074.

DISCUSSION.

(*Condensed.*)

PROFESSOR DR. A. VON ZEERLEDER * (Member): In this paper the authors describe a new method for determining the forgeability by a static and dynamic bending test. The great advantage of the new method is the elimination of the influence of friction between the test-piece and the pressure plates, which is in agreement with our earlier investigations.† These investigations on aluminium and various aluminium alloys have been carried out with small samples of a diameter of 20 mm., as shown in Fig. A (p. 108), and heated in an electric furnace under the press to different temperatures between 20° and 600° C. We so determined the necessary specific load to produce from the initial section a certain reduction of the height of the test-pieces up to 50 per cent. (similar investigations under a drop hammer with a hammer weight of 11 and 22 kg. with the same small test-pieces will be published in due course).

In Fig. B (p. 108), the results we obtained with a 5 and 10 per cent. aluminium–copper alloy at different temperatures are compared with the results obtained by the authors on alloys with 6 and 12 per cent. copper as mentioned in the paper. The figures obtained are not strictly comparable, but the parallelism of both investigations is clearly visible on the curves. It is surprising to note the increase of the maximum bending load determined by Professor Portevin and Dr. Bastien between 20° and 200° C., whereas in our curves an immediate decrease of the compression stress can be observed.

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

† *Z. Metallkunde*, 1935, **27**, 145; *Schweiz. Arch. angew. Wiss. Tech.*, 1935, **1**, (4), 1; *Aluminium*, 1936, **18**, 41.

Fig. C illustrates a similar comparison with pure magnesium and an aluminium alloy with 10 per cent. magnesium. At higher temperatures our curves are parallel to the curves of the paper. Again the increase revealed in the paper by the bending test up to 150° C. is surprising, and it would be interesting to get the opinion of the authors on this point.

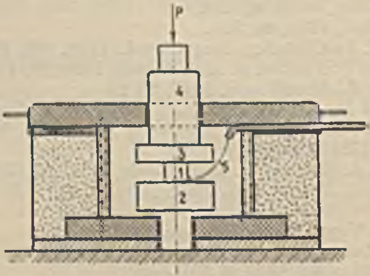

Fig. A.—Device for the Static Upsetting Test.

1 = sample.
2 = lower pressure plate.
3 = upper pressure plate.
4 = thrust die.
5 = thermoelement.

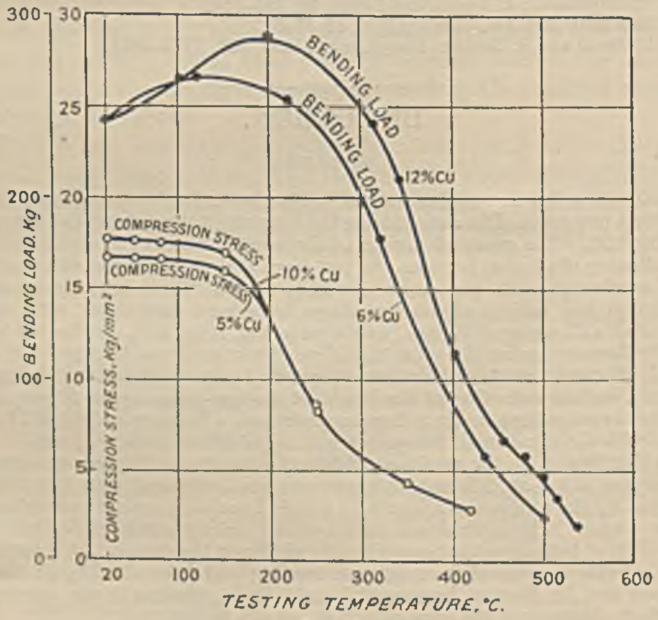

Fig. B.

Fig. D (p. 110) shows the influence of the increase of magnesium, Mg_2Si, and copper on the compression stress at different temperatures.

Professor G. B. **Waterhouse**,[*] B.Met., Ph.D. (Member): I would ask the authors whether they have carried out actual forging tests, on the alloys investigated in, order to confirm their laboratory tests.

Dr. C. H. **Desch**,[†] F.R.S. (Vice-President): I wish to refer to one small point which does not affect the subject-matter of the paper, but which it may be convenient to raise now. Some years ago a Committee of the Institute reported [‡] on the subject of nomenclature of alloys and drew up certain rules as to the order in which the metals composing an alloy should be mentioned. It was agreed, for example, that an alloy containing 90 per cent. of aluminium and 10 per cent. of copper should be called a copper–aluminium alloy and not an aluminium–copper alloy. The opposite plan has been adopted in this

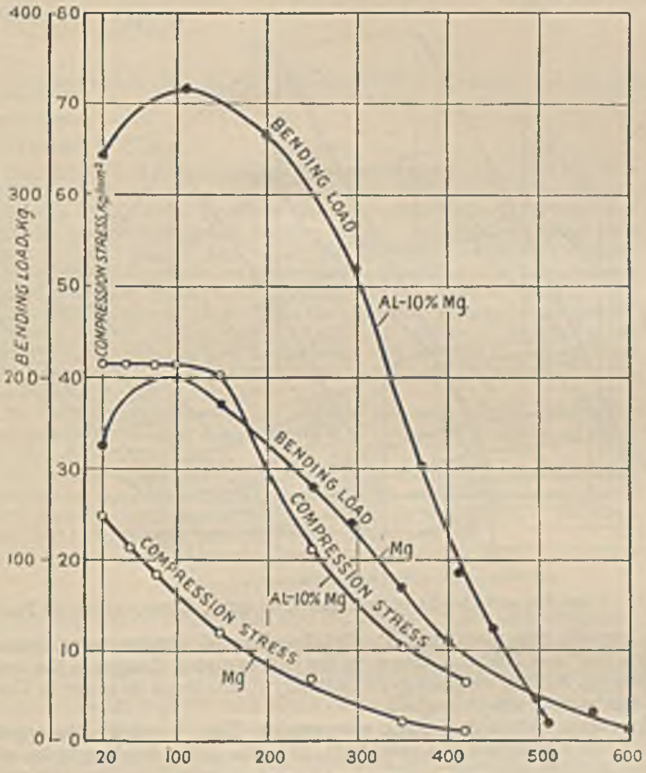

Fig. C.

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[*] Professor of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A.

[†] Superintendent, Department of Metallurgy, National Physical Laboratory, Teddington.

[‡] *J. Inst. Metals*, 1914, **11**, 45.

paper. Perhaps we have here an opportunity of raising the question of some international agreement as to the nomenclature of alloys.

Dr. Bastien (*in reply*): We have carried out forging in the case of the ultra-light alloys magnesium–aluminium and magnesium–copper and have obtained experimental practical confirmation of the results obtained in the laboratory.* As regards the light alloys, we are in process of finding out whether there is good concordance between our results in the laboratory and results in the works.

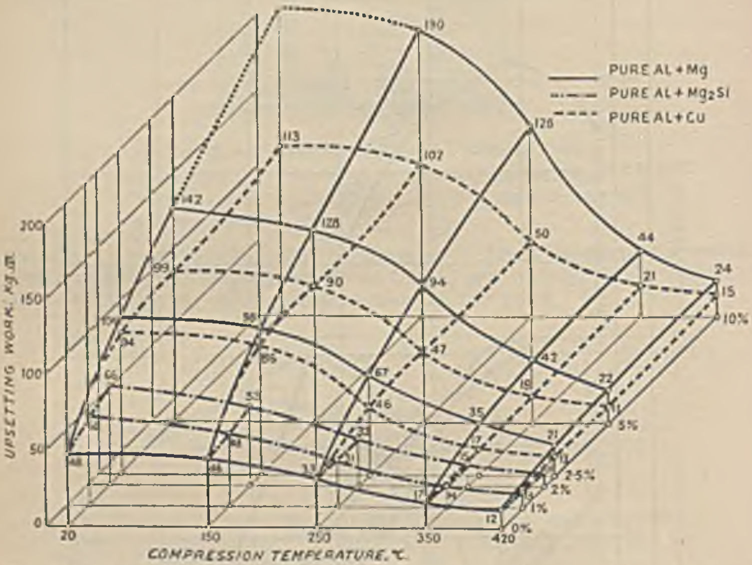

Fig. D.—Diameter and Height of Specimens, 20 mm.; Compression, 50 Per Cent.

As regards the maximum at slightly elevated temperatures (generally between 100° and 200° C.), shown on the curves giving changes in the bending load (see pp. 88–89), we have systematically found them to occur in the case of all the various alloys studied.

The curves obtained in static compression (Figs. 8 and 9) also appear to indicate the occurrence of a maximum, as in the static bending tests, which, however, is much less clearly marked. Our curves cannot be directly compared with those of Professor von Zeerleder since, in the first place they show the change in breaking load in the region in which there is complete fracture, and secondly the variation of the maximum load reached, with a 50% reduction in height, in the zone of temperatures in which this reduction occurs without fracture of the specimen.

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* P. Bastien, *Rev. Mét.*, 1933, 30, 528–542.

MECHANICAL PROPERTIES OF ALUMINIUM AND ITS ALLOYS AFTER PROLONGED HEATING.* 740

By Professor Dr.-Ing. A. von ZEERLEDER,† Member, and Dr.-Ing. R. IRMANN,‡ Met.Eng.

Synopsis.

The strength of pure aluminium and various aluminium alloys has been investigated after heating for long periods at 75°–300° C. The strength properties of the same materials were determined also in the state of complete stabilization. The heating periods employed extended over approximately 2 years. After treatments of different duration at elevated temperatures, some specimens were cooled and tested at room temperature; others were tested at the treatment temperature. For complete softening at 250° C., for instance, *i.e.* to obtain the properties observed in completely stabilized samples, heating periods of at least 6 months are required in the case of pure aluminium and Anticorodal, and of more than 2 years for Avional and "Y" alloy. A still longer heating time is necessary in the case of the alloy "R.R. 59."

To determine the decrease in strength of any material after heating for long periods at elevated temperatures it is necessary, therefore, to carry out tests of long duration.

The values of the yield-point observed in the normal short time test after heating periods of 1 year form a basis for calculations for engineers. The permissible loads can be ascertained only by observation of the creep limit, and this property is being studied by the authors.

Introduction.

The increasing use of aluminium and its alloys at elevated temperatures makes a precise knowledge of the properties at those temperatures of increasing importance. The present paper describes extensive investigations on pure aluminium and some of its alloys in this connection.

On consideration of the influence of temperature on the tensile strength of aluminium (Fig. 1) as observed by different investigators, serious discrepancies are found in the results, especially for temperatures between 100° and 300° C.—a range of special importance to the engineer. In view of the experience of the various investigators, the discrepancies cannot be attributable to errors of observation, but rather to differences in the test conditions employed.

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* Manuscript received February 15, 1936.

† Chief Engineer, Aluminium-Industrie A.G., Neuhausen, Switzerland; Professor of Technology of Aluminium at Federal Technical High School, Zürich.

‡ Head of the Mechanical Testing Department, Aluminium-Industrie A.G., Neuhausen, Switzerland.

As will be shown later, a slow, gradually increasing decrease in strength occurs on long heating within the temperature range mentioned above. The decrease in strength properties depends on the nature of the alloy. Anticorodal, for instance, softens within a comparatively short time, whereas Avional needs much more time. This is made clear in Fig. 2, which shows the time necessary at different temperatures to cause a 50 per cent. decrease in hardness. The heating time is represented logarithmically in this and the other illustrations.

Fig. 1.—Tensile Strength of Pure Aluminium as Depending on the Temperature. Tested at the Annealing Temperature.

Systematic investigations of these effects have been carried out during the past 15 years, but appropriate and reliable technique has been developed only recently. At the Autumn Meeting of the Institute in Düsseldorf in 1929, the first paper on the influence of operating temperatures on the strength properties of overhead electric transmission cables was read by one of the present authors.[7] It was stated in that paper that a hard wire of pure aluminium softens noticeably at a temperature of 80° C., and it was further stated in error that complete softening had occurred after heating at 80° C. for 1000 hrs. More accurate tests in a subsequent investigation have shown that statement to be incorrect.[14] The results of the subsequent investigation, which included tests of wires in different materials after heating for long periods at 77° C. are given in Fig. 3, and those obtained after heating at 160° C. are given in Fig. 4. These results show that the percentage decrease of strength after heating at 77° C. is much greater for copper than for pure aluminium and Aldrey, while Anticorodal and Avional show a noticeable age-hardening effect. After heating at 160° C. the latter alloys showed a distinct decrease of strength, but after heating at 100° C. no softening was observed in these materials.

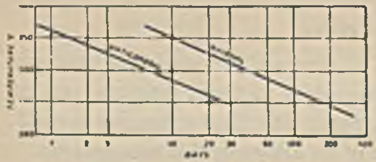

Fig. 2.—Time Necessary for a 50 Per Cent. Decrease in Hardness of Anticorodal and Avional after Heat-Treatment at Different Temperatures. Tested at 20° C.

EXPERIMENTS.

Additional experiments have been made to determine the temperature at which the softening commences. Heating at temperatures between 77° and 160° C. was carried out in an oil-bath. The strength of the samples was determined after they had been heated for suitable periods at different temperatures, and cooled to 20° C. The time required for completion of the tensile test varied between 2 and 5 minutes, according to the elongation of the material.

Tests of wires of pure aluminium of 99·0 and 99·5 per cent. purity, Anticorodal, Avional D, Aldrey, copper, nickel, and iron, at 20° after heating for 1 year at 50°, 75°, 100°, and 160° C. confirm the earlier results. The tensile strength curves are given in Fig. 5. In Fig. 6 the values are given as percentages of the original strength, and it is quite clear that copper, after heating for 1 year at temperatures up to 160° C., shows a much higher percentage decrease in strength than pure aluminium.

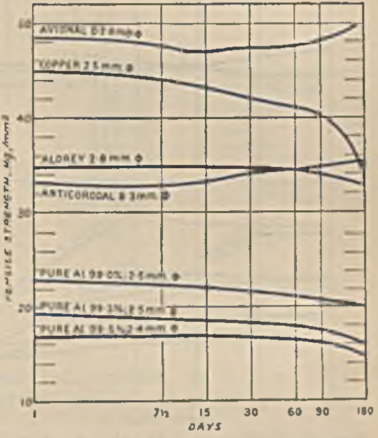

Fig. 3.—Influence of Continuous Heating at 77° C. on the Tensile Strength of Various Wire Materials. Tested at 20° C.

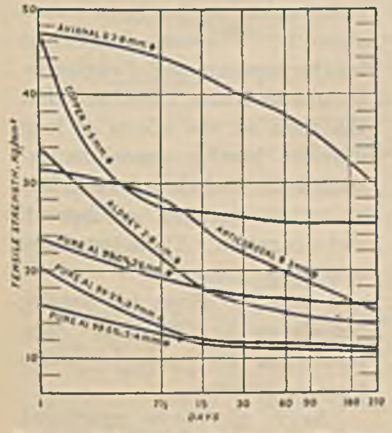

Fig. 4.—Influence of Continuous Heating at 160° C. on the Tensile Strength of Various Wire Materials. Tested at 20° C.

In previous work [14] a study was made of the influence of complete and incomplete stabilization on the strength properties of heat-treated aluminium alloys. The material was in the form of extruded bars of 20 mm. diameter.

The term "incomplete stabilization" is used in reference to samples which, before being tested, had first been given normal solution-treatment, then heated for 2 hrs. at 100°, 200°, 250°, 300°, 350°, 400°, or 450° C., and finally tested at that temperature.

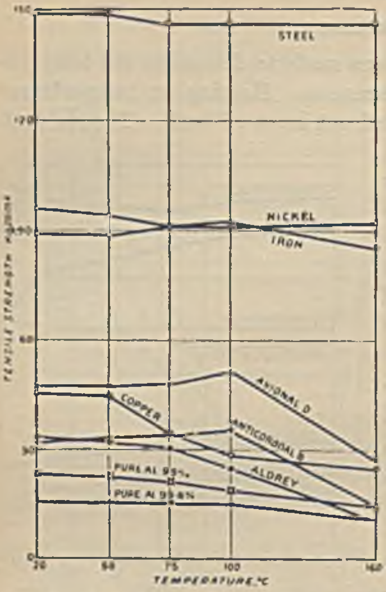

FIG. 5.—Influence of Heating for 1 Year at Different Temperatures on the Tensile Strength of Various Wire Materials. Tested at 20° C.

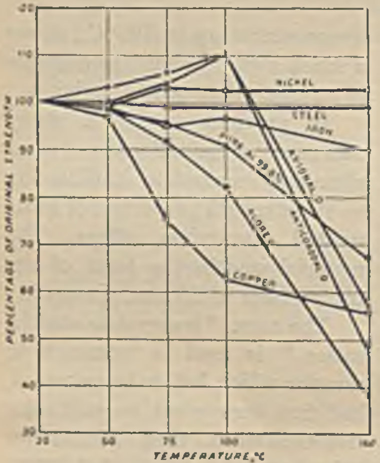

FIG. 6.—Influence of Heating for 1 Year at Different Temperatures on the Tensile Strength of Various Wire Materials Expressed as Percentage of the Original Strength. Tested at 20° C.

The term "complete stabilization" is used in reference to samples which had been first heated for 4 hrs. at their solution-treatment temperature, then allowed to cool in 24 hrs. by stages of 50° C. until the temperature of testing—450°, 400°, 350°, 300°, 250°, 200°, or 100° C. —was reached.

In connection with the earlier investigations, the decrease of the strength resulting from prolonged heating was only determined by means of the Brinell hardness test and it was found that after heating to temperatures exceeding 200° C., the Brinell hardness only approaches that of completely stabilized samples when the heating has extended over lengthy periods; at 300°–350° C. this is usually reached after a heating period of 100–300 days. Information on hardness values alone is, however, insufficient for the requirements of engineers. It was desirable, therefore, that the tests on the effects of long duration heating should be extended to include observations of tensile strength, yield-point, and elongation. These tests have now been carried out on cast and wrought alloys for heating periods up to 720 days. The results for the wrought alloys were as follows.

As in the tests mentioned above, the material was in the form of extruded bars of 20 mm. diameter. The method and conditions of testing were the same as those used previously and were, briefly described, as follows: The apparatus for tests at elevated temperatures is shown in Fig. 7. For the tests at elevated temperature the test-piece shown in Fig. 8, having threaded ends, was used. This was heated without application of stress at the temperature of testing for 20 minutes and then pulled at a rate of testing, which resulted in fracture after 2–5 minutes according to the elongation of the material used. The gauge-length was $\frac{11{\cdot}3\sqrt{F}}{2}$. ($F$ = section.)

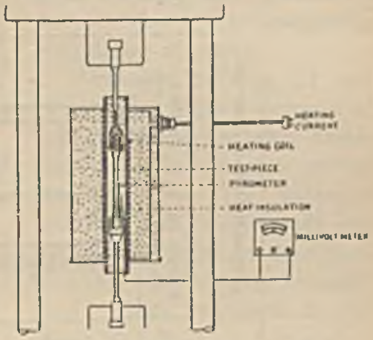

Fig. 7.—Equipment for Hot Tensile Tests.

In the investigations illustrated in Figs. 21–26 the initial points given at 0 day, plotted on the left of the figures, have been determined at room temperature, as it is not possible to heat the samples to different testing temperatures in a time sufficiently short without annealing.

In the tension tests at room temperature the same test-piece was used, but the ends were not threaded. The test-pieces were broken in 1–2 minutes. The gauge-length was $11{\cdot}3\sqrt{F}$, and the test results recorded were the average of three.

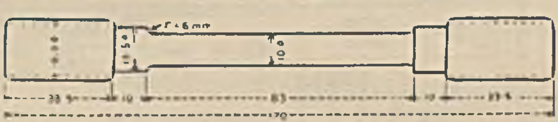

Fig. 8.—Test-Bar for Hot Tensile Tests.

Table I gives the composition and properties of the materials used. The results of the individual tests are not given on account of their very large number.

Strength Tests at Room Temperature.

The various materials—pure aluminium, Peraluman 2, Anticorodal B, Avional D, "Y" alloy, and "R.R. 59" alloy—after heating at 75°, 100°, 130°, 160°, 200°, 250°, and 300° C. for periods up to 2 years, showed different behaviour according to their previous treatment and composition.

Pure Aluminium (Figs. 9 and 10), the original material of which was half hard, shows no decrease at temperatures up to 160° C. At higher temperatures, complete softening occurs by reason of recrystallization. At 250° C., however, the lowest recorded strength properties are

TABLE I.

<table>
<tr><th rowspan="2">Material.</th><th rowspan="2">mm.
φ.</th><th colspan="7">Analysis.</th><th colspan="8">Original Mechanical Properties.</th></tr>
<tr><th>Fe.</th><th>Si.</th><th>Mn.</th><th>Mg.</th><th>Cu.</th><th>Ni.</th><th>O.</th><th colspan="2">Yield-Point (σ 0·2), kg./mm.².</th><th colspan="2">Tensile Strength σ_B, kg./mm.².</th><th colspan="2">Elongation δ, Per Cent. l = 200 mm.</th><th colspan="2">Brinell Hardness, kg./mm.².</th></tr>
<tr><td>Aluminium 99·0 wire . .</td><td>2·6</td><td>0·35</td><td>0·25</td><td>...</td><td>...</td><td>0·02</td><td>...</td><td>...</td><td colspan="2">17·7</td><td colspan="2">23·0</td><td colspan="2">2·82</td><td colspan="2"></td></tr>
<tr><td>" 99·5 " . .</td><td>2·4</td><td>0·30</td><td>0·15</td><td>...</td><td>...</td><td>0·01</td><td>...</td><td>...</td><td colspan="2">14·1</td><td colspan="2">16·4</td><td colspan="2">1·75</td><td colspan="2"></td></tr>
<tr><td>Aldrey " . .</td><td>2·4</td><td>0·25</td><td>0·55</td><td>...</td><td>0·44</td><td>0·01</td><td>...</td><td>...</td><td colspan="2">27·4</td><td colspan="2">32·9</td><td colspan="2">8·3</td><td colspan="2"></td></tr>
<tr><td>Anticorodal B " . .</td><td>3·0</td><td>0·22</td><td>1·02</td><td>0·68</td><td>0·70</td><td>0·02</td><td>...</td><td>...</td><td colspan="2">21·4</td><td colspan="2">32·3</td><td colspan="2">13·1</td><td colspan="2"></td></tr>
<tr><td>Avional D " . .</td><td>2·8</td><td>0·28</td><td>0·25</td><td>0·55</td><td>0·52</td><td>3·85</td><td>...</td><td>...</td><td colspan="2">29·2</td><td colspan="2">46·6</td><td colspan="2">16·1</td><td colspan="2"></td></tr>
<tr><td>Iron " . .</td><td>2·4</td><td>R *</td><td>0·05</td><td>0·30</td><td>...</td><td>...</td><td>...</td><td>0·05</td><td colspan="2">79·8</td><td colspan="2">95·7</td><td colspan="2">1·5</td><td colspan="2"></td></tr>
<tr><td>Steel " . .</td><td>2·0</td><td>R *</td><td>0·15</td><td>0·40</td><td>...</td><td>...</td><td>...</td><td>0·20</td><td colspan="2">119·0</td><td colspan="2">147·7</td><td colspan="2">5·5</td><td colspan="2"></td></tr>
<tr><td>Nickel " . .</td><td>2·0</td><td>0·25</td><td>...</td><td>0·15</td><td>...</td><td>0·10</td><td>R *</td><td>...</td><td colspan="2">77·9</td><td colspan="2">88·8</td><td colspan="2">1·5</td><td colspan="2"></td></tr>
<tr><td>Copper " . .</td><td>2·0</td><td>...</td><td>...</td><td>...</td><td>...</td><td>99·99</td><td>...</td><td>...</td><td colspan="2">39·3</td><td colspan="2">45·9</td><td colspan="2">1·8</td><td colspan="2"></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>Ti.</td><td>(1)</td><td>(2)</td><td>(1)</td><td>(2)</td><td>(l = 11·3$\sqrt{F}$)
(1)</td><td>(l = $\frac{11{\cdot}3}{2}\sqrt{F}$)
(2)</td><td>(1)</td><td>(2)</td></tr>
<tr><td>Aluminium 99·5 round-bar .</td><td>10·0</td><td>0·28</td><td>0·18</td><td>...</td><td>...</td><td>0·02</td><td>...</td><td>...</td><td>11·4</td><td>10·7</td><td>11·5</td><td>11·4</td><td>9·3</td><td>17·6</td><td>33·0</td><td>32·0</td></tr>
<tr><td>Peraluman 2 " .</td><td>10·0</td><td>0·22</td><td>0·25</td><td>1·45</td><td>2·20</td><td>0·02</td><td>...</td><td>...</td><td>15·7</td><td>12·9</td><td>25·6</td><td>26·5</td><td>12·7</td><td>17·1</td><td>62·0</td><td>61·0</td></tr>
<tr><td>Anticorodal B " .</td><td>10·0</td><td>0·25</td><td>0·98</td><td>0·65</td><td>0·72</td><td>0·01</td><td>...</td><td>...</td><td>36·8</td><td>30·5</td><td>38·8</td><td>33·9</td><td>7·6</td><td>14·7</td><td>106·0</td><td>104·0</td></tr>
<tr><td>Avional D " .</td><td>10·0</td><td>0·25</td><td>0·28</td><td>0·58</td><td>0·55</td><td>3·78</td><td>...</td><td>...</td><td>34·1</td><td>32·7</td><td>47·6</td><td>40·5</td><td>13·1</td><td>15·8</td><td>112·0</td><td>111·0</td></tr>
<tr><td>"Y" Alloy " .</td><td>10·0</td><td>0·22</td><td>0·25</td><td>...</td><td>1·45</td><td>3·95</td><td>1·92</td><td>...</td><td>26·0</td><td>22·9</td><td>39·9</td><td>38·9</td><td>20·1</td><td>23·7</td><td>107·0</td><td>109·0</td></tr>
<tr><td>"R.R. 59" Alloy " .</td><td>10·0</td><td>1·15</td><td>0·82</td><td>...</td><td>1·49</td><td>2·35</td><td>1·32</td><td>0·06</td><td>39·2</td><td>29·2</td><td>41·7</td><td>37·1</td><td>7·3</td><td>12·7</td><td>138·0</td><td>121·0</td></tr>
</table>

* R = remainder.

(1) = Original mechanical properties of the test-pieces tested at 20° C.

(2) = Original mechanical properties of the test-pieces tested at the annealing temperatures.

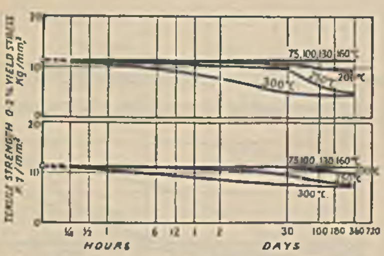

Fig. 9.—Influence of Continuous Heating at Different Temperatures on Yield-Point and Tensile Strength of Pure Aluminium. Tested at 20° C.

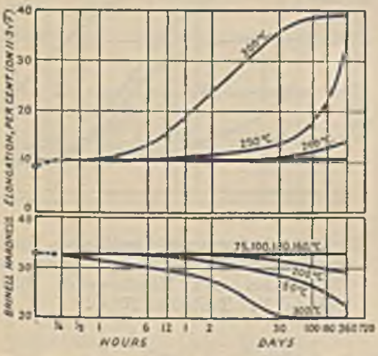

Fig. 10.—Influence of Continuous Heating at Different Temperatures on Elongation and Hardness of Pure Aluminium. Tested at 20° C.

only attained after a period of 180–360 days. The degree of purity of the metal is here of great influence, since the rate of recrystallization increases greatly with degree of purity.

Peraluman 2 (Figs. 11 and 12) does not show a decrease of strength properties after treatment at temperatures up to 200° C., since the extruded material used corresponds approximately to the soft condition, in which this alloy is normally used. After treatment in the range 250°–300° C., however, a slight decrease is seen.

Anticorodal B (Figs. 13 and 14). Treatment at the lower temperatures, between 75° and 160° C., causes an increase of the yield-point and tensile strength, showing that the material had not yet undergone maximum precipitation-hardening. Treatment at 250° C. only results

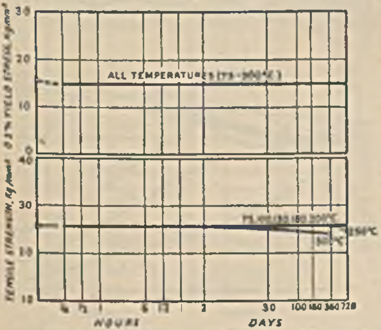

Fig. 11.—Influence of Continuous Heating at Different Temperatures on Yield-Point and Tensile Strength of Peraluman 2. Tested at 20° C.

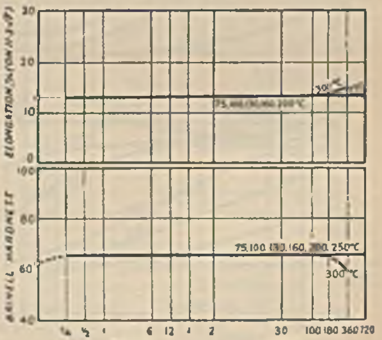

Fig. 12.—Influence of Continuous Heating at Different Temperatures on Elongation and Hardness of Peraluman 2. Tested at 20° C.

in complete softening after about 360 days, whereas for treatment at 300° C., 180 days are sufficient.

Avional D (Figs. 15 and 16) shows the phenomenon, already described elsewhere,[14] of decreasing strength and increasing elongation after short-

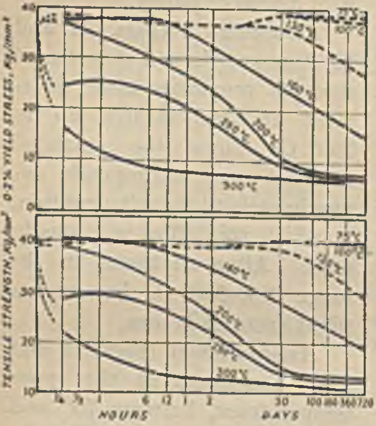

Fig. 13.—Influence of Continuous Heating at Different Temperatures on Yield-Point and Tensile Strength of Anticorodal B. Tested at 20° C.

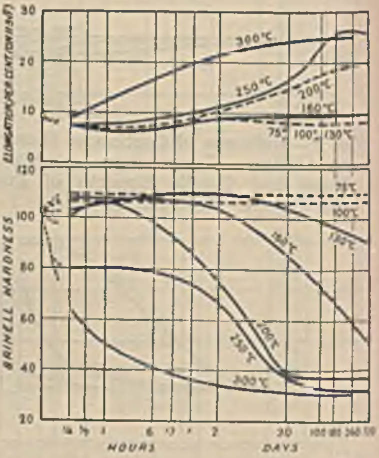

Fig. 14.—Influence of Continuous Heating at Different Temperatures on Elongation and Hardness of Anticorodal B. Tested at 20° C.

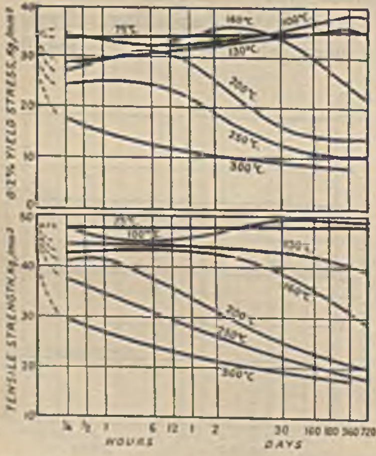

Fig. 15.—Influence of Continuous Heating at Different Temperatures on Yield-Point and Tensile Strength of Avional D. Tested at 20° C.

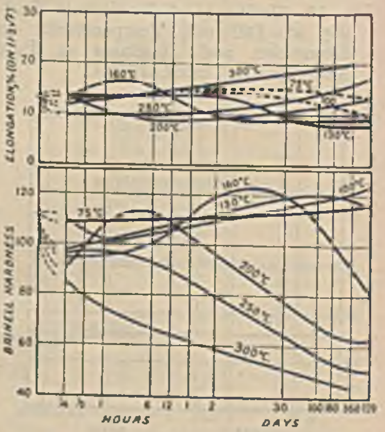

Fig. 16.—Influence of Continuous Heating at Different Temperatures on Elongation and Hardness of Avional D. Tested at 20° C.

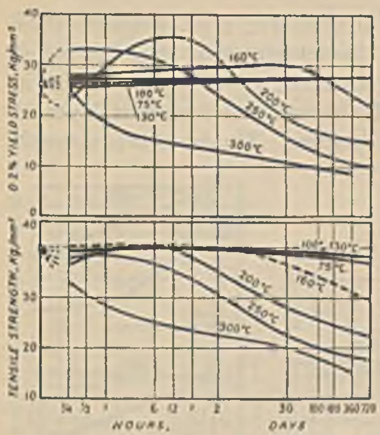

Fig. 17.—Influence of Continuous Heating at Different Temperatures on Yield-Point and Tensile Strength of "Y" Alloy. Tested at 20° C.

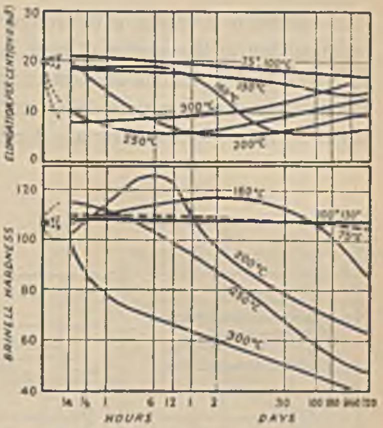

Fig. 18.—Influence of Continuous Heating at Different Temperatures on Elongation and Hardness of "Y" Alloy. Tested at 20° C.

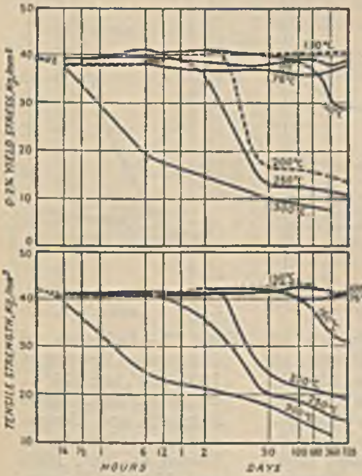

Fig. 19.—Influence of Continuous Heating at Different Temperatures on Yield-Point and Tensile Strength of "R.R. 59" Alloy. Tested at 20° C.

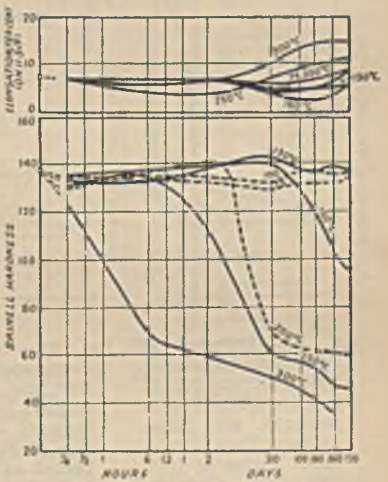

Fig. 20.—Influence of Continuous Heating at Different Temperatures on Elongation and Hardness of "R.R. 59" Alloy. Tested at 20° C.

time treatments of $\frac{1}{4}$ hr. up to 1–2 days, in which the lowest strength and highest elongation are attained the more quickly the higher the temperature of treatment. After attaining a maximum, the strength then shows a decrease after longer treatments; thus, Avional of the composition of the material used in this investigation, after heating at 75°–100° C. for periods of increasing duration, shows first a decrease in strength for heating periods up to 1 day and then for about 1 year a slight increase, followed by a second decrease. The decrease in strength occurs with an increase in elongation value and *vice versa*. Complete annealing of Avional at 300° C. requires more than 12 months.

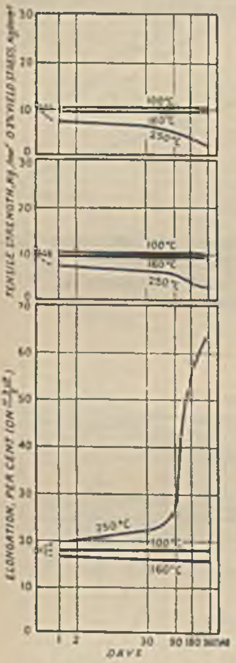

Fig. 21.—Influence of Continuous Heating at 100°, 160°, and 250° C. on Yield-Point, Tensile Strength, and Elongation of Pure Aluminium. Tested at 100°, 160°, and 250° C., Respectively.

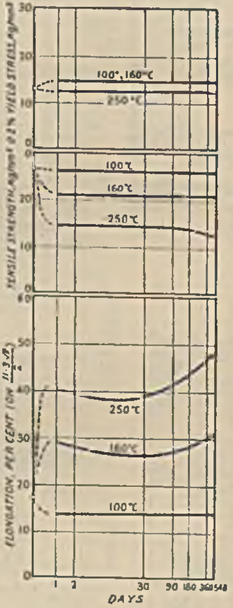

Fig. 22.—Influence of Continuous Heating at 100°, 160°, and 250° C., on Yield-Point, Tensile Strength, and Elongation of Peraluman 2. Tested at 100°, 160°, and 250° C., Respectively.

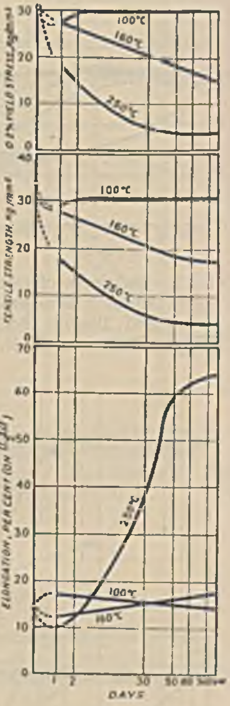

Fig. 23.—Influence of Continuous Heating at 100°, 160°, and 250° C. on Yield-Point, Tensile Strength, and Elongation of Anticorodal B. Tested at 100°, 160°, and 250° C., Respectively.

" Y " *Alloy* (Figs. 17 and 18) behaves similarly to Avional. After heating for ¼ hr. at 200° C., the strength commences to decrease and later increases, a maximum being attained after 12–24 hrs. by the effect of age-hardening; subsequently, the strength again decreases. The influence of heating for periods of 2 years up to 130° C. on the strength is, as in the case of Avional, still scarcely perceptible.

"*R.R. 59*" *Alloy* (Figs. 19 and 20). This alloy shows a similar behaviour to that of Avional and " Y " alloy after short-time heating, the decrease of the 0·2 per cent. yield stress and the subsequent increase being less strongly marked, however.

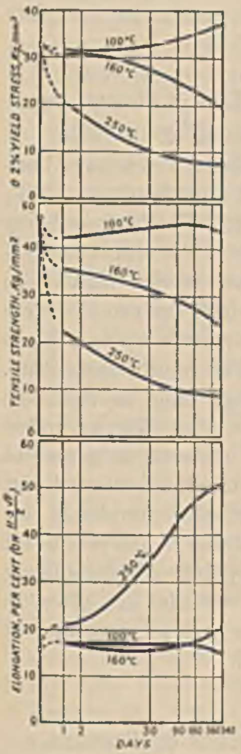

FIG. 24.—Influence of Continuous Heating at 100°, 160°, and 250° C. on Yield-Point, Tensile Strength, and Elongation of Avional D. Tested at 100°, 160°, and 250° C., Respectively.

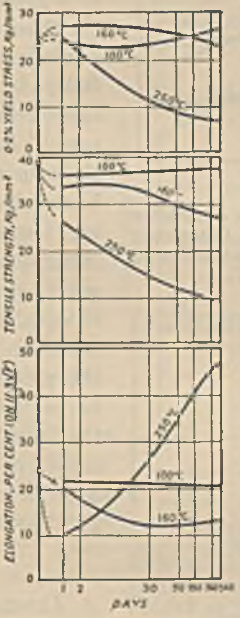

FIG. 25.—Influence of Continuous Heating at 100°, 160°, and 250° C., on Yield-Point, Tensile Strength, and Elongation of " Y " Alloy. Tested at 100°, 160°, and 250° C., Respectively.

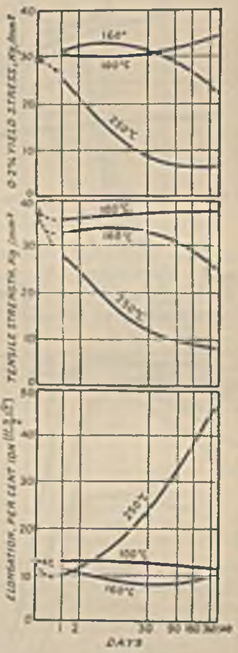

FIG. 26.—Influence of Continuous Heating at 100°, 160°, and 250° C. on Yield-Point, Tensile Strength, and Elongation of "R.R. 59" Alloy. Tested at 100°, 160°, and 250° C., Respectively.

After heating to temperatures up to 130° C. for 2 years, the strength

Fig. 27.—Yield-Point of Pure Aluminium and Aluminium Alloys Completely Stabilized as Depending on the Testing Temperature of 20°–250° C.

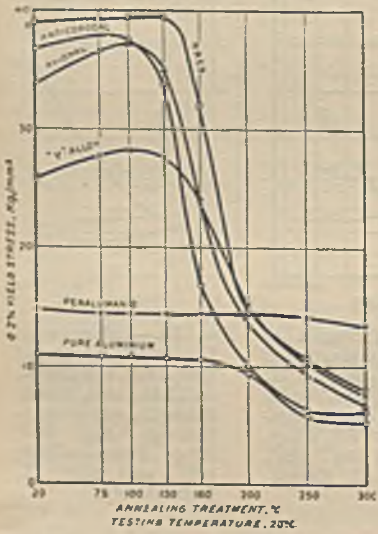

Fig. 28.—Influence of Continuous Heating for 1 Year at Temperatures up to 300° C. on the Yield-Point of Pure Aluminium and Aluminium Alloys. Tested at 20° C.

properties remain unaffected. Alloy " R.R. 59 " is exceptionally strong at elevated temperatures and differs from Avional in that heating for 1–2 years at 300° C. does not result in complete softening.

Strength Tests at Elevated Temperature (Figs. 21–26).

These tests, which have been carried out after heating at 100°, 160°, and 250° C. (the tests being carried out at the same temperatures), show results similar to those in which the samples were heated for periods up to 2 years and tested at room temperature. After a very long, or from the practical point of view, unlimited time, the material is bound to attain the minimum strength, *i.e.* the properties of completely stabilized material. The results for the yield-point of completely stabilized material are given in Fig. 27 for test temperatures of 20°–250° C.

Discussion of Results.

To get a better idea of the results of the samples tested at 20° C. and at elevated temperatures as represented by the former figures, we have produced the curves 28 and 29. We have collected the results of our investigations, carried through with different alloys in Fig. 28, showing the influence of annealing at different temperatures between

75° and 300° C. and the testing results at 20° C. on the yield-points. On Fig. 29 the yield-point tested at annealing temperature is represented. The curves for Avional and "Y" alloy show a marked increase in yield-point (room temperature) after heating to temperatures up to 100° C. "R.R. 59" is distinctly superior to Avional and "Y" alloy after heating at temperatures up to 160° C. On the other hand, the yield-point of the copper-free alloy Anticorodal decreases very rapidly after 100° C., and at 160° C. is already much lower than that of alloy Avional, "Y" alloy, and especially "R.R. 59." After heating at 200° C. the yield-point of Anticorodal is even lower than that of the alloy Peraluman 2 and nearly as low as that of pure aluminium. The same effect can also be observed in Figs. 9–20, but less clearly. Further, it can be seen that even at 160° C. "R.R. 59" is distinctly superior to "Y" alloy and Avional.

Pure, half-hard aluminium is not affected appreciably up to 160° C. For 300° C. the differences between the alloys become very small; only Peraluman 2, which is used in the soft state and is not heat-treatable, forms an exception, as would be expected. Even after heating at 300° C. it shows no substantial decrease in strength and has a higher strength than all the other alloys.

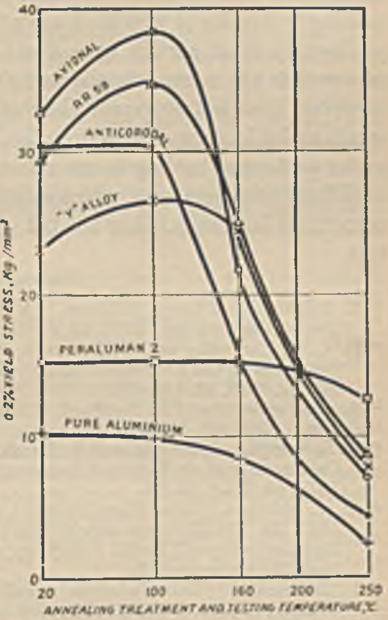

FIG. 29.—Influence of Continuous Heating for 1 Year at Temperatures up to 250° C. on the Yield-Point of Pure Aluminium and Aluminium Alloys. Tested at the Annealing Temperature.

Almost the same observation is obtained from an examination of the temperature of heating on the yield-point of the alloys heated for 1 year at 100°, 160°, and 250° C. and tested at these temperatures (Figs. 21–26 and Fig. 29). "R.R. 59" is found to be distinctly superior up to 160° C. It will be noted that the 0·2 per cent. yield-point of "R.R. 59" still increases up to 100° C. This suggests that the precipitation-hardening of the original material was incomplete.

Our investigations have shown that it would not be permissible to take as final strength after prolonged heating at a given temperature the results of tests of fully stabilized material tested at room temperature or at the temperature of heating after being heated to the temperature concerned. It appears to be necessary to carry out the lengthy procedure of prolonged heating tests for each alloy.

The curves included in the present paper give the strength of pure aluminium and of some wrought aluminium alloys after prolonged heating. Results of this kind are often required by engineers and the yield-point is of service as a basis for calculation. The yield-point observed in the normal tensile test (0·2 per cent. permanent extension), however, does not represent the strength for 0·2 per cent. permanent strain under loading of long duration. The matter of permissible stress under prolonged loading is one relating to the so-called " creep-limit " at different temperatures, which as indicated by results obtained to date, sometimes lies much below the 0·2 per cent. yield of the normal tensile test.

BIBLIOGRAPHY.

[1] R. Seligman and Percy Williams, " A Note on the Annealing of Aluminium," *Trans. Faraday Soc.*, 1916, 12, 64–65.

[2] H. C. H. Carpenter and L. Taverner, " The Effects of Heat at Various Temperatures on the Rate of Softening of Cold-Rolled Aluminium Sheet," *J. Inst. Metals*, 1917, 18, 115–168.

[3] A. von Zeerleder and M. Bosshard, " Neue Wege im Freileitungsbau," *Z. Metallkunde*, 1927, 19, 459–470.

[4] R. L. Templin, C. Braglio, and K. Marsh. " Mechanical Properties of Aluminium Casting Alloys at Elevated Temperatures," *Trans. Amer. Soc. Mech. Eng.*, 1928, 50, IS–8, 25–36.

[5] M. v. Schwarz, " Die Warmfestigkeit von Reinaluminium," *Z. Metallkunde*, 1927, 19, 170–171; see also Melchior, " Aluminium, Die Leichtmetalle und ihre Legierungen," Berlin: 1929, pp. 96–99, 107–110, and " Werkstoffhandbuch Nichteisenmetalle."

[6] F. Bollenrath, " Das Verhalten verschiedener Leichtmetallegierungen in der Wärme," *Jahrb. Wiss. Ges. Flugtech.* (*Luftf.*), 1929, 186–196.

[7] A. von Zeerleder and P. Bourgeois, " Effect of Temperatures Attained in Overhead Electric Transmission Cables," *J. Inst. Metals*, 1929, 42, 321–329.

[8] T. Kobayashi, " Einfluss der Temperatur auf die Kerbzähigkeit von Aluminiumlegierungen," *Mem. Ryojun Coll. Eng.*, 1929–1931, 3, 145–153.

[9] W. Schwinning and F. Fischer, " Versuche über den Einfluss der Temperatur auf Kerbzähigkeit und Härte von Aluminiumlegierungen," *Z. Metallkunde*, 1930, 22, 1–7.

[10] R. L. Templin and D. A. Paul, " The Mechanical Properties of Aluminium Alloys at Elevated Temperatures," *Symposium on Effect of Temperature on the Properties of Metals. Held at Joint Meeting of Amer. Soc. Mech. Eng. and Amer. Soc. Test. Mat.*, 1931, 290–313.

[11] J. A. Gann, Discussion (with original investigations) on R. L. Templin and D. A. Paul's paper (see [10] above), *ibid.*, pp. 314–315.

[12] F. Bollenrath, " On the Influence of Temperature on the Elastic Behaviour of Various Wrought Light Metal Alloys," *J. Inst. Metals*, 1932, 48, 255–272.

[13] W. Schwinning and E. Strobel, " Untersuchungen über die Warmfestigkeit von Leichtmetallen bei statischer und bei wechselnder Beanspruchung," *Z. Metallkunde*, 1932, 24, 132–137, 151–153.

[14] A. von Zeerleder, M. Bosshard, and R. Irmann, " Warmfestigkeit und Warmhärte verschiedener Aluminiumlegierungen," *Z. Metallkunde*, 1933, 25, 293–299.

[15] F. M. Howell and D. A. Paul, " Properties of Wrought Aluminium Alloys at Elevated Temperatures," *Metals and Alloys*, 1935, 6, 284–288.

DISCUSSION.

(Condensed.)

Professor A. Portevin * (Member): This paper is a valuable and useful contribution to the question of the mechanical stability of the different alloys of aluminium. It is extremely important, if grave errors and misapplications are to be avoided, to inform the users of the variations which can occur in these alloys with time and to direct their attention to the need for conducting tests of long duration. This has also been shown to be the case in connection with iron alloys designed to resist heat. The duration of the necessary tests is continually increasing, as is also the need for precision. This is evidently one way of overcoming the problem of unemployment in testing laboratories and among those engaged in making testing apparatus. The authors confirm the need for tests of long duration in the case of aluminium alloys. It is essential to know these facts, but such studies must be continued, so as to bring to light the evolution and the laws of the different phenomena which govern the modifications of properties which have been found to occur.

The rôle of science is not merely to discover facts but also to establish laws in order to systematize research and to enable metallurgists to forecast the properties of materials. If it is necessary, in order to judge a metal, to submit it to a test which lasts as long as the metal will be expected to last in service, that would give security, but it would be quite impracticable. What makes the scientific perfection of astronomy is that it enables us to predict the return of phenomena, such as comets, with precision and over immense periods of time. An astronomer does not have to say: " In a few hundred years' time I shall be able to tell you when this comet will come back." As Henri Poincaré has said, science is constructed of facts as a house is constructed of bricks, but an accumulation of facts does not represent science any more than a heap of bricks makes a house. Now that these very interesting results have been obtained, I should like to see an attempt made to disentangle the complex phenomena which underlie the modifications which occur and to establish laws, even if only approximate laws, so as to be able to classify material by means of tests which would not only be of reasonable length but would indeed be of short duration and could thus be greatly multiplied. I hope that the research workers who have carried out the interesting investigations described in this paper will try to find the law—mathematical, if possible—which will enable us to say that a certain result obtained from a short-time test means that after two or three years the result will probably be such and such.

Professor D. Hanson,† D.Sc. (Vice-President): All those who spend their time in research in any science live in a world of shocks—shocks of all kinds, large and small. This paper is, I think, one of the larger shocks to some of us. I remember as a young man, working in collaboration with Dr. Haughton, realizing that the times for which we heated our alloys in order to get them into a state of equilibrium were deplorably short, and we set ourselves to meet the problem so presented by designing a thermostat furnace which could be left to control itself and which we used in the study of the constitution of alloys. In the earlier days, we were content to heat our alloys for 2 or 3 days, but we slowly came to realize that 2 or 3 days was not enough, and now we heat in these investigations for 1, 2, 3, or 4 weeks. The authors now show that in the case of some aluminium alloys

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† Professor of Metallurgy, Birmingham University.

equilibrium at important temperatures such as 300° C. cannot be reached even in 1 year. That is very disturbing; it is one of the major shocks of life!

In the case of "Y" alloy at 300° C. the Brinell hardness seems to decrease in a linear manner over the whole of the time between 1 hr. of heating and 360 days, and there is nothing to indicate any cessation of this process.

It is clearly necessary to know the kind of information which the authors have presented to us, but it is quite clear also, as they themselves indicate, that we must know more than this. In one respect their tests are not nearly sufficient for practical purposes. They have shown us that these changes occur, but if an alloy is to be used at 200° or 300° C. for a long time, it is presumably in many instances subjected to stress for that long time; and tensile tests, hardness tests, and so on, which occupy the space of a few minutes or even a few hours, will not reveal to us the essential properties of these materials when they are used at elevated temperatures. In many metals—iron alloys, copper alloys, and so on—the tensile strength does not depend, within the range of temperature up to perhaps 500° C. or higher, on the rate of testing, but in the case of the aluminium alloys it does depend on the rate of testing. It depends very much on the rate of testing at temperatures above atmospheric temperature, but even at the ordinary atmospheric temperature, tests have shown that an alloy which is subjected to a prolonged load breaks at a stress markedly less than that shown by the ordinary tensile test. In other words, creep phenomena manifest themselves at ordinary temperatures, and to a very marked degree at elevated temperatures such as 100° or 200° C., in aluminium alloys. The authors are faced with the problem of determining the real strengths of these alloys within the temperature range at which they are working, for periods of application of load extending perhaps up to the length of their time of heating, 1 year. That is a terrible problem to have to face, but I think that they have brought it on themselves by showing the necessity for it! The total time of this piece of research so far is about 8 years, and I can see that it is only just beginning!

Dr. R. **Seligman**,* F.Inst.Met. (Past-President): It is now more than 20 years since this same subject was discussed before the Institute by Sir Harold Carpenter.† Memories are short and apparently that work has been completely forgotten. The work in question was done at my instigation by Sir Harold, and in discussing it ‡ I reached the same conclusions as those in the penultimate paragraph of the present paper. Sir Harold and his colleagues continued their work, which had been limited to aluminium, for over 5 years, and showed in the case of pure metals very much the same results which the present authors have now found. I have a few figures here with which I will not trouble you, but I think that such differences as those which the authors' work shows, can be explained by slight differences in the composition of the metals. Since then similar work has been done on aluminium alloys by others who are also not cited by the authors.

Professor **von Zeerleder** (*in reply*): I thank Dr. Seligman for the information he has given with regard to the work of Sir Harold Carpenter. There is one difficulty in the way of tests of shorter duration, and it is this: at each annealing temperature age-hardening occurs in many alloys and continues for some time before the annealing effect manifests itself.

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* Managing Director, Aluminium Plant and Vessel Company, Ltd., London.

† *J. Inst. Metals*, 1917, **18**, 115.

‡ *J. Inst. Metals*, 1917, **18**, 159.

CORRESPONDENCE.

The Authors (*in reply to the discussion at the Meeting*): In reply to Professor Portevin we would say that in carrying out our investigations we hoped to find a formula allowing us to determine by a short-time test the influence of prolonged heating, but we regret that it was impossible to do so.

A glance at the curves 13–23 shows their complete irregularity, which makes it impossible to determine the course of a curve illustrating a long-time test from the curve obtained by a short-time test. If, for instance, in Fig. 2 the curves were extrapolated, a 50 per cent. hardness decrease would result in the case of Anticorodal heated at 150° C. for 400 days. From the values in Fig. 14, however, it can be seen that even at a temperature of 160° C., a 50 per cent. hardness decrease cannot be fully reached after a heating period of 720 days.

Professor Hanson mentioned that in the case of the "Y" alloy, for instance, after heating at 300° C. the Brinell hardness seems to decrease in a linear manner over the whole of the time between 1 hr. of heating and 360 days, and that there is nothing to indicate any cessation of this process.

It must be pointed out that the investigations referred to by Professor Hanson have been carried out for a period of 360 days only, whereas the investigations at other temperatures were extended to 720 days. The logarithmic recording of the time always gives the impression of a more rapid decrease at the end of the curves.

In reply to Professor Hanson's question regarding the long heating under load we would say that such tests, in which the creep limit at elevated temperatures is by Rohn's method, have been carried out for 2 years, and that a report on them should soon be available for publication.

We must apologize for not having included a full reference to other publications such as we gave in our earlier paper published in the *Zeitschrift für Metallkunde*. We shall repair this omission.

We are much indebted to Dr. Seligman for his reference to the paper by Sir Harold Carpenter, which we overlooked when publishing the results of our tests, as we did also the very interesting note on the annealing of aluminium published by Dr. Seligman and Mr. P. Williams,* showing that they—as well as other investigators—had observed as early as 1916, that an annealing at 100° C. has an influence on hard-worked pure aluminium sheet.

* *Trans. Faraday Soc.*, 1916, **12**, 64.

THE CONDUCTIVITY OF SUPER-PURITY ALUMINIUM: THE INFLUENCE OF SMALL METALLIC ADDITIONS.* 743

By GASTON G. GAUTHIER,† Member.

Synopsis.

This paper deals with the effect on the conductivity of super-purity aluminium (exceeding 99·99 per cent.) of additions of those elements which may occur as impurities in commercial aluminium.

It is shown that aluminium follows the universal law that the conductivity and the temperature coefficient of conductivity both increase with the purity: Mathiessen's Law has been confirmed. The data presented in this paper on the effect of small additions on the conductivity of aluminium are of value in that they have been determined under favourable experimental conditions, owing to the extreme purity of the basis metal and the large amount which has been available. This high purity has made it possible to determine, with a stated accuracy, the effect of each one of the added elements in the almost complete absence of other impurities. Further, the figures given for iron and silicon, for these elements with titanium and vanadium, and for magnesium and silicon, make it possible to calculate the conductivity of aluminium of accurately known purity.

Norbury's Law does not appear to hold in the case of aluminium.

Introduction.

In employing aluminium for electrical conductors it is necessary to use commercial metal of the highest possible purity. It is essential, therefore, to know accurately the effect on the electrical resistivity of those elements which may be introduced into the metal during its manufacture from the ore stage onwards, and hence to carry out research directed to the elimination of the most harmful of them. Further, accurate curves showing the effect of impurities make it possible to calculate, from the chemical analysis alone, the approximate conductivity which would be expected from a sample of metal which had been given the same thermal and mechanical treatment as those used in establishing the curves.

Numerous investigations have already been carried out on this

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subject. To attempt to refer to them all would involve the risk of committing the injustice of omitting some; reference will only be made to those in which the conditions of testing were such as to permit comparison with the data now presented: the author apologizes in advance for the omission of any work of which he is ignorant. The majority of previous investigations have been carried out, moreover, on commercial aluminium of which the content of impurities was not negligible: certain of these impurities can combine with the added elements and so modify their influence. Further, in other cases, the amount of element added was too great to allow of any conclusion being reached as to its effect when present merely as an impurity.

The author has been fortunate in having at his disposal super-purity aluminium (of which the purity exceeds 99·99 per cent.) made by the process of the Cie. Alais, Froges et Camargue. Additions of other elements were made in amounts comparable with those likely to be met with in practice, and in general not exceeding the limit of solid solubility in the cold. Additions in excess of this amount—which should lead to its accurate determination—will form the subject of further work. Conductivity determinations were made on annealed and on quenched specimens, and precise details will be given below.

The author has thought it advisable to mention some of his data regarding the conductivity and the temperature coefficient of super-purity and of commercial aluminium, since these data appear to afford an explanation of an anomaly found previously in the relationship between purity and conductivity.

DESCRIPTION OF TESTS.

In preparing the alloys, considerable precautions had to be taken to prevent accidental contamination. Acheson graphite crucibles were used, and in order to ensure that the compositions of the samples conformed as closely as possible with those intended, rich alloys were prepared of suitable composition. These were chill-cast into shallow ingots in order to minimize segregation, and analysis samples were taken by drilling through the ingot. In order to provide sufficient samples, two and sometimes four for each test, and to ensure the greatest accuracy, at least 3 kg. of alloy were prepared each time.

The alloys were cast in small cylindrical billets 64 mm. in diameter, extruded under identical conditions as regards temperature and time of pre-heating, and temperature of extrusion, into rods 10 mm. in diameter; these were cold-drawn to wires 8 mm. in diameter, using a tungsten carbide die in order to ensure a constant and known final thickness (7·975 mm.).

For annealing, the samples were placed, in small quantities at a time, in a large electric furnace of which the temperature was carefully maintained at 320° C. After annealing for 3 hrs., the samples were slowly cooled during 24 hrs. to 100° C., and were then removed, so as to liberate the furnace. For quenching, the samples were placed in the furnace which had previously been heated to 500° C.; after 1 hr. at this temperature they were quenched in cold water.

Frequent checks were carried out by putting billets from the same cast through the whole series of operations, and no abnormal results were obtained. The accuracy of the bridge was checked during each series of measurements against samples of known conductivity serving as standards.

For the measurements a Kelvin double bridge was used, having 4 series of decade resistances. The specimens were about 1·10 m. long, and the resistance was measured over a length of 1 m., at least two and sometimes four specimens being used for each test. All measurements were made at approximately 20° C. in order to reduce to a minimum the necessary correction for temperature, and in order to ensure a constant temperature over the whole length of the specimen, a 70-litre oil-bath was used, of which the temperature was accurately known to 0·1° C. Under these conditions, and having regard to other factors, the maximum relative error was approximately 0·2 per cent.

Using metal cast direct from the refining furnace and analyzing:

	Per Cent.
Iron	0·0011
Silicon . . .	0·0015
Copper . . .	0·0005
Aluminium . . .	99·997 (by difference),

a sample annealed as above at 320° C. gave a resistivity of 2·63 microhms/cm. cube * at 20° C., corresponding with a conductivity of 65·45 per cent. of that of copper. So far as the author is aware, this figure is the highest ever recorded. Edwards [1] gives 64·6 per cent. of copper for aluminium of 99·971 per cent., and the Bureau of Standards [2] give 63·4 per cent. for metal of 99·968 per cent. purity. These differences, which cannot be accounted for by the analyses, suggest that the purities were not as high as those stated. The author's figures for aluminium annealed at 320° C. are given in Table I.

TABLE I.

Purity, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.	Copper, Per Cent.	Conductivity, Per Cent. of Copper.
99·997	0·0012	0·0015	0·0003	65·45
99·991	0·0013	0·0037	0·0035	65·35
99·97	0·012	0·008	0·008	64·90

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* *i.e.* conductivity = 38·0 recip. ohms/m./mm.^{2}.

A sample of metal quenched from 500° C. gave a conductivity of 64·3 per cent. This reduction is evidently due to a structural change during heating.

In order to ascertain whether re-melting introduced any appreciable amount of impurities, several kg. of this metal were re-cast into billets. The analysis was :

	Per Cent.
Iron	0·0023
Silicon . . .	0·0032
Copper . . .	0·0015
Aluminium . . .	99·993 (by difference).

No difference could be detected between the conductivity of this and of the original metal.

In order to verify that this amount of contamination was never exceeded, iron, silicon, and copper were determined on an average sample made up of samples taken from each specimen used in each series. The increase in iron + silicon + copper due to re-melting never exceeded 0·005 per cent.

The effect of introducing a single element was next studied, the intended additions being given in Table II.

TABLE II.

Impurities.	Limit of Solid Solubility at Room Temperature.	Intended Additions, Per Cent.				
Iron . .	0 ?	0·2	0·4	0·6	0·8	1·0
Silicon . .	0·05	0·2	0·4	0·6	0·8	1·0
Copper . .	0·5	0·05	0·10	0·15	0·20	0·25
Zinc . .	13·5	0·25	0·50	0·75	1·00	1·25
Nickel . .	0·5	0·05	0·20	0·30	0·40	0·50
Manganese .	0·1	0·005	0·01	0·015	0·020	0·025
Magnesium .	4	0·25	0·50	0·75	1·00	1·25
Titanium . .	0·2	0·005	0·010	0·015	0·020	0·025
Vanadium .	0·2	0·005	0·010	0·015	0·020	0·025
Chromium .	0·03	0·0025	0·005	0·0075	0·010	0·0125

This was followed by an investigation of the effect of adding more than one element at a time : silicon + iron, magnesium + silicon, and silicon, iron, titanium, and vanadium together, and the results were examined to see if the effects were additive or not.

Finally, in order to see if there was any physical law determining the effect of additions, an investigation was made of the effect of elements not usually occurring, namely silver, gold, and gallium.

CONDUCTIVITY OF SUPER-PURITY AND OF COMMERCIALLY PURE ALUMINIUM.

In some previous work, the author had occasion to measure the resistivity and the temperature coefficient of resistivity not only of super-purity aluminium, but also of aluminium of various purities. It was found that, as for other metals, the temperature coefficient of resistivity of aluminium increased with purity. This is contrary to the experience of Holborn.[3]

The author's measurements also confirmed Mathiessen's law, namely that for alloys approximating to pure metals, the product of the temperature coefficient of resistivity at $t°$ into the resistivity at the same temperature is a constant whose value depends on the pure metal in question and on the temperature $t°$ under consideration.

Table III gives the analyses and electrical measurements on specimens annealed for 3 hrs. at 320° C. and slowly cooled.

TABLE III.

Sample.	Analysis, Per Cent.				ρ 20.	α 20.	ρ 20 × α 20.
	Iron.	Silicon.	Titanium.	Vanadium.			
Super-purity aluminium	0·0005	0·0023	...	...	2·620	0·00433	0·01134
Al 99·5%, annealed	0·34	0·10	0·0096	0·0044	2·767	0·0040	0·01107
Al 99%, annealed	0·56	0·32	0·016	0·0039	2·780	0·00413	0·01152
Al 98·5%, annealed	0·96	0·41	0·0168	0·0044	2·835	0·0040	0·01134

The maximum error in the product $\rho\,\alpha$ is of the order of 25/1000, so that, taking a mean value of 0·01135, the experimental values should lie between 0·01164 and 0·01106. The above figures, therefore, confirm Mathiessen's law.

The coefficient α is higher for very pure aluminium than for the ordinary metal. Holborn found the following values for the coefficient α for specimens annealed at 320° C. :

for 0·1 per cent. of impurities, α = 0·00422
0·4 ,, ,, = 0·00443
1·2 ,, ,, = 0·00446
1·6 ,, ,, = 0·00429

It is probable that Holborn's anomalous results are due to impurities other than those usually estimated, as Bosshard has already indicated.[4] Mathiessen's relation shows that those impurities which increase the resistivity the most are those which most reduce the temperature coefficient. A very small content of such impurities as titanium, vanadium, manganese, and chromium would suffice to explain Holborn's anomalous results.

THE EFFECT OF DIFFERENT ELEMENTS.

(1) *Iron.*

A rich alloy containing 8·07 per cent. iron was used. The analyses and conductivity measurements are given in Table IV.

TABLE IV.

Mark.	Intended Iron Content, Per Cent.	Analysis, Per Cent.			Conductivity at 20° C.			
					Annealed.		Quenched.	
		Fe.	Si.	Cu.	m./mm.^{2}.	Cu, Per Cent.	m./mm.^{2}.	Cu, Per Cent.
Fe 1	0·20	0·22	0·0047	on mean sample 0·001	37·18	64·05	36·92	63·65
Fe 2	0·40	0·41	0·0042		36·92	63·65	36·65	63·2
Fe 3	0·60	0·61	0·0037		36·80	63·45	36·60	63·05
Fe 4	0·80	0·82	0·0042		36·72	63·35	36·52	62·95
Fe 5	1·00	0·99	0·0051		36·52	62·95	36·40	62·75

A further point determined for 0·1 per cent. iron gave a conductivity as annealed of 37·55 or 64·8 per cent. of copper. The solid solubility of iron is, therefore, less than 0·1 per cent. at 100° C. All investigators are in agreement that iron is practically insoluble in aluminium. The slope of the curve, indicates, however, a certain small solubility, although part of the difference may be due to a change of crystallization due to the heating before quenching. A similar feature occurs in some of the following curves.

(2) *Silicon.*

A rich alloy containing 10·19 per cent. silicon was used, made from a ferro-silicon containing 98·5 per cent. silicon. The intended compositions, analyses, and conductivity measurements are given in Fig. 1 and in Table V.

It follows that at 100° C., the solid solubility of silicon, in the absence of iron, is approximately 0·06 per cent., in agreement with Dix and Heath,[5] who reported 0·05 per cent. at a temperature of 200° C.

In this series the effect of quenching is very considerable. The curve for the quenched samples is almost a straight line, showing that the solid solubility of silicon at high temperatures is greater than the maximum content investigated.

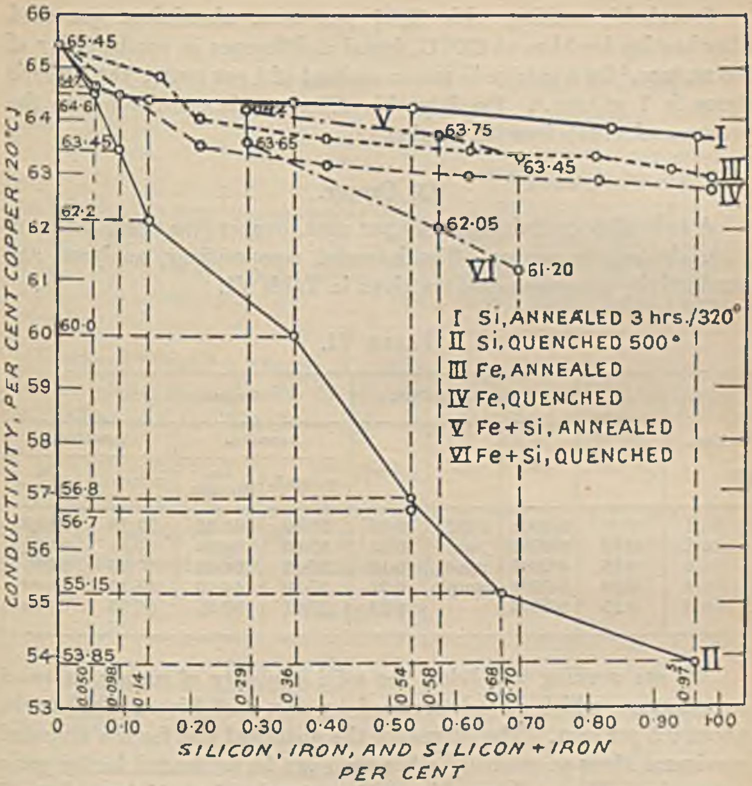

FIG. 1.—Effect of Iron and Silicon and of Iron + Silicon on the Conductivity of Aluminium.

TABLE V.

Mark.	Intended Silicon Content, Per Cent.	Analysis, Per Cent.			Conductivity at 20° C.			
					Annealed.		Quenched.	
		Fe.	Si.	Cu.	m./mm.^{2}.	Cu, Per Cent.	m./mm.^{2}.	Cu, Per Cent.
Si 0·5	0·05	on mean sample 0·0027	0·05	on mean sample 0·0011	37·53	64·70	37·49	64·60
Si 1	0·1		0·098		37·42	64·55	36·80	63·45
Si 1·5	0·15		0·142		37·38	64·45	36·12	62·20
Si 3·5	0·35		0·36		37·38	64·45	34·80	60·00
Si 5	0·50		0·54		37·28	64·25	32·85	56·80
Si 7	0·70		0·68		37·18	64·05	32·01	55·15
Si 10	1·00		0·975		36·95	63·70	31·24	53·85

Fraenkel,[6] working with 99·97 per cent. aluminium quenched after heating for 6 hrs. at 450° C., found a difference in conductivity of 8·6 m./mm.^{2} for a change in silicon content of 1 per cent.; the author's figure is 7 m./mm.^{2}. Possibly this difference is mainly due to the presence of a little iron (cf. Section 12).

(3) *Copper.*

A rich alloy containing 49·40 per cent. copper was used, made up from electrolytic copper. The intended compositions, analyses, and conductivity measurements are given in Table VI.

TABLE VI.

Mark.	Intended Copper Content, Per Cent.	Analysis, Per Cent.			Conductivity at 20° C.			
					Annealed.		Quenched.	
		Fe.	Si.	Cu.	m./mm.^{2}.	Cu, Per Cent.	m./mm.^{2}.	Cu, Per Cent.
Cu 1	0·05	0·0004	0·0023	0·06	37·80	65·25	37·78	65·10
Cu 2	0·10	0·0004	on	0·13	37·65	64·90	37·51	64·65
Cu 3	0·15	0·0004	mean	0·16	37·49	64·60	37·35	64·35
Cu 4	0·20	0·0004	sample	0·21	37·20	64·15	37·16	64·00
Cu 5	0·25	0·0004		0·26	37·01	63·85	36·95	63·70

We are working well below the solid solubility of copper, at room temperature, which was determined by Dix and Richardson [7] to be about 0·5 per cent. The curves for the quenched and for the annealed specimens show no anomaly other than can be accounted for by grain coarsening. Fraenkel,[6] working with a sample of aluminium of 99·97 per cent. purity, of American origin, found a decrease of conductivity of 0·8 m./mm.^{2} per 0·25 per cent. copper added. Bosshard,[4] in his work on binary aluminium alloys, using a specimen of 99·7 per cent. purity, annealed at 300° C. and quenched, found a difference of 1·5 m./mm.^{2} conductivity per 0·35 per cent. copper. These two results are a little different from the author's, one being greater and the other less. It is possible that the explanation lies in small differences in the preparation of the specimens.

(4) *Zinc.*

A rich alloy analyzing 10·44 per cent. zinc was used, made from electrolytic zinc. The intended compositions, analyses, and conductivity measurements are given in Table VII.

As the solid solubility of zinc is far higher than the maximum content studied, the two curves show no abnormalities.

TABLE VII.

Mark.	Intended Zinc Content, Per Cent.	Analysis, Per Cent.				Conductivity at 20° C.			
						Annealed.		Quenched.	
		Fe.	Si.	Cu.	Zn.	m./mm.^{2}.	Cu, Per Cent.	m./mm.^{2}.	Cu, Per Cent.
Zn 1	0·25	0·0022	0·0028 on mean sample	0·0014 on mean sample	0·24	37·70	65·05	37·55	64·80
Zn 2	0·50	0·0012			0·53	37·38	64·45	37·28	64·25
Zn 3	0·75	0·0013			0·78	37·05	63·90	36·97	63·75
Zn 4	1·00	0·0010			1·00	36·78	63·40	36·70	63·30
Zn 5	1·25	0·0010			1·21	36·48	62·90	36·45	62·80

Bosshard[4] found a change of conductivity of 5·5 m./mm.^{2} for an addition of 5 per cent. zinc to aluminium of 99·65 per cent. purity annealed at 240° C. This is roughly what the author finds.

(5) *Nickel.*

Using electrolytic nickel, a rich alloy containing 6·12 per cent. nickel was prepared. Table VIII gives the intended compositions, analyses, and conductivity measurements.

TABLE VIII.

Mark.	Intended Nickel Content. Per Cent.	Analysis, Per Cent.				Conductivity at 20° C.			
						Annealed.		Quenched.	
		Fe.	Si.	Cu.	Ni.	m./mm.^{2}.	Cu, Per Cent.	m./mm.^{2}.	Cu, Per Cent.
Ni 0·5	0·05	0·0020	0·0028 on mean sample	0·0005 on mean sample	0·050	37·93	65·40	37·80	65·25
Ni 2	0·2	0·0012			0·177	37·89	65·35	37·77	65·15
Ni 3	0·3	0·0019			0·27	37·80	65·25	37·69	65·00
Ni 4	0·4	0·0020			0·37	37·77	65·15	37·65	64·90
Ni 5	0·5	0·0020				37·69	65·00	37·64	64·85

Bohner,[8] working on commercial aluminium and a specimen quenched from 300° C., found a change in conductivity of 0·8 m./mm.^{2} on increasing the nickel from 0·1 to 0·5 per cent. This is roughly three times the change found by the author. This is probably due to the formation of complex constituents of nickel, iron, and silicon which increase the lowering of the conductivity.

(6) *Magnesium.*

A rich alloy was used containing 4·25 per cent. magnesium, made from electrolytically refined magnesium. The intended compositions, analyses, and conductivity measurements are given in Table IX.

TABLE IX.

Mark.	Intended Magnesium Content, Per Cent.	Analysis, Per Cent.				Conductivity at 20° C.			
						Annealed.		Quenched.	
		Fe.	Si.	Cu.	Mg.	m./mm.^{2}.	Cu, Per Cent.	m./mm.^{2}.	Cu, Per Cent.
Mg 1	0·25	0·0018	0·0037 on mean sample	0·0025 on mean sample	0·23	35·71	61·50	35·65	61·45
Mg 2	0·50	0·0013			0·54	33·81	58·30	33·75	58·20
Mg 3	0·75	0·0014			0·83	31·67	54·65	31·60	54·50
Mg 4	1·00	0·0014			1·04	30·37	52·35	30·30	52·20
Mg 5	1·25	0·0022			1·40	28·71	49·50	28·68	49·40

In addition, measurements have been carried out on samples containing lower percentages of magnesium. These were prepared from an alloy containing 0·82 per cent. magnesium. It is not easy to analyze such small quantities accurately, and it is only possible to indicate the intended composition (Table X).

TABLE X.

Mark.	Intended Magnesium Content, Per Cent.	Conductivity at 20° C.			
		Annealed.		Quenched.	
		m./mm.^{2}.	Cu, Per Cent.	m./mm.^{2}.	Cu, Per Cent.
Mg 01	0·01	37·80	65·25	37·79	65·20
Mg 02	0·05	37·53	64·70	37·51	64·65
Mg 03	0·1	37·18	64·05	37·10	63·95

All these results are in perfect agreement and show that magnesium exerts a considerable effect on the conductivity of very pure aluminium.

Fraenkel found a decrease of conductivity of 6 m./mm.^{2} per 1 per cent. magnesium working with aluminium of 99·97 per cent. purity. This figure is rather lower than the author's, and the presence of silicon is insufficient to account for the difference.

(7) *Manganese.*

A rich alloy was prepared by the action of potassium permanganate on super-purity aluminium, and analyzed 0·69 per cent. The intended compositions, analyses, and conductivity measurements are given in Table XI.

Rather low manganese contents have been investigated, since no useful comparison could be made with previously published data.

TABLE XI.

Mark.	Intended Manganese Content, Per Cent.	Analysis, Per Cent.				Conductivity at 20° C.			
		Fe.	Si.	Cu.	Mn.	Annealed.		Quenched.	
						$m./mm.^2$.	Cu, Per Cent.	$m./mm.^2$.	Cu, Per Cent.
Mn 1	0·005	0·0008	0·0014	0·0005	0·0048	37·80	65·25	37·78	65·10
Mn 2	0·010	0·0007	on	on	0·010	37·53	64·70	37·51	64·65
Mn 3	0·015	0·0007	mean	mean	0·016	37·30	64·30	37·28	64·25
Mn 4	0·020	0·0008	sample	sample	0·021	37·05	63·90	36·99	63·80
Mn 5	0·025	0·0008			0·026	36·83	63·50	36·78	63·40

(8) *Vanadium.*

In order to prepare a rich alloy free from impurities, vanadium was introduced by the interaction between vanadic acid and super-purity aluminium. The alloy so obtained analyzed 0·58 per cent. An earlier analysis gave 0·21 per cent.; hence the difference between the intended and the actual compositions. The intended compositions, analyses, and conductivity measurements are given in Table XII.

TABLE XII.

Mark.	Intended Vanadium Content, Per Cent.	Analysis, Per Cent.				Conductivity at 20° C.			
		Fe.	Si.	Cu.	V.	Annealed.		Quenched.	
						$m./mm.^2$.	Cu, Per Cent.	$m./mm.^2$.	Cu. Per Cent.
V 1	0·005	0·0011	0·0033	0·0018	0·012	37·35	64·35	37·28	64·25
V 2	0·010	0·0011	on	on	0·027	36·62	63·15	36·60	63·05
V 3	0·015	0·0011	mean	mean	0·040	36·03	62·10	35·95	62·00
V 4	0·020	0·0011	sample	sample	0·051	35·24	60·80	35·22	60·75
V 5	0·025	0·0012			0·067	34·85	60·10	34·80	60·00

As we are working well below the limit of solid solubility, the curves show no anomalous features, and there is only a small difference between the quenched and the annealed samples. Here also the author is unaware of any published data dealing with such low contents.

(9) *Titanium.*

A rich alloy was prepared from very pure potassium fluotitanate and analyzed 0·21 per cent. titanium. The intended compositions, analyses, and conductivity measurements are given in Table XIII.

As we are working below the limit of solid solubility, the curves show no anomalous features.

TABLE XIII.

Mark.	Intended Titanium Content, Per Cent.	Analysis, Per Cent.				Conductivity at 20° C.			
						Annealed.		Quenched.	
		Fe.	Si.	Cu.	Ti.	m./mm.².	Cu, Per Cent.	m./mm.².	Cu, Per Cent.
Ti 1	0·005	0·001	0·0023 on mean sample	0·0010 on mean sample	0·0056	37·69	65·00	37·67	64·95
Ti 2	0·010	0·0014			0·010	37·53	64·70	37·51	64·65
Ti 3	0·015	0·0014			0·015	37·28	64·25	37·25	64·20
Ti 4	0·020	0·0015			0·022	37·10	63·95	37·05	63·90
Ti 5	0·025	0·0018			0·026	36·84	63·55	36·83	63·50

Working with a sample of aluminium analyzing 99·5 per cent., and annealed at 240° C., Bosshard found a decrease of conductivity of 5·7 m./mm.^{2} on addition of 0·2 per cent. titanium. This figure is almost half that found by the author for the range 0–0·02 per cent. The reason for this is not clear; the limit of solid solubility of titanium is greater than 0·2 per cent., and, as will be shown below, the effect of titanium on conductivity is additive to that exerted by the iron and the silicon.

(10) *Chromium.*

The rich alloy was prepared from refined chromium of 99 per cent. purity, and contained 0·29 per cent. chromium. The intended compositions and conductivity measurements are given in Table XIV.

TABLE XIV.

Mark.	Intended Chromium Content, Per Cent.	Conductivity at 20° C.			
		Annealed.		Quenched.	
		m./mm.².	Cu, Per Cent.	m./mm.².	Cu, Per Cent.
Cr 1	0·0025	37·89	65·35	37·79	65·20
Cr 2	0·005	37·77	65·15	37·67	64·95
Cr 3	0·0075	37·65	64·90	37·59	64·75
Cr 4	0·010	37·51	64·65	37·44	64·50
Cr 5	0·0125	37·37	64·40	37·28	64·25

It has not been possible to give analyses for such small quantities of chromium, and the intended compositions have, therefore, been used in preparing the curves. This is permissible by reason of the precautions taken in preparing the specimens, and spectrographic analyses confirm the compositions. Nothing appears to have been published dealing with such low percentages of chromium.

(11) *Silver, Gold, and Gallium.*

Table XV gives the intended compositions and the results of the conductivity measurements. The compositions have been checked spectrographically and conform closely to those intended.

TABLE XV.

Alloy and Mark.	Intended Composition, Per Cent.		Conductivity at 20° C.	
			Annealed.	
			m./mm.^{2}.	Cu, Per Cent.
Argent Ag 1	Silver	0·2	37·18	64·05
Or Au 1	Gold	0·1	37·93	65·40
Gallium Ga 1	Gallium	0·05	37·93	65·40

As regards silver, Fraenkel, using aluminium of 99·97 per cent. purity quenched from above 500° C., found a change of conductivity of 8·3 m./mm.^{2} corresponding with an addition of 2 per cent. of silver. This is approximately that found by the author.

As regards gallium, the same author found a decrease in conductivity of 2·1 m./mm.^{2} for an addition of 1·28 per cent. of gallium, rather less than that found by the author.

(12) *Effect of Iron and Silicon.*

Having established a curve showing the effect of these two elements, which are invariably present in commercial aluminium, the author prepared a series of synthetic samples of overall purity varying between 99·3 and 99·8 per cent. Rich alloys containing 9·1 per cent. iron and 10·20 per cent. silicon were used, in conjunction with super-purity aluminium, for the work. The analyses and conductivity measurements are given in Table XVI.

TABLE XVI.

Mark.	Analysis, Per Cent.		Purity.	Conductivity at 20° C.			
				Annealed.		Quenched.	
	Fe.	Si.		m./mm.^{2}.	Cu, Per Cent.	m./mm.^{2}.	Cu, Per Cent.
FES 1	0·21	0·09	99·7	37·25	64·20	36·92	63·65
FES 2	0·23	0·10	99·67	37·16	64·00	...	...
FES 3	0·365	0·21	99·42	36·97	63·75	36·00	62·05
FES 4	0·34	0·23	99·43	36·95	63·70	...	...
FES 5	0·47	0·23	99·3	36·80	63·45	35·55	61·20
FES 6	0·41	0·30	99·29	36·84	63·55	...	...

It is clear—as could have been foreseen—that the effects of these two elements are not additive. This is due to the formation of complex constituents of aluminium, iron, and silicon, whose effect is different from that of the individual elements. To illustrate this, Table XVII gives the conductivity of the preceding samples annealed at 320° C. as measured and as calculated from the curves for iron and silicon (Sections 1 and 2). The difference between the observed and calculated figures is relatively large, and depends essentially on the ratio of iron to silicon contents. In calculating conductivity from the chemical analysis, therefore, due cognisance must be taken of this fact.

Table XVII.

Mark.	Conductivity at 20° C.			
	Calculated		Measured.	
	m./mm.².	Cu, Per Cent.	m./mm.².	Cu, Per Cent.
FES 1	36·62	63·15	37·25	64·20
FES 2	36·60	63·05	37·16	64·00
FES 3	36·36	62·65	36·97	63·75
FES 4	36·40	62·75	36·95	63·70
FES 5	36·30	62·55	36·80	63·45
FES 6	36·30	62·55	36·84	63·55

(13) *Effect of Titanium and Vanadium.*

In order to obtain data of practical value, it was considered necessary to study the effect of titanium and of vanadium on aluminium containing iron and silicon in such quantities as occur in the metal normally used for electrical conductors. A basis alloy was, therefore, prepared from iron- and silicon-rich alloys and super-purity aluminium, and analyzed:

	Per Cent.
Iron	0·14
Silicon . . .	0·07

Titanium and vanadium were added, using the bars which had been used for the work on these individual elements, in the ratios of 2 : 1 and of 5 : 1. The results are summarized in Table XVIII.

In Fig. 2 have been included the curves for titanium, for vanadium, and two other curves for ratios $\frac{\mathrm{Ti}}{\mathrm{V}} = 2$ and $\frac{\mathrm{Ti}}{\mathrm{V}} = 5$, respectively. The intended compositions have been used in drawing these curves, since the analyses were not sufficiently accurate: there is a systematic error in the analysis for vanadium.

Contrary to what occurs in the case of iron and silicon together, and in the case of magnesium and silicon together (see below), the effects of

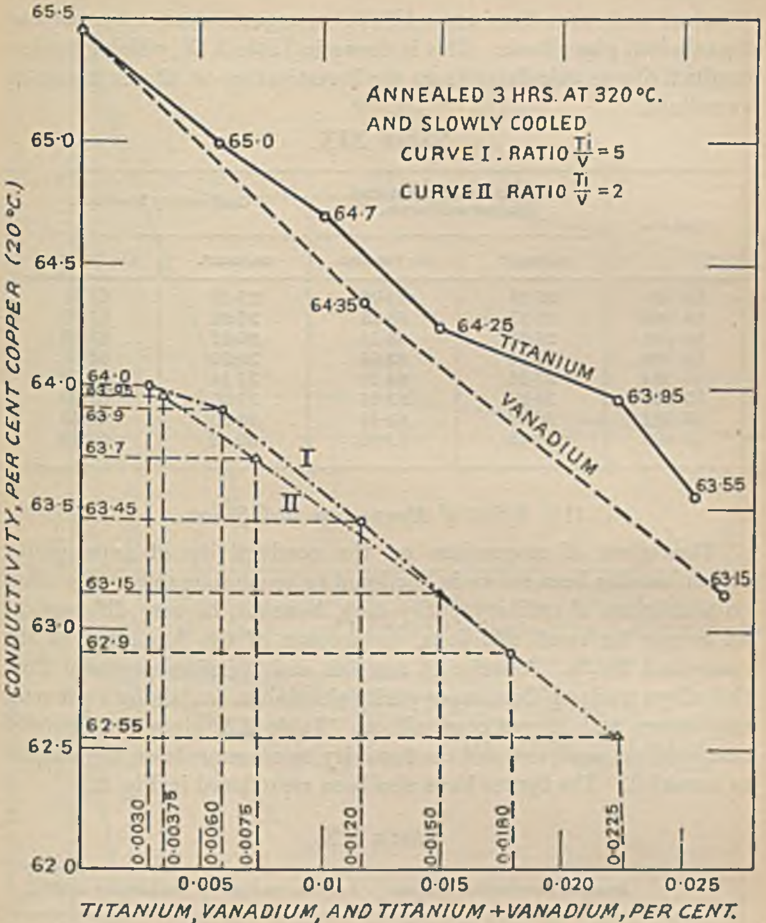

FIG. 2.—Effect of Titanium and Vanadium on the Conductivity of Aluminium.

TABLE XVIII.

Cast No.	Amount Introduced, Per Cent.		Analysis, Per Cent.					Conductivity at 20° C.	
	Ti.	V.	Fe.	Si.	Ti.	V.	Ti + V.	m./mm.².	Cu, Per Cent.
15 787	0·0025	0·00125	0·14	0·070	0·0024	...	0·0024	37·10	63·95
15 788	0·005	0·0025	0·15	0·0655	0·0058	0·0011	0·0069	36·95	63·70
15 789	0·010	0·005	0·15	0·061	0·0108	0·0033	0·0141	36·62	63·15
15 790	0·015	0·0075	0·15	0·056	0·0160	0·0067	0·0227	36·30	62·55
15 794	0·0025	0·0005	0·15	0·07	0·0030	...	0·0030	37·16	64·00
15 801	0·0050	0·001	0·16	0·065	0·0048	0·00055	0·0053	37·05	63·90
15 802	0·010	0·002	0·14	0·061	0·0098	0·0011	0·0109	36·80	63·45
15 803	0·015	0·003	0·17	0·0608	0·0166	...	0·0166	36·48	62·90

titanium and vanadium are additive as regards each other and as regards iron plus silicon. This is shown in Table XIX, which gives the conductivity as calculated from the investigation on titanium and on vanadium.

TABLE XIX.

Cast No.	Conductivity Calculated from Analysis and Curves.		Conductivity Measured.	
	m./mm.^{2}.	Cu, Per Cent.	m./mm.^{2}.	Cu, Per Cent.
15 787	37·18	64·05	37·10	63·95
15 788	36·97	63·75	36·95	63·70
15 789	36·62	63·15	36·62	63·15
15 790	36·30	62·55	36·30	62·55
15 794	37·22	64·10	37·16	64·00
15 801	37·03	63·85	37·05	63·90
15 802	36·78	63·40	36·80	63·45
15 803	36·48	62·90	36·48	62·90

(14) *Effect of Magnesium and Silicon.*

The effect of magnesium on the conductivity of super-purity aluminium has been shown in Section 6 to be considerable. The effect on aluminium of ordinary purity may, however, be very different, at all events for small additions, on account of the formation of the compound Mg_2Si. A series of samples was therefore prepared from rich alloys made up from super-purity aluminium containing 1 per cent. magnesium and 10 per cent. silicon. Table XX gives the intended compositions, analyses, and conductivity measurements on the samples as annealed. The figures have also been reproduced in Fig. 3.

TABLE XX.

Mark.	Intended Composition, Per Cent.			Analysis, Per Cent		Conductivity at 20° C.	
	Mg.	Si.	Mg_2Si.	Mg.	Si.	m./mm.^{2}.	Cu, Per Cent.
M.S. 1	0·0175	0·01	0·0275	...	0·01	37·67	64·95
M.S. 2	0·044	0·025	0·069	0·042	0·018	37·44	64·50
M.S. 3	0·09	0·050	0·140	0·060	0·055	36·87	63·60
M.S. 4	0·175	0·10	0·275	0·166	0·099	36·78	63·40
M.S. 5	0·44	0·25	0·69	0·486	0·235	36·65	63·20

The effect of Mg_2Si is practically that of magnesium within the region of solid solubility. From this work the limit of solubility would appear to be less than 0·14 per cent., whereas Kishino[9] found 0·47 per cent. He did not, however, state the purity of the metal used.

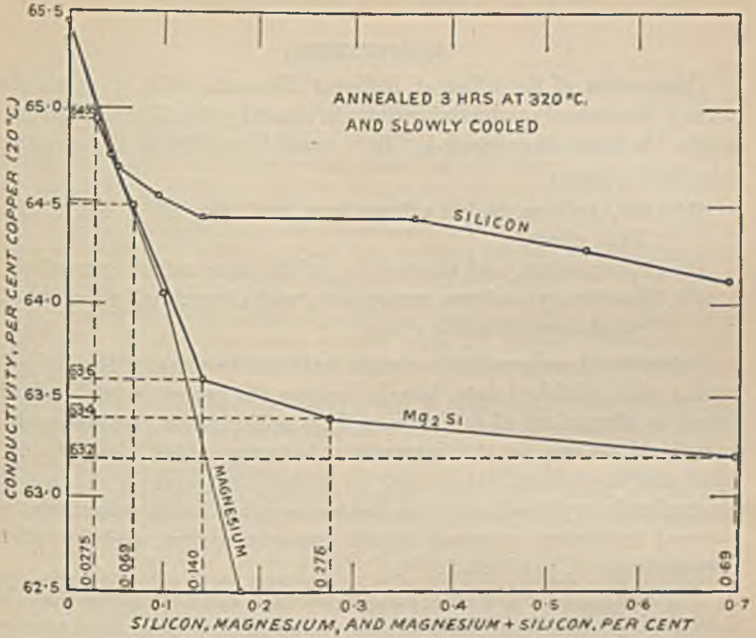

FIG. 3.—Effect of Magnesium and Silicon on the Conductivity of Aluminium.

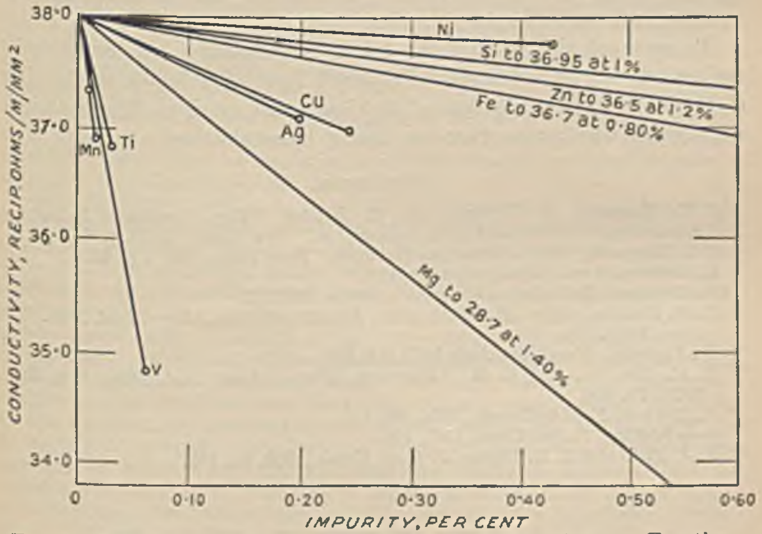

FIG. 4.—Mean Decrease of Conductivity in Alloys of Aluminium as a Function of the Content of Alloying Element Added.

CONCLUSIONS.

Comparison of the Effect of Different Elements.—Fig. 4 shows the average decrease of conductivity brought about by the different elements within the limits investigated. It is possible to divide the elements into three groups:

1. Gold, gallium, nickel, silicon, iron, and zinc, all of which have little effect.
2. Copper, silver, and magnesium, which have rather more effect.
3. Titanium, vanadium, manganese, and chromium, all of which exert a considerable effect.

It has only been possible in certain instances to compare the author's results with published data, largely because the present work has been based on aluminium of particularly high purity, thus eliminating the complications due to the interaction between added elements and incidental impurities. It should be added that certain differences, incompletely explained, may be due to variation in the mechanical or thermal treatment as used by the present author and by other investigators (cf. particularly [10]).

Norbury's Law.—Norbury has put forward the hypothesis that the increase in resistivity brought about by the addition of the same number of atoms is larger, the greater the separation between the added element and the basis metal in the periodic system.

In spite of the precautions taken in preparing his samples the author's figures do not support Norbury's Law. This confirms the view of Fraenkel, using aluminium of 99·97 per cent. purity. The author is considering whether another law cannot be established.

REFERENCES.

[1] J. D. Edwards, F. C. Frary, and Z. Jeffries, "The Aluminium Industry: Aluminium Products and their Fabrication," New York: **1930**, p. 44.
[2] J. D. Edwards, "The Aluminium Industry," New York: **19** , p. 43.
[3] L. Holborn, *Ann. Physik*, 1919, **59**, 155.
[4] M. Bosshard, *Bull. Assoc. Electrotech. Suisse*, 1927, 3.
[5] E. H. Dix, Jr., and A. C. Heath, *Proc. Inst. Metals Div., Amer. Inst. Min. Met. Eng.*, **1928**, 164.
[6] W. Fraenkel, *Metallwirtschaft*, 1933, **12**, 159.
[7] E. H. Dix, Jr., and H. H. Richardson, *Trans. Amer. Inst. Min. Met. Eng.*, 1926, **73**, 560.
[8] H. Bohner, *Z. Metallkunde*, 1934, **26**, 45.
[9] —— Kishino, *J. Soc. Chem. Ind.*, 1932.
[10] A. J. Field and J. H. Dickin, *J. Inst. Metals*, 1933, **51**, 183.

DISCUSSION.

(*Condensed.*)

Dr. A. G. C. Gwyer,* B.Sc. (Vice-President): This paper is of great interest to a wider circle than those concerned with aluminium, because it is the first that we have had dealing with a product of so-called super-purity, namely aluminium *raffiné*. The highest purities which have been obtained with this metal approximate to those reached in America, for example, in the case of zinc. We have, in fact, now reached the stage where aluminium can be obtained of practically spectroscopic purity, and this is, of course, of much importance not only to those interested in aluminium but also to those who desire to investigate the fundamental properties of metals. For example, I am sure that many workers upon the subject of corrosion will be as eager to experiment with this super-purity aluminium as with spectroscopic zinc, &c.

Another great advantage, brought out in this paper, is that this very high degree of purity seems to stimulate the workers to a very high degree of accuracy, which is also a matter for congratulation. My staff and I have read this paper on more than one occasion, and with the exception of one small point, there seems nothing to criticize in it, which is why my remarks are of a rather general nature. It is a record of work done with the greatest care and accuracy, and work which is of the greatest value.

Turning to some of the points raised in the paper, Fig. 4 shows, for the first time, the effect of the individual elements commonly found in aluminium in decreasing the conductivity. Looking back 10 or 20 years, we used to be very puzzled by the fact that we did not always obtain the required conductivity from metal of apparently the correct purity. It was extraordinarily difficult at that time to arrive at the real cause, because, as the author has shown, elements like titanium, vanadium, manganese, and chromium all exert an important effect on the conductivity. In those days, when there was no control over the minor elements present in the higher purity material, there was no means of dealing with the subject at all. We investigated the effect of titanium by adding small amounts, but we never thought of considering the effect of vanadium. In the intervening period has come a great need for improvement in analytical methods, because one must be able to determine these small amounts accurately.

Referring again to Fig. 4, it would be of interest if the author would include in it a curve showing the effect of the silicon when completely in solid solution. Turning to Fig. 1, it will be noticed that even with quite small amounts of silicon present, of the order of 0·30 per cent., the conductivity is lowered to approximately 64 per cent. That is when the material is out of solid solution, in the graphitic form. When it is in solid solution, it will be seen from curve II of Fig. 1 that the conductivity decreases to about 60 per cent. At the end of the paper the author classifies silicon as one of those elements which have little effect. No doubt that is true with regard to silicon in the graphitic form, but in the ordinary way in which aluminium wire is produced by drawing, heat-treatment, and so on, one does not get the silicon in a graphitic form but in a mixture of dissolved and free silicon; therefore its effect is very much greater than would be expected from the author's conclusion. It would be of value, therefore, if the author would indicate what is the relative effect of silicon entirely in solid solution as compared with copper, silver, or, if it falls in the other group, with titanium, manganese, and other elements.

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Dr. L. H. **Callendar**,* B.Sc., A.R.C.S. (Member): I have been particularly interested in this contribution, since I read a paper to the Institute some 3 years ago on the effect of annealing on the conductivity of aluminium.†

I notice that M. Gauthier anneals his metal for 3 hrs. at 320° C. and slowly cools for 24 hrs. down to 100° C. In the case of silicon this would not be nearly sufficient to bring about equilibrium. The author is scarcely justified, therefore, in stating that the solid solubility at 100° C. is 0·06 per cent. silicon, as his metal is certainly not in equilibrium at that temperature. I found by two different chemical methods, which largely eliminated the effect of other impurities, dissolved silicon figures of 0·06 and 0·05 per cent. for metal annealed to equilibrium at 300° C.‡ Allowing for the iron in Dix and Heath's metal, their results give about 0·05 per cent. at 300° C., and I think that we must conclude that M. Gauthier's result of 0·06 per cent. more nearly represents the solid solubility at 300° C. than at 100° C. To obtain the solubility at 100° C., annealing for 1000 hrs. or more would be required.§ From Tables I and V, I calculate the nearest figure for the silicon in solution in the author's annealed metal to be 0·044 per cent. silicon.

With regard to the effect of iron alone, the author's results confirm some comments that I made on a former paper on the same subject by Field and Dickin,|| namely, that the effect of this element alone was much less than was generally supposed and that the relatively large effects on conductivity attributed by Field and Dickin to the iron were really due to the formation of a complex with the silicon and aluminium. This is well illustrated by the results in Table XVI, where the author has investigated the effect of iron and silicon together in the proportions found in the commercial metal. The conductivities for the quenched metal are extremely close to those obtained for silicon alone, *i.e.* the iron has no effect, and for the annealed metal they are only a little lower, owing, as I previously pointed out,¶ to the tendency of the iron to slow down the separation of the silicon. The iron does not seem to form a true compound with the silicon, since, as I have found, a longer anneal than the author's would give a higher conductivity and a further separation of silicon.

The author does not refer to the presence of calcium or sodium in his metal; these used always to be present in small amounts in our metal, but he may have discovered some way of eliminating them.

The author's work on the relatively large effects of vanadium and titanium are particularly important, as I believe the effect of small amounts of these elements has not previously been fully appreciated.

Professor A. **Portevin** ** (Member): The results of the author's determinations are very valuable, because the influence of each element on the conductivity of aluminium is studied separately, thanks to the high purity of the aluminium employed. They confirm in particular, as I have previously stated,†† the important influence of two elements which are found as impurities in commercial aluminium—titanium and vanadium, which are of very similar atomic volume and position in the periodic table. If Norbury's law does not appear to apply to aluminium, at least it may be possible to complete it by noting that the influence of a small addition on the conductivity grows with

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† *J. Inst. Metals*, 1933, **51**, 199.

‡ *J. Inst. Metals*, 1933, **51**, 212, 213.

§ Cf. Gwyer and Phillips, *J. Inst. Metals*, 1927, **38**, 35.

|| *J. Inst. Metals*, 1933, **51**, 214.

¶ *J. Inst. Metals*, 1933, **51**, 214.

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

†† *Metal Progress*, 1932, **21**, (3), 69.

the atomic volume, the distance in the periodic system, and the difference in the crystal network as compared with aluminium.

An element which, it is interesting to note, had but little effect on the conductivity of aluminium, is gallium. As has been pointed out by Goldschmidt, owing to the equality of the crystals of aluminium and gallium, which is shown by the remarkable and sometimes extraordinary resemblance of the reticular dimensions of corresponding combinations, all natural sources of aluminium contain gallium. It is therefore found in commercial aluminium, where it is, as Goldschmidt puts it, "camouflaged." On the other hand, one must not deduce from this the solubility in the solid state of the two metals, which is, as Jenckel has shown, in fact somewhat limited, due to the difference between the face-centred cubic system of aluminium and the orthorhombic system of gallium. An analogous result is found in the case of alloys of indium and lead, which are chemical neighbours but show a gap in solid solubility, as indicated by the work of N. W. Ageew and V. Ageewa * published in connection with the present meeting.

It would be interesting to verify that this super-purity aluminium does not show the super-conductivity mentioned by Tuijn and Onnes, because, according to the ideas of Kapitza † and Bernal,‡ all absolutely pure metals should be super-conductors, the abrupt drop of the resistance to zero being, according to them, due to an instantaneous expulsion of impurities.

Professor Dr. A. VON ZEERLEDER § (Member): The author has investigated the influence of additions of other elements on extra pure aluminium and of annealing at temperatures of 320° and 500° C. M. Gauthier has compared his results with investigations of my collaborator, Mr. Bosshard, published about 10 years ago.‖ He found in the case of certain metals, in particular silicon, iron, and copper, a difference between the results he obtained with this super-purity aluminium and the results obtained by Bosshard. We think that this difference is chiefly due to the fact that our metal had a purity of 99·7 per cent., so that it probably contained other impurities which we did not determine exactly but which may have had a certain influence on the results of the conductivity tests and on the effect of the other elements. On the other hand, we consider that, as Dr. Callendar has pointed out, the time of annealing and cooling was not long enough at and from the temperature employed by the author. At 320° C., especially with additions like titanium and manganese which go into solution in aluminium very slowly, it would be better to allow more than 3 hrs. for annealing and 24 hrs. for cooling. Moreover, we found that to obtain a complete solid solution, especially with titanium, vanadium, and manganese, a temperature of 500° C. was not sufficient, and we went to over 600° C. for that purpose. I think these are the reasons of the difference between the results found by Bosshard and those obtained by the present author. In general, the results with all the other elements are in good agreement, and I should like to congratulate the author on his interesting work, which gives us a great deal of useful information for the investigations which will be carried out in various laboratories with this super-purity metal. We have to thank the author's firm, La Compagnie de Produits Chimiques et Electrometallurgiques Alais, Froges et Camargue, for having developed the refining process of Hoopes (Aluminum Company of America), by changing the electrolyte and also by the construction of the cell, to such a perfection that they are now able to

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* *J. Inst. Metals*, 1936, **59**, 311–316. † *Proc. Roy. Soc.*, 1929, **123**, 292.

‡ *Trans. Faraday Soc.*, 1929, **25**, 367.

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

‖ Bosshard, *Bull. Assoc. Electrotech. Suisse*, 1927, **18**, 113.

produce an aluminium of higher purity than 99·99 per cent., reaching sometimes even 99·998 per cent. This metal is produced not on a laboratory scale but industrially. A similar refining process is in use at the S.A. pour 'Industrie de l'Aluminium, Neuhausen.

CORRESPONDENCE.

Herr H. Röhrig * (Member) : The author states that with an aluminium of high purity containing iron 0·0012, silicon 0·0015, and copper 0·0003 per cent., a conductivity of 65·64 per cent. was found after annealing at 320° C. and a conductivity of 64·3 per cent. when annealing at 500° C. This difference is attributed to a change in structure. It would be most valuable to know exactly what change occurred. Is there an indication of the possibility that, in spite of the very low content of impurities, the concentration of the solid solution after annealing at 500° C. is greater than after annealing at 320° C. ? We noted the same effect when making some conductivity measurements on aluminium from the same source.

The Author (*in reply*) : I thank all those who took part in the discussion for their valuable criticisms. The primary object of my work was essentially of a practical nature, namely, to determine the individual influence of all the impurities likely to be present in 99·5 per cent. aluminium on its electrical conductivity. That is why not only the concentration of the impurities, but also the times and temperatures of heat-treatment were selected to correspond closely to those encountered in industrial practice. Nevertheless, I shall bear in mind the justifiable criticisms that were made on certain points. Dr. Gwyer's remarks on the effect of silicon in solid solution and those of Dr. Callendar's and Professor von Zeerleder's on the precipitation of silicon are recognized as true criticisms of my work, but I should like to reserve for a future paper the results of work I am carrying out with the object of obtaining scientific results on these points, and of determining the actual solubility of silicon at various temperatures.

Herr Rohrig raised the question of the reduction of the conductivity when the annealing temperature is increased. I do not think this is a question of a change in the concentration of the solid solution, but rather that this change in concentration should be in relation either to the crystallographic structure or to the greater concentration of the impurities at the grain boundaries (the latter decreasing in volume as the crystals grow in size).

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AN ANODIC TREATMENT FOR THE PRODUCTION OF ALUMINIUM REFLECTORS.* 744

By N. D. PULLEN.†

SYNOPSIS.

A description is given of a dual anodic process designed for the treatment of aluminium surfaces in order to produce a high degree of reflectivity. The first bath in which the electrolytic brightening is produced is a mixture of sodium carbonate and sodium phosphate in the approximate proportions of 3 : 1 having a strongly alkaline reaction. The second bath in which a reinforcing film is produced consists preferably of a strong solution of acid sodium sulphate. Data are given showing the reflectivity of aluminium surfaces treated by this method compared with a standard silver mirror and other surfaces such as chromium plate, nickel plate, &c.

It is well known that the power to reflect incident light is possessed by various metal surfaces to a very varying degree even when such surfaces have been reduced to the same condition so far as possible by grinding, polishing, &c. Not only does the reflectivity vary over the visible range taken as a whole, but it also varies for different wave-lengths and not always in the same manner. The reflectivity of a silver mirror, for instance, is very high when measured on the longer waves, but decreases to almost vanishing point over a narrow band in the ultra-violet. This paper is not concerned, however, with reflectors designed for a particular or specialized purpose, but with an electrochemical method for the production of aluminium surfaces having a high reflectivity value when measured in the normal manner using daylight or an artificial light as source of illumination.

At this point it might be desirable to define what is meant by a reflector as distinct from a mirror. A mirror might be defined as a surface designed to reflect the maximum amount of light with the minimum amount of diffusion. A reflector on the other hand, whilst still required to reflect the maximum amount of light might be, and in many cases is, designed to give maximum diffusion. Since the amount of diffusion depends on the evenness of the reflecting surface, only those

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substances capable of being ground accurately to a predetermined shape and then highly polished without "flowing" or otherwise becoming distorted are suitable for mirrors. This condition, together with the desire for high reflectivity and freedom from liability to tarnish, reduces the choice to a very small number of substances. For reflectors, the production of optically correct surfaces is not required nor is the minimum diffusion of paramount importance. The maximum total reflectivity combined with freedom from tarnishing must, however, still be attained.

It would appear that the above definitions preclude the use of aluminium as a reflecting medium to a very large extent, since in its normal commercial state it is rather too soft to give optical surfaces, its reflectivity is not of the highest order, and it is not free from the liability to tarnish or to acquire a dull surface. The tarnishing trouble has been overcome by the application of anodic oxidation, using various electrolytes producing material which is practically immune to this type of atmospheric corrosion, but the reflectivity of such material is appreciably less than that of the untreated metal and considerably less than the value given by a highly polished specimen. The problem concerning the production of reflectors, therefore, consisted in designing a process which would in the first place increase the reflectivity of a normal aluminium surface to an appreciable extent and then render such surface permanent.

The method of brightening a metal surface by anodic treatment in a suitable electrolyte is not new, as Figour and Jacquet * described a process for copper using orthophosphoric acid and ether solution, whilst more recently a process for aluminium has been patented in America and elsewhere using a hydrofluoric–boric acid mixture.

A still later process † which I shall describe, has a strongly alkaline solution for electrolyte. Its discovery was more or less an accident which happened during an investigation of the possible use of alkaline electrolytes for anodic oxidation in place of the more popular acid type; its development, however, has proceeded along more orthodox lines. This process is divisable into two main parts : (*a*) the production of the brightened highly reflective surface, and (*b*) the application of a protective layer which layer must not reduce the degree of reflectivity already attained.

For the production of brightened surfaces on aluminium, it is essential to remove the thin surface layer consisting of the natural oxide skin and such impurities, dirt, &c., as might be introduced during production; this can only be done by chemical means, using

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* French Patent 707,526.

† British Patent applications.

an acid or alkaline solvent. Without this preliminary treatment improved reflectivity is not obtained. This removal of the oxide skin is carried out without the application of any current, and the time during which solution occurs needs to be carefully controlled. The actual brightening is done under an applied e.m.f. and follows immediately after the chemical treatment in the same bath.

The solution which we use for this part of the process contains a relatively high proportion of alkali plus a smaller proportion of an alkaline phosphate. The actual amounts are not very critical although one particular mixture appears to give rather better results than others. The electrolyte is an aqueous solution containing approximately 15 per cent. sodium carbonate (anhydrous) and 5 per cent. tribasic sodium phosphate, the working temperature being about 80° C.

The material to be treated is immersed in this solution connected to the anode bar, with the current off, and allowed to remain until a vigorous etching action, which starts almost immediately, has persisted for about 20 seconds. Direct current at about 10 v. is then switched on with a current density of about 35 amp./ft.^{2} of anode surface. Within about 30 seconds of switching on, the initial etching of the metal should cease entirely and at the same time the current density should decrease to about half its original value, the voltage being kept within 9–12 v. The anodic treatment is then continued for about 5 minutes, after which the metal is removed from the bath and rapidly washed in clean cold water.

The reflectivity of the surface compared with the original mill finish is now considerably improved, and if the specimen is allowed to dry brilliant interference colours may be seen indicating the presence of an extremely thin transparent film presumably of aluminium oxide. This seems to be confirmed by the fact that the surface is now capable of being dyed by aniline dyes. This film is, however, too thin to withstand much wear and needs to be reinforced, and some difficulty was experienced in finding a suitable type of film for this purpose.

Of the normal electrolytes, chromic acid is useless, as its film is almost opaque; oxalic acid and sulphuric acid are better, particularly the latter, but both films reduce the original reflectivity. By carrying out the second treatment in sodium bisulphate the desired protective film is formed without causing any reduction in the degree of reflectivity obtained in the first process; in fact, in some cases a slight increase has been found. This effect is undoubtedly due to the presence of the sodium ions, since experiments carried out using equivalent solutions of sulphuric acid show a tendency to decrease the reflectivity. For the second part of the process, therefore, an aqueous solution is used containing approximately 20 per cent. sodium bisulphate worked at about 35° C. It is a straightforward anodic treatment using d.c. at 10 v. and a current density of about 5 amp./ft.^{2} anode surface, treatment being continued for 15 minutes.

The working details given above are those which have been found to give the most consistent results. The working, however, is not very critical, the permissible variations being indicated in Table I.

TABLE I.

	Normal.	Permisaible Range.
First Treatment.		
Electrolyte:		
Sodium carbonate anhyd., % . . .	15	12–20
Tribasic sodium phosphate, % . .	5	2·5–7·5
Temperature, ° C.	80–82	75–90
Voltage D.C.	9–12	7–16
Time, minutes	6–9	3–20
Second Treatment.		
Electrolyte:		
Sodium bisulphate, %	20	15–30
Temperature, ° C.	35	30–40
Voltage D.C.	10	8–12
Time, minutes	12–15	10–20

It should be noted, however, that working the process at the extreme limits of the permissible range will not necessarily give good results particularly with the first electrolyte; for instance, a composition of 12 per cent. carbonate and 7·5 per cent. phosphate is not good.

Some care is necessary in the finishing of treated material if a rather unpleasant defect is to be avoided. If a sheet is treated by both processes and finally washed and allowed to dry in air, a very brilliant surface is obtained which remains so until it is rubbed or fingered, when a permanent white streak appears which is rendered worse by further rubbing. This appears to be due to the formation in the first bath, of an extremely thin powdery layer, which is only rendered visible when rubbed in the dry state. The layer can be readily removed, however, without damage to the surface, by light scrubbing using clean water and a rubber sponge; this treatment must be applied before drying.

Several difficulties have arisen in the after-treatment or sealing of these reflector films, as most of the oils, waxes, &c., in general use reduce the reflectivity value, but very good results have been obtained by the application of soap and water. The soap should be applied with a second rubber sponge and worked into a good lather evenly over the reflector surface; this treatment produces a rather greasy effect on rinsing which disappears, however, when the metal is dried by rubbing in hot sawdust. Subsequent cleaning with soap and water and drying with a cloth may be done as often as desired.

Preliminary tests on the corrosion-resistance of the double film produced by the process described above—such as their resistance to dilute alkalis and dilute acids—show that they are at least as good as, and probably better than, anodic films produced by more orthodox means. Additional tests on the effect of atmospheric influences are now being carried out. The effect of heat is worthy of notice, since it is possible to heat metal treated by this process to its melting point without any apparent effect on the total reflectivity. Other tests have been carried out with metal used as reflectors for electric and gas heating elements. A reflector used behind a 1 kw. element after burning for 1500 hrs. showed a decrease in reflectivity of not more than 5 per cent. The element had been burning intermittently over a period of 18 months and the reflector was washed with soap and water as and when the normal accumulation of dirt and dust warranted it. In the case of the gas heaters, the reflector was so arranged that a portion of it was immediately above the heater and therefore subjected to the direct action of the gas fumes. After 1000 hrs. a slight milky haze was noticeable over this portion, the rest of the reflector being unaffected. Even over the hazy portion, however, there was no sign of definite corrosive action.

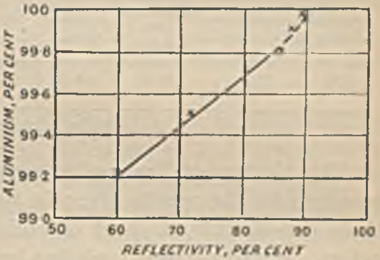

Fig. 1.

The films absorb dye-stuffs very readily, producing very brilliant colours. Here again the effect of the double process is noticeable, since the bisulphate film applied after the first treatment dyes more readily and to a deeper colour than a similar bisulphate film produced under exactly the same conditions but without the first treatment.

That the final results are dependent on the total overall purity of the metal used is shown in Fig. 1, in which reflectivity is plotted against purity. To obtain these results, metal was used varying in purity from 99·2 to 99·992 per cent. The curve is practically a straight line up to 99·8 per cent., after which the increase in reflectivity is less marked. It becomes evident, therefore, that if high results are required high-purity metal must be used.

The reflectivity values for aluminium of 99·8 per cent. purity treated by this process are given in Table II and compared with similar values for nickel, silver, and chromium plate, and other materials generally used for mirrors or reflectors. The silver, nickel, and chromium specimens were in the form of plated brass sheet as supplied by manufacturers for reflectors. Each specimen was flat and highly polished. The aluminium specimen was a piece of commercial sheet also polished and electrolytically brightened. The measurements were made in an apparatus using a photoelectric cell, and, since the conditions of each experiment were identical, the results are comparable. The figures represent the percentage of incident light reaching the cell after reflection by the metal surface compared with a standard silvered mirror taken as 100.

TABLE II.

							Plate Glass Mirrors.	
Standard Mirror.	Aluminium Mirror.*	Brightened Aluminium.	Stainless Steel.	Silver Plate.	Nickel Plate.	Chrome Plate.	Thick Plate Glass.	Thin Plate Glass.
100	101·5	86·0	54·0	97·0	72·0	72·0	91·5	95·0

* Distilled aluminium on glass.

That the type of film applied as reinforcement is of major importance is shown by the results given in the first column of Table III. For these experiments, a sheet of polished metal of the same purity as before, *i.e.* 99·8 per cent., was first brightened in the alkaline electrolyte, then cut into a number of smaller pieces each of which was further treated in one of the various electrolytes named, using the normal anodic process for that electrolyte.

In the second column, reflectivity values are given for a further series of specimens treated exactly as those shown in the previous column except that they did not receive the brightening treatment; that is to say, the figures show the comparative reflectivity values for normal good-quality polished and anodized sheet.

TABLE III.

Type of Final Film.	Brightened Metal.	Unbrightened Metal.
Sodium bisulphate . .	84·0	71·0
Sulphuric acid, d.c. . .	78·0	67·0
Oxalic acid, d.c. . .	73·0	66·0
Oxalic acid, a.c. . .	74·0	71·0
Chromic acid . . .	60·0	54·0

Value for plain polished sheet = 85
Standard silver mirror = 100

The measurements were made using a photoelectric cell, as previously mentioned. The general outlay of the apparatus was as follows :

The source of light was a 100 watt projection lamp worked from the 230 v. mains. By means of a condenser, a parallel beam of light from this lamp was thrown on to the reflecting surface arranged at an angle of 30° to the incident beam. In the path of the reflected beam a collimator tube was placed carrying at one end a large lens and at the other a Weston Photronic cell, the length of the tube and position of the lens being such that an image of the illuminated area was thrown on the cell surface. The cell was connected directly to a low-resistance micro-ammeter. Under these conditions the response is linear.

As it is important that the incident illumination shall remain constant, some means of control is necessary. This was obtained by inserting a suitable variable resistance in the mains lead to the lamp. Using the standard silvered mirror and the collimator arranged so that $\angle i = \angle r$, the resistance was adjusted to give a reading on the micro-ammeter of exactly 100. Frequent checks were made during any series of measurements.

Since most metal surfaces give some diffuse reflectivity, the collimator tube was arranged to swing about the reflected ray, and measurements were also taken at various points towards and away from normal. By calculation, therefore, it was possible to arrive at a value indicating the total reflectivity. This arrangement also helped to reduce errors due to a reflecting surface not being optically flat.

The preceding remarks have only dealt with surfaces treated to give high specular reflection and little or no diffusion. The brightening process is equally efficient when applied to surfaces designed to give maximum diffusion. It has also been stated above that for maximum results high-purity metal should be used, but it can also be said that with any normal commercial purity, treatment by this process will result in increased permanent brightness though it may be necessary with metal of the order of 99·2 per cent. purity to increase the electrolyte temperature to 90° C. with a current density of 50 amp./ft.^{2}, or higher.

Although the experimental work described was carried out using pure aluminium sheet, the reaction of a certain number of alloys was also investigated. In a certain number of cases the results were disappointing, but a few alloys have been found with which the results were quite successful. The operation of the process on a scale considerably larger than is possible in a laboratory has already been tested and few difficulties were experienced.

ACKNOWLEDGMENTS.

The author desires to thank Messrs. The British Aluminium Company, Ltd., for permission to publish this paper, the Research Department of Messrs. Metropolitan-Vickers, Ltd., for the loan of the special distilled aluminium mirror, and in particular he wishes to acknowledge the valuable help given by Mr. J. T. Richmond, M.A., B.Sc., who carried out a very large proportion of the experimental work. He also desires to thank Dr. A. G. C. Gwyer for his continued interest throughout the investigation.

DISCUSSION.

(*Condensed.*)

Dr. H. Sutton * (Member): Is any difference observed when daylight is used instead of the artificial light which the author employed in his experiments? The comparison given in Table II between quite a number of mirrors is interesting and must necessarily appeal to many users of mirrors. I would like to know whether these reflectivity values would stand in the same relative order after about 12 months' exposure to a British atmosphere. In the anodic treatment itself, is it possible partially to immerse the work without causing any appreciable trouble at the surface of the liquid? Sometimes in anodic treatment processes there is a tendency for the work to become pitted there. Is there any such tendency in connection with the present electrolytes and anodic treatment?

Dr. A. G. C. Gwyer,† B.Sc. (Vice-President): I would direct attention to the extraordinary stability of these films to temperature. When the mirror finish is produced, it is possible to heat the sheets up to the melting point and retain their brightness absolutely unimpaired.

Mr. Pullen (*in reply*): We attempted to carry out some tests using daylight, but Warrington daylight is somewhat uncertain. However, it appeared that the reflectivity values came in the same relative order. Aluminium is always brighter than the nickel and chromium, and slightly less bright than the silver. With regard to corrosion effects, I have made tests on some of the material which has been exposed for 2½ months, and as compared with chromium plate, nickel plate, and stainless steel which are definitely affected, particularly the nickel, the aluminium reflectivity only decreases about 3 per cent. The specimens are washed as and when required, to remove the accumulation of dust and dirt, but there is no sign of corrosion on the mirrors. Treatment by partial immersion does not work; one does not obtain water-line corrosion but the splashing of the metal above the water-line with a very fine soda spray.

There is one point in connection with this treatment which I have not mentioned in the paper, and that is that the electrolyte must not be stirred during treatment. Before we put the material in we stir to get the temperature up to 80°–82° C., but during the treatment the electrolyte must be quite still; in fact, it is necessary to put wooden baffle boards at the two ends on the cathode plates to keep the hydrogen stream away. Dr. Sutton might try to discover where the oxygen goes to; I have not discovered this yet. A peculiar feature about this process is that, although much hydrogen is evolved, one has to look very carefully indeed to find any gas on the anodes. Even using eudiometer tubes there is plenty of hydrogen, but no oxygen.

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THE CREEP OF TIN AND TIN ALLOYS.—PART I.* 733

By Professor D. HANSON, D.Sc.,† Vice-President, and E. J. SANDFORD, B.Sc.,‡ Member.

Synopsis.

The paper describes results of creep tests of long duration on tin and some of its alloys in the rolled condition. Silver up to 3·5 per cent. greatly improves the creep-resistance of tin. Bismuth–tin alloys are more resistant to flow than pure tin at stresses above about 300 lb./in.^{2}, but at lower stresses they are inferior to pure tin. Antimony improves the creep properties of tin: the alloy containing 8·5 per cent. antimony withstands a stress three times that of pure tin for an equal duration. Cadmium–tin alloys are greatly improved by heat-treatment and offer considerable resistance to creep. The mechanism of failure of these alloys is discussed. Results are given of tests on lead–tin solders and on the cadmium–tin eutectic alloy: these flow under stresses as low as 130–150 lb./in.^{2}. It is shown that in many cases there is no relationship between resistance to creep and ultimate tensile strength.

Introduction.

This paper describes the results of the first part of a systematic investigation of the creep properties of tin and its alloys. Previous papers [1,2,3] have shown that suitable additions of other metals considerably increase the tensile strength and hardness of tin. Whilst such quick tests are useful as a method of investigation for many purposes, they cannot be relied on in the case of tin and its alloys as a measure of the true strength under loads applied for a long time as in many service applications, for at normal temperatures tin is within the range in which pronounced creep phenomena must be anticipated.

Previously, most creep tests on alloys have been confined to endurances of a few days' or weeks' duration, and tests for more than 1 month are comparatively rare. Periods of this order seemed to the authors to be inadequate, and they have attempted, therefore, to adopt an endurance period of the order of 1 year, a procedure which is simple in tests carried out at room temperature. The only serious disadvantage of this procedure is that it limits the number of tests

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which can be carried out simultaneously and makes progress slow. The results obtained, however, have amply justified the decision.

PREVIOUS WORK.

The literature on creep is extensive, but a full discussion of the subject has been given by Tapsell.[4] Little work has been done on tin and its alloys. Jenkins [5] compared a lead–tin and a cadmium-zinc solder, and found that both alloys have a much better resistance to creep in the cast than in the rolled condition; Jenkins' paper contains a general discussion on the flow of metals above the temperature of recrystallization. Freeman and Quick [6] tested pure tin, pure lead, and a 50:50 lead–tin solder in the form of wire; their tests extended to 28 days only, although extensive tests were carried out on soldered joints.

PART I.—DESCRIPTION OF METHOD OF CREEP TESTING.

All the tests described in this paper were carried out at room temperature on rolled material. Ingots, 10 in. × 2 in. × 0·5 in., were chill-cast, cold-rolled to 0·1 in. in thickness, and machined into specimens, the dimensions of which were: overall length, 8 in.; parallel portion 3 in.; gauge-length 2 in.; width at ends 1 in.; width at parallel portion 0·5 in.; thickness 0·1 in. Holes, 0·1 in. in diameter, were drilled about 0·5 in. from each end of the specimens, exactly on the axis of the parallel portion.

Four frames were constructed to carry the specimens and weights, each frame consisting of two 4 in. × 2 in. channel sections, supported at the ends and at the centres. Each girder was drilled with 12 countersunk holes, from each of which was hung a specimen on a hemispherical seating. Two stirrups were fastened to every specimen, one at each end, by silver–steel pins, 0·1 in. in diameter, which passed through the holes in the specimens. These pins were found satisfactory up to loads of 200 lb., and in the tests reported in this paper no specimen was torn out of the stirrups before fracture. Direct loading with weights was adopted, as this method is simpler in construction than a lever system. The hemispherical seating and the pins supporting the specimen ensured axial loading at all times.

The extension of every specimen was measured at frequent intervals during the test. A pair of dividers was used at first, giving an accuracy of 0·25 per cent.; later, greater accuracy was found necessary with certain alloys which broke with small extension, and a cathetometer reading to 0·001 cm. (0·02 per cent.) was obtained. The gauge-length was 2 in. although for use with the cathetometer this was reduced slightly to 5 cm (1·97 in.) for ease of calculation.

The temperature of the room fluctuated, especially in the winter and during the Christmas and Easter vacations; the maximum temperature variation was from 27° to 9° C., whilst the mean daily variation was 5° C. Such variations might be serious in tests occupying only a short time, and might produce appreciable differences in those carried out at extremes of temperature, *e.g.* summer heat and winter cold, but in view of the policy adopted of carrying the tests to approximately 1 year's duration, these variations cancel out to a large extent, and the results at long endurances may fairly be taken as mean figures for the behaviour of the alloys at atmospheric temperatures.

The results are given as graphs obtained by plotting the initial stress in lb./in.^{2} against the time, in days, taken to fracture. The results of many other tests under lower loads, in which fracture did not occur, and which, therefore, do not lend themselves to graphical treatment, are incorporated in tables, which also include information concerning the extensions of the specimens. Typical time–extension curves for various alloys are also given, together with photographs of the types of fracture obtained.

TABLE I.—*Tensile Properties of Alloys Investigated.*

Composition, Per Cent.	Reference No.	Ultimate Tensile Strength, Lb./in.^{2}.	Elongation, Per Cent. on 2 in.	Heat-Treatment.
Tin	...	2,370	96	Self-annealed †
Silver, 0·1	A1	2,600	87	,,
0·02	A2	2,710	89	,,
0·04	A4	2,760	94	,,
0·1	A10	2,960	90	,,
3·5	A350	8,140	...	,,
Bismuth, 1	BI1	5,350	75	,,
2	BI2	...	...	,,
3	BI3	8,870	49	,,
5	BI5	10,390	56	,,
Antimony, 1	SB1	3,340	57	,,
5	SB5	6,790	68	,,
8·5	SB8·5	10,300	63	,,
10	SB10	9,210	61	,,
Cadmium, 1	CD1(QT)	5,820	48	Quenched and tempered *
4	CD4(QT)	8,360	38	,, ,,
6	CD6(QT)	9,270	29	,, ,,
6	CD6(SA)	4,700	...	Self-annealed †
33	CD33	11,270	45	,,
Lead, 40	P40	7,660	63	,,
50	P50	6,810	88	,,
60	P60	6,270	88	,,
Cadmium, 33	CD33	8,870	198	Tested at 0·1 in./in./min.

* 1 day at 168° C., quenched: tempered for 1 day at 120° C.

† For at least 1 month, after which no further softening takes place.

Rate of testing 0·4 in. per in. per minute, except where otherwise stated.

Table I gives a list of alloys investigated, their identification numbers, tensile strength, and elongation (rate of testing 0·4 in. per in. per minute) and heat-treatment, if any. The materials used were "Chempur" tin (99·99 per cent.), fine silver (99·97 per cent.), "Tadanac" cadmium (99·95 per cent.), pure antimony (99·7 per cent.), bismuth (99·+ per cent.), and pure lead (99·97 per cent.). The silver was added as a temper alloy, containing 3·5 per cent. silver, and the antimony as a temper alloy containing 50 per cent. antimony. Cadmium, bismuth, and lead were added as the pure metals.

PART II.—RESULTS OF CREEP TESTS.

(a) *Pure Tin and Silver–Tin Alloys.*

Table II gives the results of creep tests on pure tin and silver–tin alloys, and Fig. 1 shows the duration plotted against the initial stress.

TABLE II.—*Results of Creep Tests on Pure Tin and Silver–Tin Alloys.*

Tin.			0·01% Silver.			0·02% Silver.		
Stress, Lb./in.^{2}.	Duration, Days.	Final Extension, Per Cent.	Stress, Lb./in.^{2}.	Duration, Days.	Final Extension, Per Cent.	Stress, Lb./in.^{2}.	Duration, Days.	Final Extension, Per Cent.
1,025	0·5	78	1,027	0·6	102	1,002	1	81
611	4·6	105	603	7	95	604	10	97
468	21	119	460	27	117	472	37	110
402	79	132	407	92	147	404	143	64
327	173	101	323	199	95	324	307	98
196	(551)	(7)	...	...	...	...	...	...
157	(551)	(3·5)	...	...	...	...	...	...
0·04% Silver.			0·1% Silver.			3·5% Silver.		
1,006	1·6	73	1,011	3	49	1,996	10	62
602	24	67	603	44	59	1,845	15	60
475	71	72	462	236	59	1,614	34	52
405	250	68	406	369	74	1,407	74	76
347	602	62	339	644	66	1,193	157	66
...	...	...	200	(541)	(3·5)	1,100	211	50
...	...	...	160	(541)	(1·5)	1,002	449	57
...	...	...	...	...	...	800	(220)	(1·74)
...	...	...	...	...	...	700	(220)	(0·84)

The figures in parentheses are for specimens which have not fractured.

An increase in life can be effected by small additions of silver to tin; thus 0·1 per cent. causes a four-fold increase at stresses of about 300 lb./in.^{2}. The strength of the same alloy for any particular duration is about 1·5 times that of pure tin. The alloy A350 has a considerably greater resistance to creep than pure tin; under a stress of 1000 lb./in.^{2}, this alloy fails only after 449 days, whereas pure tin fails in less than 1 day, whilst for the same duration, A350 is nearly three times as strong as pure tin.

The load-duration curves for tin and alloys A1, A2, A4, and A10 all take about the same form (the curves for A1 and A2 are not shown in the figure to obviate overcrowding one part of the diagram). For short durations (less than about 25 days) the curves slope steeply; for durations exceeding about 70 days the curves slope relatively slightly and are not markedly curved. With the alloy A350, the curve still has a considerable slope up to at least 200 days' duration; this type of curve is the more difficult to extrapolate, since long-time tests are needed before the portion of the curve is reached where a further small reduction in stress will produce a considerable increase in life. It is possible to extend as a straight line (it then passes through the point represented by a stress of 250 lb./in.^{2} and a life of 1000 days) the latter part of the curve for alloy A4, and to predict that since the downward slope of the curve becomes less than the straight line, a stress of 250 lb./in.^{2} will *not* cause failure in 1000 days. A similar method applied to alloy A350 would probably greatly underestimate the creep-resistance of the material.

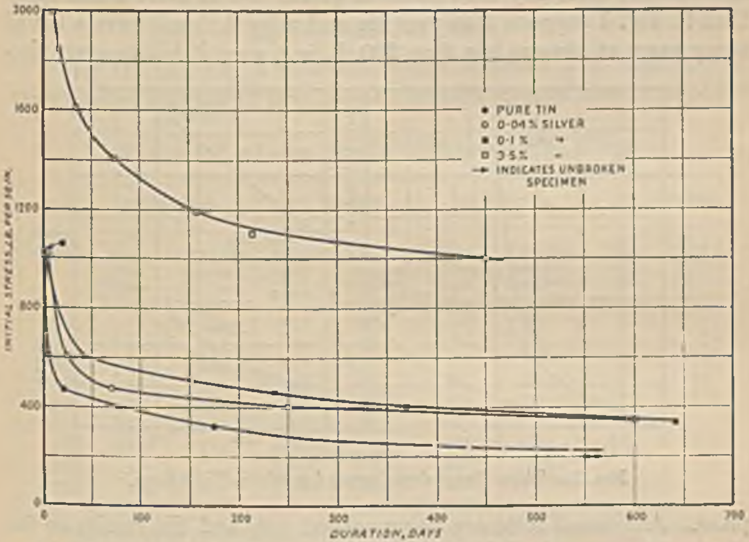

Fig. 1.—Stress–Duration Curves for Silver–Tin Alloys.

Fig. 2 gives some typical time–extension curves for these alloys. Within the accuracy of measurement, the first application of the stress causes creep, the rate of which increases continuously throughout the test. The shape of the curves suggests that if any strain-hardening takes place it is quickly removed; this might be anticipated in view of the definite self-annealing properties of these alloys at room temperature. The form of these curves (both Figs. 1 and 2) does not disclose the existence of any limiting creep stress at which the alloy will not break. In all such cases it is debatable whether any stress, however small, will cause failure after any time however great; *i.e.* Is there a real creep limit? Fig. 1 suggests that pure tin and alloy A10 will have a life of many years at stresses less than 200 lb./in.^{2}, even if failure ever takes place. Additional tests are being carried out, and the results so far obtained are given in Table II (the figures in parentheses). At 200 and 160 lb./in.^{2}, pure tin has extended 7 and 3½ per cent., respectively, and A10 has extended 3·5 and 1·5 per cent. in 540 days. The time–extension curve for pure tin is also shown in Fig. 2. In all cases a small amount of strain-hardening takes place, *e.g.* Fig. 2 shows that pure tin at a stress of 196 lb./in.^{2} extends 0·75 per cent. in the first 20 days and only a further 0·25 per cent. in the next 40 days; however, the rate of creep then increases and although, between 150 and 500 days, the time-extension curve appears almost as a straight line, the results show that the rate of creep is increasing slightly. This suggests that pure tin will ultimately fail even at 196 lb./in.^{2}. Similarly, the results indicate a probable failure at 157 lb./in.^{2}.

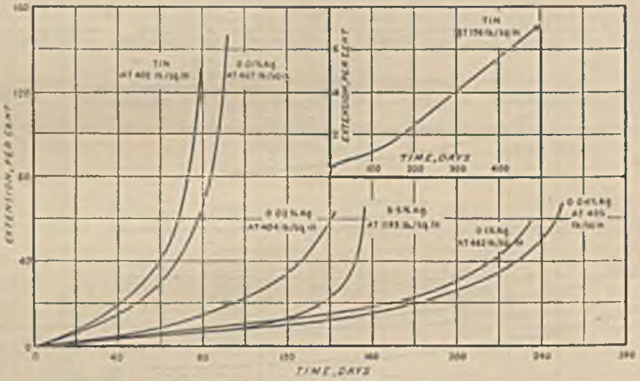

FIG. 2.—Time–Extension Curves for Silver–Tin Alloys.

Alloy A350 will have a very long life at stresses of about 800 lb./in.^{2}. Tests on this alloy are in progress at 800 and 700 lb./in.^{2} (Table II).

Under the former stress, the extension is 1·74 per cent. in 220 days, and 0·84 per cent. in the same time under the latter stress. In both cases the creep rate appears to be increasing, but the tests have not progressed sufficiently to judge whether failure will ever take place.

The appearance of the test-pieces of these alloys after fracture by creep differs little from that after rapid fracture in a tensile test. The final elongation does not vary much in the two tests. The characteristic "orange peel" effect due to the (comparatively) large grain-size is always found; no signs of intercrystalline failure were found with these alloys.

(b) *Bismuth–Tin Alloys.*

Table III and Fig. 3 show the results obtained with these alloys; their marked superiority over pure tin at high stresses may be expected from their tensile strengths. Alloy BI3 has the greatest resistance to creep, being considerably better in this respect than alloy BI5, although the latter has a higher tensile strength. At 1000 lb./in.^{2}, alloy BI3 has a life of 137 days, as compared with pure tin which at that stress has a life of less than 1 day. At low stresses, however, alloy BI3, the best of the bismuth–tin alloys, extends more rapidly, and will probably, therefore, have a shorter life than pure tin. At 150 lb./in.^{2}, alloy BI3 extends 16·72 per cent. in 329 days, whereas pure tin (at 157 lb./in.^{2}) extends only 3·5 per cent. in 551 days. It is to be expected, therefore, that tin will have the longer life. This reversal of creep strength at low stresses is shown clearly by a comparison of the shape of the creep curves; those of the bismuth–tin alloys consist of gradual sweeping curves, whereas that for pure tin has a sharp change of direction and

TABLE III.—*Creep Results of Bismuth–Tin Alloys.*

Stress, Lb./in.^{2}.	1% Bismuth.		2% Bismuth.		3% Bismuth.		5% Bismuth.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
1,600	7	91	22	95	30	70	12	83
1,400	10	121	31	88	45	73	15	84
1,200	19	123	47	97	77	86	26	98
1,000	37	134	94	102	137	91	37	102
700	185	138	255	133	378	108	130	133
600	355	150	(185)	(49)	...	...	...	...
500	(476)	(85)	(330)	(78)	(330)	(55)	443	148
300	...	...	(330)	(42)	(322)	(30)	...	...
150	...	...	(335)	(18·26)	(329)	(16·72)	...	...

The figures in parentheses are for specimens which have not fractured.

becomes nearly horizontal. This causes the curves to cross at a point where pure tin and alloy BI3 have an equal life at an equal stress. This point will be below 300 lb./in.^{2}, since alloy BI3 will have a life of over 600 days at that stress (judging from the uncompleted test) whereas it seems that pure tin will fracture in from 300 to 400 days.

The very low resistance of bismuth–tin alloys to flow under low loads may be due to their small crystal structure. It has already been shown [2] that bismuth–tin alloys, self-annealed at room temperature, possess a very fine crystal structure, which is confirmed by Figs. 5 and 6 (Plate V) in the case of alloys used in this research.

The behaviour of the alloy BI5 is anomalous; in spite of a higher tensile strength, its creep properties are inferior to those of alloy BI1 at stresses below 1000 lb./in.^{2}. This alloy shows no anomalies in a tensile test; the elongation is 56 per cent. with substantial local reduction in area. After a creep test, although the extension is over 100 per cent., there are a number of fine cracks across the edge of the parallel portion of the test-piece, shallow cracks on the face near to the fracture, and no local reduction in area. Fig. 4 (Plate IV), shows the difference between this alloy in a tensile and a creep test, and also shows that there are no cracks in alloy BI3 after a creep test. These facts are sufficient to account for the impaired properties of alloy BI5. Figs. 5 and 6 (Plate V) show the microstructures of these alloys. Alloy BI3 (Fig. 5) is a bismuth–tin solid solution, with a few isolated pieces of free bismuth; alloy BI5 (Fig. 6) is similar but contains much more free bismuth. The presence of a considerable amount of free bismuth in alloy BI5 is probably the cause of the formation of cracks, and thus of the lower strength. In addition to the particles shown in these figures, some free bismuth also existed between the grains; in alloy BI5 it was

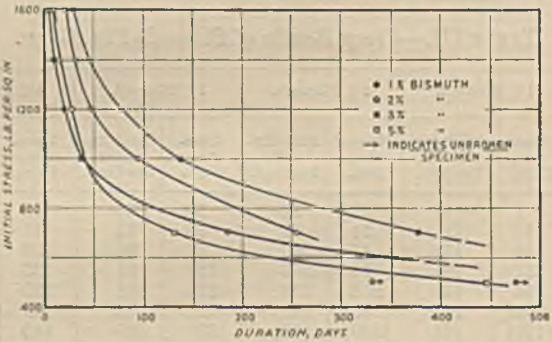

FIG. 3.—Stress–Duration Curves for Bismuth–Tin Alloys.

present as a practically continuous and very thin film, whereas in alloy BI3 the intergranular bismuth consisted of small isolated particles. High-power microscopic examination is required to show these intergranular films and particles.

Fig. 7 shows some typical time-extension curves for the bismuth–tin alloys. At low stresses, the rate of extension is almost constant, in spite of the increasing stress caused by the reduction in cross-sectional area. This suggests that some strain-hardening takes place. The curves show that there are times when the rate of creep increases above, or decreases below, the average rate. This may be an effect of the temperature variation. If strain-hardening is constantly counteracting an increase in the rate of creep, it would be expected that such a balance would be greatly influenced by small changes in temperatures. This, however, is being investigated further.

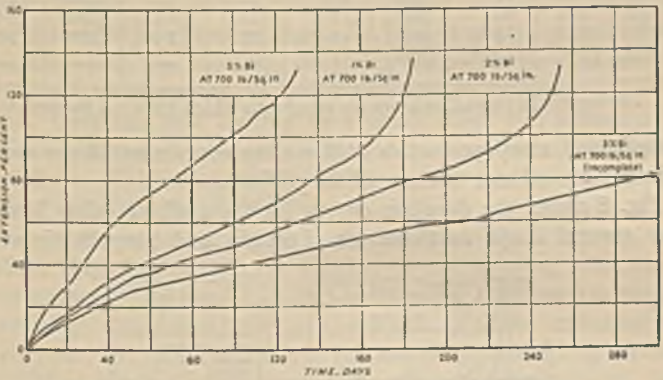

Fig. 7.—Time–Extension Curves for Bismuth–Tin Alloys.

(c) *Antimony–Tin Alloys.*

Table I shows the alloys of this series which have been investigated, together with their tensile strengths. The results of creep tests are given in Table IV.

The addition of 1 per cent. of antimony to tin improves the creep properties. At 400 lb./in.^{2}, pure tin fails in 79 days, whereas alloy SB1 extends only 13·5 per cent. in 365 days, indicating a life of over 3 years. Additions of antimony up to 8·5 per cent. produce further improved properties, so that alloy SB8·5 is better under 600 lb./in.^{2} (4·12 per cent. in 339 days), than alloy SB1 under 300 lb./in.^{2}, and is approximately equal to pure tin under 200 lb./in.^{2}. The tensile

TABLE IV.—*Creep Results of Antimony–Tin Alloys.*

Stress, Lb./in.².	1% Antimony.		5% Antimony.		8·5% Antimony.		10% Antimony.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
1,400	...	...	4	114	19	66	7	26
1,200	...	...	...	...	54	54	...	...
1,100	...	...	...	...	71	37	...	...
1,000	4	65	19	79	155	42	48	58
900	...	...	...	...	198	49	145	83
800	37	88	132	77	360	98	324	99
700	79	71	249	88	...	...	(232)	(12)
600	201	63	(366)	(18·5)	(339)	(4·12)	(396)	(6·24)
400	(365)	(13·5)	(386)	(2·68)	(337)	(1·06)	(388)	(2·02)
300	(340)	(5·50)	(344)	(1·10)	...	...	...	...

The figures in parentheses are for specimens which have not fractured.

strength and creep properties of the alloy containing 10 per cent. of antimony are inferior to those of alloy SB8·5.

Fig. 8 shows the duration curves for these alloys; they have the same general shape as those for silver–tin and bismuth–tin alloys.

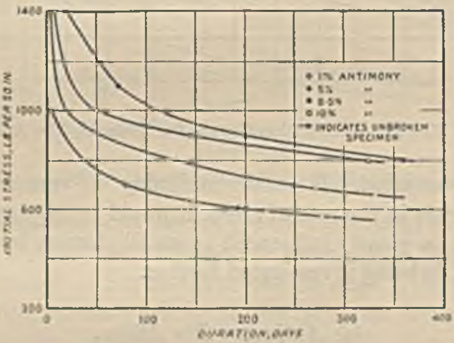

FIG. 8.—Stress–Duration Curves for Antimony–Tin Alloys.

Several of the results do not fit a smooth curve. Some specimens which were loaded to small stresses for a period, and which extended by only a small amount (less than 1 per cent.) were subsequently stressed to a higher amount, to supplement the results. Table V gives a list of these alloys. The result which is apparently greatly in error (alloy SB8·5 at 900 lb./in.²) relates to the alloy which underwent the greatest amount of previous strain (0·84 per cent.). On the other hand, the result for alloy SB10 at 900 lb./in.² seems to fit the curve, although it was previously strained 0·48 per cent. Further, alloy SB8·5 at 1200

TABLE V.—*Antimony–Tin Alloys, Loaded to Low Stresses and Subsequently Fractured at a Higher Stress.*

Antimony, Per Cent.	Stress for Fracture, Lb./in.^{2}.	Duration, Days.	Previous Stressing.
1	700	79	72 days at 200 lb./in.^{2}, extension 0·2%
5	700	249	68 ,, ,, ,, ,, 0·1%
8·5	1,200	54	44 ,, ,, ,, ,, nil
8·5	900	198	148 ,, 300 ,, ,, 0·84%
10	900	145	155 ,, 300 ,, ,, 0·48%
10	700	not fractured	44 ,, 200 ,, ,, nil

lb./in.^{2} (previously stressed at 200 lb./in.^{2} for 44 days) apparently had a duration which was too long, assuming the result for that alloy at 1100 lb./in.^{2}, to be correct, as it had no previous stressing. It seems possible, therefore, that loading to a small stress will influence the duration when the stress is increased, but to what extent, the results do not show. This effect may be similar to the raising of the fatigue limit by "understressing."

None of the curves of Fig. 8 approximated to the horizontal and, therefore, they do not indicate whether or not, a creep limit exists. For example, alloy SB1 at 300 lb./in.^{2}, is extending slowly at a rate which is increasing; from the 100th to the 200th day, the extension was 1·54 per cent., but from the 200th to the 300th day, it was 3·12 per cent. Alloy SB5 at 300 lb./in.^{2}, is also creeping at an increasing rate; from the 100th to the 200th day, its extension was 0·30 per cent., and from the 200th to the 300th day it was 0·46 per cent. On the other hand, alloy SB8·5 at 400 lb./in.^{2} shows distinct signs of creep at a decreasing rate; the average daily rate from the 100th to the 150th day was 0·0055 per cent; from the 150th to the 200th day—0·0040 per cent.; from the 200th to the 340th day—0·0038 per cent. This test has not been carried sufficiently far to show whether the creep rate will begin to increase, and thus it cannot be said whether this specimen will fail or not. The test on alloy SB8·5 at 600 lb./in.^{2} does not reveal whether the rate of creep is increasing or decreasing. Fig. 9 shows some typical time–extension curves for these alloys. There is some indication of a little strain-hardening since the creep-rate decreases at first during a short portion of the total test. This is confirmed by the discussion given above on alloy SB8·5 at 400 lb./in.^{2}.

A comparison of Tables I and IV shows that the extensions under creep are at least as great as those under tensile tests. The appearance of the test-pieces fractured by creep does not differ from those fractured in a tensile test; alloy SB1 exhibits the "orange-peel" effect, typical of an alloy with a comparatively coarse grain-size. The other alloys SB5, SB8·5, and SB10 show smooth surfaces after fracture, indicating that they have a fine grain-size.

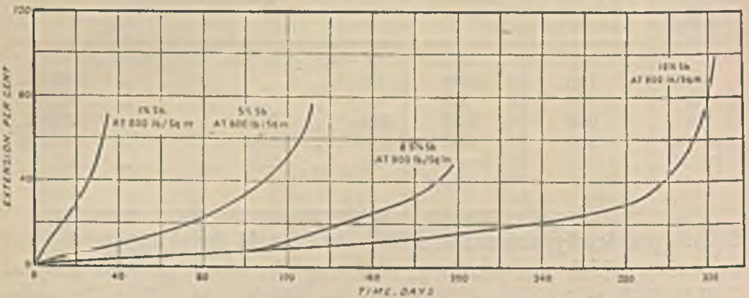

Fig. 9.—Time–Extension Curves for Antimony–Tin Alloys.

(d) *Cadmium–Tin Alloys.*

Table I shows the alloys of this series which have been investigated. Hanson and Pell-Walpole [3] showed that the tensile properties of these alloys can be greatly improved by quenching and tempering. Therefore the alloys have been quenched from 168° C., after 1 day at that temperature, and tempered for 1 day at 120° C. This treatment gives stable properties. For comparison, alloy CD6 was also investigated in the self-annealed condition. The prefix " Q.T." or " S.A." indicates to which treatment reference is made. Table VI shows the results. These alloys in the heat-treated condition have a greater resistance to creep; the alloy CD6(Q.T.) has a duration of 53 days at 2240 lb./in.^{2}. The order of superiority of the quenched and tempered alloys is that of their tensile strengths; no anomalies are found in this respect.

Hanson and Pell-Walpole [3] have shown the constitution of these alloys; the creep resistance of alloy CD1(Q.T.) is that of the cadmium-tin solid solution; alloys CD4(Q.T.) and CD6(Q.T.) will consist mainly of eutectoid. The results show that, whilst the α solid solution has a remarkable creep strength, the presence of eutectoid causes a further improvement. Furthermore, a comparison of alloys CD6(Q.T.) and CD6(S.A.) reveals that the heat-treatment given to the former is responsible for greatly improved creep properties.

The duration curves for these alloys are shown in Fig. 10. The shape of these is roughly similar to those of the other alloys previously discussed. In the diagram, however, several results, when plotted, do not form a smooth curve. Alloy CD6(Q.T.) at 1400 lb./in.^{2} failed before alloy CD4(Q.T.) at the same stress, although the curve for the former is, in general, above that for the latter. Again, alloy CD1(Q.T.) failed sooner at 1200 lb./in.^{2} than at 1400 lb./in.^{2}. The explanation of this is in the method of failure. Table VI shows that the extensions after failure are of the order of only a few per cent., although, after a tensile test (Table I) an elongation of 30–40 per cent. was recorded. Figs. 11 and 12 (Plate VI) show the ends of alloy CD1(Q.T.) fractured by creep and in a tensile test, respectively. The fracture of the latter

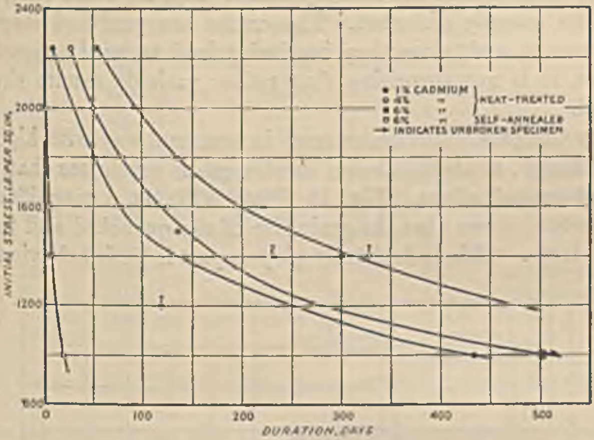

FIG. 10.—Stress–Duration Curves for Cadmium–Tin Alloys.

TABLE VI.—*Creep Results of Cadmium–Tin Alloys.*

Stress, Lb./in.^{2}.	1% Cadmium, Heat-Treated.*		4% Cadmium, Heat-Treated.*		6% Cadmium, Heat-Treated.*		6% Cadmium, Self-Annealed.	
	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.	Duration, Days.	Final Extension, Per Cent.
2,240	8	7·3	27	5·0	53	2·5	...	...
2,000	...	...	50	5·0	92	2·0	1	110
1,800	51	5·0	80	...	135	2·5	1·5	111
1,600	79	5·5	125	2	221	5·0	2·5	102
1,500	...	...	135	1·8	...	...	...	...
1,400	232	3·8	327	2·5	300	1·2	6	156
1,200	117	3·6	...	...	...	...	...	...
1,000	434	3·5	505	2·0	(481)	(0·38)	18	108

* One day at 168° C., quenched; tempered for a day at 120° C.

The figures in parentheses are for specimens which have not fractured. The extension figures for the heat-treated alloys are probably too high, as it was not possible to fit the fractured parts together closely.

is normal for a coarse-grained material. The specimen pulls down to a wedge and the surface is severely rumpled. Broken in a creep test, the extension is small and cracks are seen in the surface of the parallel portion; these cracks are intercrystalline (Fig. 13, Plate VII), and the grains are scarcely distorted. The cracks are produced long before failure occurs, and, since they inevitably lead to local concentrations of stress, it is not surprising that rather variable results should be obtained.

Alloy CD6(S.A.) fails under creep in a normal way with high extension, although, as stated above, its strength is much less than that of the heat-treated alloys. Fig. 13 (Plate VII), at a magnification of 10 diameters, shows that the grain-size of the quenched and tempered alloys is large. This undoubtedly plays a part in their behaviour under creep. The authors are investigating this and will not discuss it further in this paper.

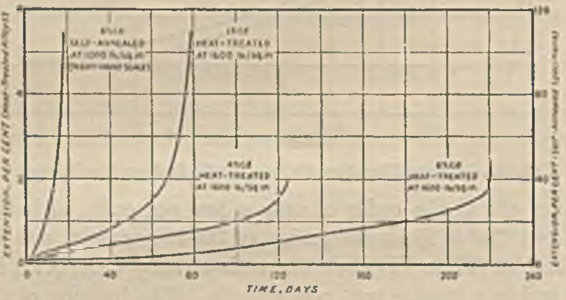

FIG. 14.—Time–Extension Curves for Cadmium–Tin Alloys.

Fig. 14 shows typical time–extension curves for these alloys. There is a well-marked period where the rate of extension is decreasing, suggesting that the alloy can be hardened slightly by cold-work. The self-annealed 6 per cent. alloy shows no such period, and the rate of creep increases continuously, if not from the moment of application of the load, from a time very soon afterwards.

(e) *Lead–Tin Solders and the Cadmium–Tin Eutectic.*

Tests were carried out on three lead–tin solders, and on the cadmium–tin eutectic (33 per cent. cadmium) to ascertain whether the latter has any definite advantages as a solder, in spite of its increased cost. The reference numbers, compositions, and tensile strengths of the alloys used are given in Table I, the creep results being summarized in Table VII.

Table VII.—*Creep Results of Lead–Tin Solders and the Cadmium–Tin Eutectic.*

Stress, Lb./in.².	40% Lead.		50% Lead.		60% Lead.		33% Cadmium.	
	Duration.	Final Extension, Per Cent.	Duration.	Final Extension, Per Cent.	Duration.	Final Extension, Per Cent.	Duration.	Final Extension, Per Cent.
1,000	5½ hrs.	197	5 hrs.	267	5½ hrs.	225	26 hrs.	230
800	...	...	...	...	...	...	30 ,,	300
600	less than 22 hrs.	256	less than 22 hrs.	300	less than 22 hrs.	325	4 days	315
400	56 hrs.	235	less than 48 hrs.	435	less than 48 hrs.	397	9 ,,	445
300	5 days	325	...	...	...	...	...	...
200	19 ,,	145	...	...	...	...	132 days	525
150	53 ,,	255	...	...	...	...	(164 days)	(21)
130	95 ,,	140	...	...	...	...	...	...
100	(165 days)	(35)	...	...	...	...	...	...

The figures in parentheses are for specimens which have not fractured.

Lead–tin solders in the rolled and self-annealed condition are easily deformed by static stresses. At 130 lb./in.², alloy P40 has a life of only 98 days, in spite of a tensile strength of over 7000 lb./in.². Few tests were carried out on alloys P50 and P60, as they appear to be inferior even to alloy P40.

Alloy CD33 is only slightly better than alloy P40 at stresses above 400 lb./in.², but between 400 and 200 lb./in.² its life increases from 9 to 132 days, whereas the life of alloy P40 increases only from 56 hrs. to 19 days. This is clearly shown in Fig. 15, which gives these results as duration curves. The curve for alloy CD33 has a sharp change in direction between 400 and 200 lb./in.². However, the possible increase in stress between alloys P40 and CD33 for an equal duration is only 50 per cent.

The extension of these alloys is very great in a creep test, usually over 200 per cent., and the specimens often show several necks. In Table I two figures are given for the tensile strength of alloy CD33, one at a rate of testing of 0·4 in. per in. per minute and the other at 0·1 in. per in. per minute. The slow rate of testing usually results in a lower tensile strength, the difference being about 650 lb./in.² with an alloy of the strength of alloy CD33. The extension increases about 5 per cent. With alloy CD33, however, a change from the fast to slow rate of testing produces a reduction in tensile strength of 2400 lb./in.², and an increase in elongation from 45 to 198 per cent. This indicates that the alloy is very susceptible to the rate of testing. Since a creep test may be likened to a tensile test at an extremely slow rate (this analogy holds for alloys such as the one under discussion), it would be expected that alloy CD33 would flow appreciably at low stresses, and that the final extension would increase as the load which caused failure decreased; this is so, in spite of a tensile strength of 11,270 lb./in.^{2}, creep at 150 lb./in.^{2} is rapid, being 21 per cent. in 164 days.

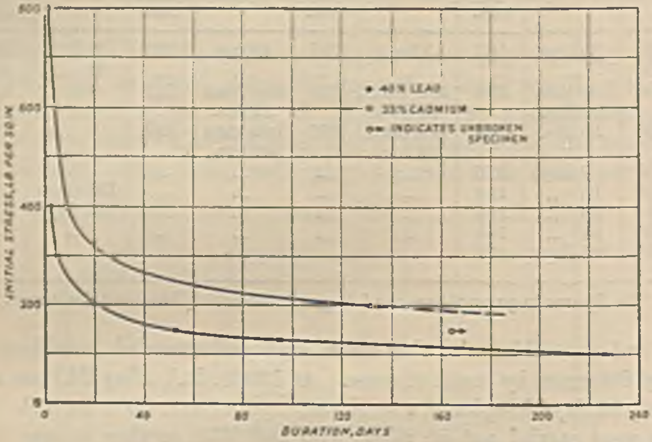

FIG. 15.—Stress–Duration Curves for a Lead–Tin Solder and the Cadmium–Tin Eutectic.

GENERAL DISCUSSION OF RESULTS.

The figures given in the tables are, in many cases, the results of creep tests extending over a period of 1 year. The results are sufficient to show that short-time tests may, in some cases, give a false impression. This is shown by a comparison of the bismuth–tin and silver–tin alloys; the former have a life many times that of the latter at 1000 lb./in.^{2}, but are considerably poorer at 150 lb./in.^{2}.

Table VIII gives several pairs of results for alloys of opposite tensile and creep properties. This is sufficient to show that there is no relation between tensile strength and creep properties of alloys of different constituent metals, nor is there always any relation between those of the same constituents; the results of the bismuth–tin alloys show this. It seems, therefore, that long-time creep tests are essential for a full understanding of the behaviour of these metals under prolonged loading.

No limiting creep stress was found for any alloy and, in most instances, tests carried out from 200 to 300 days are required to enable any estimate, even approximate, to be made of the creep characteristics of the alloys. Tests of 1 year's duration are probably satisfactory for all practical needs, since it is doubtful whether a part of any structure is subjected to the maximum stress for such a long time in the life of the structure.

TABLE VIII.—*Comparison of Tensile Strength and Creep Properties.*

Alloy.	Ultimate Tensile Strength, Lb./in.^{2}.	Creep Data.
SB1	3,340	5·5 per cent. extension in 340 days at 300 lb./in.^{2}
BI3	8,870	18·3 ,, ,, ,, 150 ,,
CD1(Q.T.)	5,820	Life of 434 days at 1000 lb./in.^{2}
BI5	10,390	,, 443 ,, 500 ,,
SB5	6,790	Life of 132 days at 800 lb./in.^{2}
P40	7,660	,, 95 ,, 130 ,,
SB8·5	10,300	Life of 155 days at 1000 lb./in.^{2}
CD33	11,270	,, 132 ,, 200 ,,

Small additions of silver and antimony improve the creep strength of tin in the self-annealed condition, whilst heat-treated cadmium–tin alloys containing 1–6 per cent. cadmium are greatly superior to the self-annealed alloys. To what extent this is due to an increased grain-size, or to constitutional changes is not yet known.

Bismuth–tin alloys have a longer life than pure tin at stresses exceeding 300 lb./in.^{2}, but they appear to flow more quickly than tin at 150 lb./in.^{2}. Lead–tin solder and the 33 per cent. cadmium–tin eutectic are particularly weak in the cold-rolled and self-annealed condition.

The work described in this paper is continuing and is embracing a wider range of tin alloys. Tests at elevated temperatures and tests on cast material, especially bearing metals, are in hand. It is hoped to publish the results in subsequent papers.

ACKNOWLEDGMENTS.

The research described has been made possible by grants from the International Tin Research and Development Council, to whom the authors are greatly indebted. They are particularly grateful to Mr. D. J. Macnaughtan, Director of Research, for his keen interest in and helpful criticism of the work.

REFERENCES.

[1] D. Hanson, E. J. Sandford, and H. Stevens, *J. Inst. Metals*, 1934, **55**, 115.
[2] D. Hanson and E. J. Sandford, *J. Inst. Metals*, 1935, **56**, 191.
[3] D. Hanson and W. T. Pell-Walpole, *J. Inst. Metals*, 1935, **56**, 165.
[4] H. S. Tapsell, "Creep of Metals." London: 1931.
[5] C. H. M. Jenkins, *J. Inst. Metals*, 1928, **40**, 21.
[6] J. R. Freeman, Jr., and G. W. Quick, *Met. Ind.* (*N.Y.*), 1926, **24**, 7.

DISCUSSION.

(*Condensed.*)

DR. M. BALLAY * (Member): I have investigated the effect of the time factor in ball-hardness tests on lead, and have ascertained as the result of tests on as-cast, rolled, and rolled and annealed lead specimens, that the speed of penetration of the ball is a function of the grain-size.

In tin alloys no doubt other factors have an influence but, apparently, in the case of my experiments on lead the only factor is that of grain-size.

Freiherr VON GÖLER † (Member): We cannot praise this work too highly; we have carried out a similar series of measurements on lead alloys and can thus fully appreciate the sacrifice of time and care entailed. In our work we used a logarithmic scale for the time in the stress–duration graphs and found the resulting curves to be straight lines except for slight deviations at low stresses. This logarithmic relation facilitates not only the experimental representation of the results, but also their theoretical interpretation. It appears to me that the authors' results can be interpreted in a similar way.

The authors' observation that bismuth–tin alloys behave worse than pure tin at low stresses is especially interesting. H. F. Moore and his collaborators at the University of Illinois, as well as Hanemann at the Technische Hochschule in Berlin, have made similar observations on antimony-lead alloys, and we have also observed in the case of a number of lead alloys, that at high stresses, *i.e.* in short-time tests, the alloys are greatly superior to pure lead, but at low stresses, *i.e.* with increased time of testing, this superiority is much less marked; in no case, however, have we observed the transition from superiority to inferiority which occurs with bismuth–tin alloys. This behaviour should interest not only the practical man, therefore, but also the theorist; the latter particularly, since it should do much to elucidate the nature of creep, and the former since it warns him to be cautious in selecting alloys on the basis of short-time tensile tests, the results of which are compared with those given by pure metals in similar tests.

Mr. G. BLACKMAN ‡: I address the meeting not as a metallurgist but as a plant physiologist. Statistical methods as applied to research in plant physiology should be of value in metallurgical and other scientific work. By means of statistics it is possible to interpret data which would be intelligible only with difficulty by other means. If any of those present are interested in trying to assess the errors of any metallurgical process, let them read Professor R. A. Fisher's book "Statistical Methods for Research Workers."

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† Metallgesellschaft A.-G., Frankfurt a. Main, Germany.
‡ London.

PLATE IV.

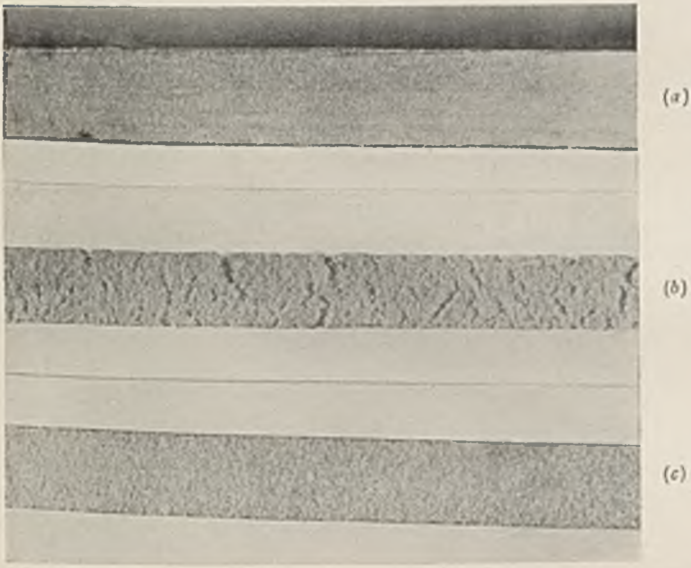

FIG. 4.—Edge of Fractured Specimens. (*a*) 5% Bi, Fractured in Tensile Test; (*b*) 5% Bi, Fractured in Creep Test; (*c*) 3% Bi, Fractured in Creep Test.

[*To face p.* 176.

FIG. 5.—3% Bi. Etched Electrolytically in Dilute Hydrochloric Acid. × 150.

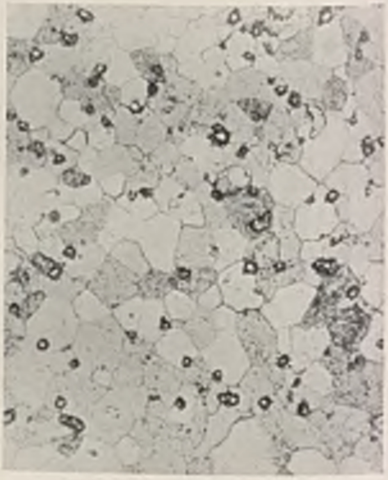

FIG. 6.—5% Bi. Etched Electrolytically in Dilute Hydrochloric Acid. × 150.

FIG. 11.—Creep Fracture. 1% Cadmium, Quenched and Tempered. × 3.

FIG. 12.—Tensile Fracture. 1% Cadmium, Quenched and Tempered. × 3.

FIG. 13.—Intercrystalline Cracks in Creep Specimen. 1% Cadmium, Quenched and Tempered. × 10.

Sir Robert Mond,* Kt., M.A., LL.D., F.R.S.E. (Member): For many years, as Chairman of the British Fire Prevention Committee, I was concerned with the question of the use of fusible alloys in sprinklers and other apparatus. An important question is whether the fusing point varies with time. In the case of sprinklers it may be necessary to renew them from time to time; if so, at what rate should they be renewed? Does crystallization or any other factor arise which might alter the temperature at which these easily fusible alloys fuse?

Mr. J. R. Green,† B.Sc. (Member): I am a little surprised to find that no alloys of copper with tin have been investigated. As is well known, once copper is alloyed with tin, it is extremely difficult to get it away again. In practice almost all solders which are found in commerce contain anything up to 0·15 or even 0·2 per cent. of copper. It seems to me that if such alloys were investigated, say, ordinary lead–tin solders both antimonial and non-antimonial, and containing up to perhaps 0·1 per cent. of copper, some interesting results might be obtained.

CORRESPONDENCE.

The Authors (*in reply to the discussion at the meeting*): We are glad to know that Dr. Ballay finds that grain-size is a function of the speed of penetration of a loaded ball in lead, because we have evidence that grain-size plays a large part in determining the rate of creep and the duration of tin alloys under load.

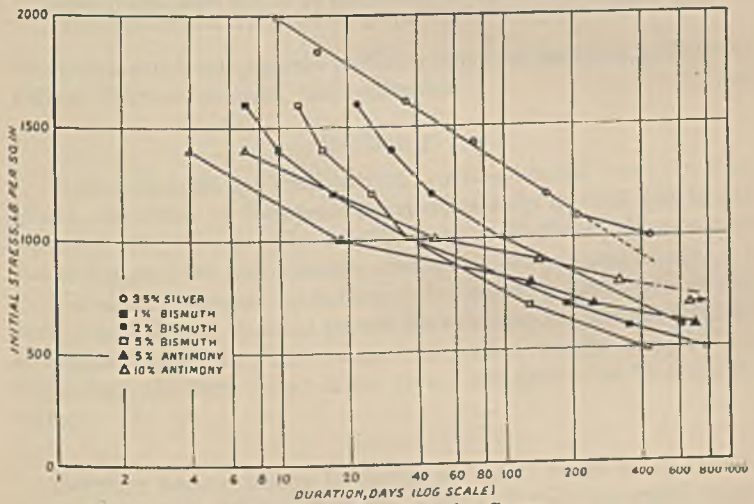

Fig. A.—Stress–Log. Duration Curves.

We have not found that much advantage is to be gained by using a logarithmic time scale in stress–duration curves, nor do we find that this

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* Director, International Nickel Company of Canada, Ltd.

† Chief Chemist, Batchelor, Robinson & Co., Ltd., Llanelly.

method of plotting always gives straight lines. Fig. A shows a selection of curves so plotted: a few results have been included which have been obtained subsequent to writing this paper. Only the curve for the alloy of 3·5 per cent. silver approximates to a straight line. Even here, the result at the lowest stress departs considerably; a continuation of the straight line indicates a life of 300 days at 1000 lb./in.^{2}, whereas the actual result was 449 days. We find that, although the equation $S = \alpha D^n$ (S = stress, D = duration) sometimes fits the results approximately, other equations are as close. We are glad to receive further proof of our contention that short time creep tests are often misleading as a criterion of the behaviour of a material under lower stresses.

Mr. Blackman's remarks are of great importance to metallurgists. To apply statistical methods to an investigation on creep, however, would prolong the investigation beyond the patience of a generation of workers.

In reply to Sir Robert Mond, we see no reason to suppose that the fusing point of a fusible alloy alters with time. Of course, where the alloy is being used at such a temperature that oxidation takes place, the oxide layer may support the plug when actually molten. Again, where a fusible alloy is under pressure, creep may take place and lead to a premature operation of the sprinkler.

We are attempting to investigate a large number of tin alloys under creep, and the only reason why alloys of tin containing copper have not been dealt with, is, that it is impossible to examine a large number of alloys at a time.

METALS OF THE PLATINUM GROUP.* 734

ORES, RECOVERY AND REFINING, FABRICATION AND USES, AND PROPERTIES.

By R. H. ATKINSON,† M.A., MEMBER, and A. R. RAPER,‡ M.A., MEMBER.

SYNOPSIS.

An attempt is made to present up-to-date metallurgical information about the six metals of the platinum group. After a brief description of the discovery of the metals and an account of the ores, particular attention is devoted to the recovery and refining of the metals produced from the Canadian nickel industry. This is followed by a full description of the methods of fabrication of the metals and their alloys. It is shown that the two ductile metals of the group platinum and palladium are readily worked, while rhodium and iridium are worked with much greater difficulty. The two metals osmium and ruthenium, belonging to the hexagonal system, have not up to the present been thoroughly investigated. Finally, an account is given of the properties of the metals and their uses.

THE metals which comprise the platinum group are platinum, palladium, iridium, rhodium, osmium, and ruthenium.

DISCOVERY.

Platina (Spanish for small silver), a strange metal from the New World, was noted by European travellers as early as 1538, but it was not until 1741 that samples were brought to England. Watson and Brownrigg gave the first scientific description of the metal in 1751.

Wollaston discovered palladium and rhodium in 1804, and in the same year Smithson Tennant proved the existence in platinum residues of two new metals to which he gave the names osmium and iridium. Ruthenium, the sixth metal of the group, was discovered by Claus in 1845.

ORES.

Platinum usually occurs in nature as native metal alloyed with one or more of its allied metals in the form of very fine grains more

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or less flattened; sometimes in the form of irregular nuggets; and occasionally, though rarely, in small cubic crystals. It is sometimes coated with a black layer of iron oxide, which may be magnetic, in which case it is not easily recognizable. When unrefined it is referred to as "crude" platinum.

Up to 1915 more than 95 per cent. of the whole supply of platinum metals was derived from alluvial deposits; the remainder was obtained from the refining of copper and gold bullion, particularly from the copper–nickel deposits of Sudbury, Ontario.

The first commercially important discovery of native platinum in a primary deposit was made at the Onverwacht mine, Lydenburg, South Africa, which yielded approximately 30,000 oz. during the years 1926–1930.

The principal alluvial deposits of crude platinum at the present time in order of importance are found in the Ural Mountains, Colombia, and Abyssinia. Typical analyses of Ural, Colombian, and Onverwacht platinum are given in Table I.

TABLE I.

	Platinum, Per Cent.	Iron, Per Cent.	Palladium, Per Cent.	Rhodium, Ruthenium, Osmium, Iridium, Per Cent.
Ural platinum . .	73–86	8–17	0·3–1·8	2·5–7·7
Onverwacht platinum .	80–84	11	0·4	0·5–1·0
Colombian platinum .	84–86	5–8	0·5–1·0	3–6

There are also very extensive primary deposits of platinum metals in sulphide-bearing norite in the Potgietersrust and Rustenburg districts of the Transvaal. These deposits contain about 5 dwt. of platinum metals per ton; platinum and palladium are present in about equal proportions, with subordinate amounts of the other platinum metals. The platinum metals in the concentrates prepared from this ore are said to be in combination, mostly with sulphur.[1] Two new minerals, cooperite, PtS, and braggite, (Pd, Pt, Ni)S, have been discovered in these deposits. Copper and nickel sulphides are present in the ores but not in sufficient quantities to pay working costs, which consequently fall almost entirely on the platinum metals.

Platinum is also found mostly in combination with arsenic as sperrylite in the well-known copper- and nickel-bearing deposits of the Sudbury district of Ontario, Canada. Palladium, in about the same amount as platinum, and subordinate amounts of other platinum metals are also present.

The main sulphide mineral is pyrrhotite or magnetic pyrites (Fe_3S_4). With this is associated the copper mineral chalcopyrite or copper pyrites ($CuFeS_2$) and the nickel mineral pentlandite (NiS).

Although the amount of the platinum metals per ton of these deposits is very small, yet owing to the fact that big tonnages of ore (over 1,800,000 tons in 1934) are treated for the recovery of the main products, copper and nickel, very substantial amounts of platinum metals are produced as by-products. For instance, during the period 1928–1934 the production of platinum metals from these deposits corresponded to 1·7 oz. for every ton (2000 lb.) of nickel.

The principal source of palladium is the above-mentioned Sudbury copper–nickel ores, and there is a small amount from the South African sulphide norite deposits.

Rhodium, ruthenium, osmium, and iridium accompany platinum in all the deposits which have been mentioned, and are recovered when the platinum is refined.

The principal source of osmium and iridium is the mineral osmiridium, which is now recovered as a by-product of gold mining operations on the Witwatersrand. The composition of this mineral is variable: osmium from 23 to 40, iridium from 21 to 35, ruthenium + rhodium from 9 to 15, and platinum from 5 to 15 per cent. There is also a fluctuating production of this mineral, depending on the market price, from alluvial deposits in Tasmania.

PROPERTIES OF THE METALS OF THE PLATINUM GROUP WHICH AFFECT THEIR REFINING.

The six metals of the platinum group are white in colour and are permanent in air under normal atmospheric conditions when in compact metallic form. As would be expected from their position in the Periodic Table, their chemical properties are similar. For instance, rhodium, ruthenium, and iridium are not attacked by *aqua regia*; platinum is dissolved by *aqua regia* but is not attacked by any single acid; palladium is easily soluble in *aqua regia*, and it is also attacked by hot concentrated sulphuric acid and to a less degree by nitric acid, but with these exceptions it is resistant to the common acids. The metals in the finely divided state are less resistant to chemical attack than the compact metals; for instance, osmium black dissolves in nitric acid and rhodium black is attacked by hot concentrated sulphuric acid.

In solution the metals readily form very stable complex salts, many of which are isomorphous. For this reason clean separations of the metals are rarely accomplished.

It will be obvious from this brief reference to the chemical properties, that the refining of the platinum metals is likely to be a complicated chemical process. Electrolytic refining methods which are so helpful in the case of many other metals cannot be used because palladium is the only one of the group which easily dissolves anodically in an aqueous electrolyte. Further, all the metals have relatively high melting points ranging from 1550° C. for palladium to 2700° C.* for osmium; consequently it is customary to market the metals in the form of sponge or meal and they are not melted until required for fabrication.

RECOVERY AND REFINING.

Native platinum is recovered from alluvial deposits by gravity concentration methods which yield a concentrate (for typical analyses see Table I) rich enough for refining.

The essential steps in the refining of native platinum are probably the same now as when described by Wollaston in his Bakerian Lecture to the Royal Society in 1828.[2] The crude platinum is dissolved in hot concentrated *aqua regia*; ammonium chloride is added to the filtered solution to precipitate ammonium chloroplatinate which is filtered off, washed, dried, and ignited to convert it into platinum sponge. If a purer metal is required the operations are repeated as often as may be necessary.

McDonald[1] has described an alternative refining process based on the recrystallization of sodium chloroplatinate.

If the platinum metals present in a deposit cannot be concentrated by gravity methods, lengthy and costly treatments may be necessary to prepare a concentrate rich enough for *aqua regia* treatment unless the metals are recovered as the by-products of the recovery and refining of some other metal. In the case of the Sudbury copper–nickel deposits, the platinum metals follow the nickel through the various operations; finally, when the nickel is separated in a pure form the platinum metals remain behind as a residue which at very little additional expense can be concentrated sufficiently for refining by the *aqua regia* process.

In view of the growing importance of by-product platinum metals, a brief outline will be given of the treatment of the Sudbury copper–nickel ores.

The ore after concentration and partial roasting is smelted either in blast furnaces or in reverberatory furnaces to give a furnace matte or sulphide of iron, nickel, and copper which acts as a collector of platinum metals. This matte is blown in converters to remove the

* This temperature is not known accurately.

iron, yielding a Bessemer matte having the approximate composition copper 35, nickel 46, iron 0·8, and sulphur 17 per cent. The subsequent treatment of this matte depends on whether electrolytic metal or Mond pellets are to be produced; in the latter case, the matte is shipped to the refinery of the Mond Nickel Co., Ltd., at Clydach, South Wales.[3]

The matte as it is received is ground in ball mills and then calcined to convert the nickel and copper sulphides into the corresponding oxides:

$$(Cu,Ni)S + 2O_2 = CuO + NiO + SO_2.$$

The copper oxide is then leached out by treatment with 12 per cent. sulphuric acid:

$$NiO + CuO + H_2SO_4 = NiO + CuSO_4 + H_2O.$$

After drying, the copper-extracted matte is reduced by treatment with water-gas in a special reducer at a temperature of 330°–350° C.:

$$NiO + H_2 + CO = Ni + H_2O + CO.$$

The reduced nickel is submitted to the action of carbon monoxide in volatilizers at a temperature of about 50° C., when the following reaction takes place:

$$Ni + 4CO = Ni(CO)_4.$$

The nickel carbonyl from the volatilizers is blown by fans into the decomposers where, at a temperature of about 180°–200° C., the nickel carbonyl decomposes according to the equation:

$$Ni(CO)_4 = Ni + 4CO.$$

As the reactions are incomplete, it is in practice found necessary to pass the material through the plant three times to get good yields of nickel and copper. After the third pass, the residue is roasted and then leached with sulphuric acid to remove most of the residual copper and nickel. According to Langer and Johnson [4] an analysis of a typical leached residue gave: platinum 1·85, palladium 1·91, rhodium 0·20, ruthenium 0·16, iridium 0·04, gold 0·56, and silver 15·42 per cent.

For the production of electrolytic nickel,[5] the treatment of the ore is the same as already described as far as the Bessemer matte stage. The nickel sulphide is then separated from the copper sulphide by the Orford process, also known as "tops and bottoms" process. For this purpose the Bessemer matte is mixed with coke and sodium bisulphate and smelted in blast furnaces, as a result of which the charge separates into two layers—the "tops" which consist of a double sulphide of sodium and copper, and "bottoms" which consist of nickel sulphide. In this process the platinum metals mainly go with the nickel, whereas the silver and gold follow the copper. As the separation is not clean, it is necessary in practice to repeat the operation separately with the "tops and bottoms" portions. The final "tops" are blown in converters whereby the sodium sulphide is oxidized to sodium sulphate and the copper sulphide is converted into blister copper which is shipped to a copper refinery for electrolytic purification. Nickel sulphide "bottoms" are crushed, leached, and then roasted on Dwight–Lloyd sintering machines. The oxide thus obtained is reduced to metal in reverberatory furnaces, and the resulting metal (containing about 2 per cent. of copper and some iron) cast into anodes for electrolytic treatment. The first anode slimes, which, of course, contain the precious metals, are roasted and then smelted to give secondary or P.M. anodes (containing about 24 per cent. copper and 73 per cent nickel). Secondary slime contains about 2 per cent. of platinum group metals and is concentrated by acid treatment to a product containing about 50 per cent. platinum group metals.

Powell and Deering have patented a modified nickel extraction process for the treatment of low-grade sulphide flotation concentrates.[6] The modification consists in generating a small proportion of iron–nickel metallics in the body of the molten matte which act as collectors of the platinum metals. The metallics are subsequently separated by gravity or magnetic treatment and smelted to give a nickel matte sufficiently rich to be treated economically either by a wet chemical or electrochemical process for the recovery of the metals of the platinum group.

Operations at the Acton Refinery of the Mond Nickel Company.

The Acton Refinery receives residues from the Clydach nickel refinery besides concentrates from the electrolytic nickel refinery and a smaller amount of concentrates from the electrolytic copper refinery which treats the Company's blister copper.

The residues from the Clydach refinery require further concentration before the platinum can be extracted economically with *aqua regia*. For this reason the residues are smelted with litharge, fluxes, and charcoal in small basic-lined tilting furnaces to collect the precious metals in lead and at the same time to slag off silica and base metals. Subsequent cupellation of the ingots in similar furnaces removes the excess of lead as litharge (which is used again in further smelting charges) and yields a silver-rich precious metal alloy about four times richer than the Clydach residue. This alloy is parted with boiling concentrated sulphuric acid, which removes most of the silver and about one-third of the palladium as sulphates. The residue contains the platinum, gold, and the rest of the palladium in a form particularly suitable for extraction with *aqua regia* which is the next operation. From the solution of chlorides thus obtained, the gold is precipitated as brown gold by means of ferrous sulphate, and then the platinum as ammonium chloroplatinate by the addition of ammonium chloride, and lastly, the palladium is precipitated as palladosammine chloride. The only one of these operations which calls for special comment is the precipitation of palladosammine chloride. The palladium present as chloride is converted into soluble tetrammino-palladous chloride by the addition of excess ammonia solution according to the equation

$$PdCl_2 + 4NH_3 = [Pd(NH_3)_4]Cl_2.$$

When excess of hydrochloric acid is added, the sparingly soluble yellow compound known as palladosammine chloride is precipitated according to the equation

$$[Pd(NH_3)_4]Cl_2 + 2HCl = [Pd(NH_3)_2Cl_2] + 2NH_4Cl.$$

The impure platinum salt is converted into metal by ignition, dissolved in *aqua regia* and re-precipitated as pure ammonium chloroplatinate, which, on ignition, yields pure platinum sponge. The impure palladosammine chloride is purified by dissolving in ammonia and reprecipitating with hydrochloric acid; the pure salt is converted into sponge by igniting.

The silver and the gold are purified electrolytically, by the Moebius and Wohlwill processes, respectively, special attention being given to the recovery of small amounts of platinum metals.

The final insolubles and reduction residues from the above wet process treatment are smelted to concentrate the rhodium, ruthenium, and iridium (which are known as by-metals). From the precious metal alloy thus obtained, the individual metals are separated and refined by chemical processes.

Refining of the richer concentrates from the nickel and copper refineries which contain more than 50 per cent. platinum metals and very little silver, commences with the *aqua regia* treatment.

In precious metals refining, the order of operations depends on the ratio in which the precious metals are present. The order which is here described is followed because it has been found to be the most suitable for these by-product concentrates, although it is realized that other sequences of operations might be more suitable for other types of material.

The average purities of the metals recovered from these concentrates are: platinum 99·93, palladium 99·94, iridium 99·7, rhodium 99·7, ruthenium 99·7, gold 99·97, and silver 99·97 per cent.

The high intrinsic value of the materials treated makes it imperative to reduce working losses to a minimum and to obtain the maximum yield as quickly and directly as possible. In practice, not more than 0·25 per cent. of the platinum metals contained in the concentrates is lost, while 1·25 per cent. is temporarily retained in furnace slags which are returned to the nickel refinery for re-treatment. The remaining 98·5 per cent. is produced directly as refined metal. The losses occurring in the processes of extracting the nickel and copper are also very small, and it is estimated that 90 per cent. of the precious metals contained in the ore is ultimately recovered.

FABRICATION.

PLATINUM.

Historical Review.

The history of the development of methods of fabricating platinum is of considerable metallurgical interest. The early chemists soon found that they were unable to melt platinum in any quantity with the means then at their disposal, and realizing the value of the metal to aid them in their experimental work, they sought other means of converting the spongy metal into foil and wire.

One of the first processes for working the metal depended on the observation of Scheffer [7] that platinum could be fused with the help of arsenic and the later observation of Achard [8] that this alloy on ignition leaves a residue of malleable platinum. Janetty in Paris was celebrated for his platinum work and was able to make crucibles, &c., of the low melting point arsenic alloy, subsequently removing the arsenic by volatilization. This process and also one involving the use of mercury must have been particularly poisonous, and the methods were not successful in the hands of British experimenters.

At the beginning of the nineteenth century several workers in this country attempted to solve the problem of rendering platinum sponge malleable by mechanical means, and interesting papers were published by Richard Knight [9] in 1800, by Alexander Tilloch [10] in 1805, and by W. H. Wollaston [2] in 1828. In the course of this work they laid the foundations of powder metallurgy. The method described by Wollaston is in essentials still used in this country and will be described in a later section of the paper.

A further stage of progress in the metallurgy of the platinum metals became possible with the invention of the oxy-hydrogen blowpipe by Robert Hare, who showed [11] in 1847 that it was possible to melt large quantities of platinum and small amounts of rhodium and iridium.

Prior to this only very small quantities of platinum had been fused, although as early as 1758 Macquer and Baumé [12] had succeeded in melting the metal with the aid of a powerful burning glass. A further significant advance was made by Deville and Debray [13] in 1859 when they recommended the use of lime as a refractory hearth for platinum melting, and designed an excellent type of furnace.

In more recent years the chief advance has been in the use of the high-frequency induction furnace.

Powder Method.

The description of Wollaston's process is given in the 1828 Bakerian Lecture to the Royal Society,[2] and he remarked that it was so successful that he did not see any occasion to wish for further improvement.

In order to prepare platinum powder, pure ammonium platinichloride was heated with the utmost caution, with so low a heat as just to expel the whole of the ammonium chloride and so that the particles of platinum cohered as little as possible, for on this depended the ultimate ductility of the product. The grey powder was then rubbed between the hands of the operator to obtain by the gentlest means a powder which passed through a fine lawn sieve. The coarser particles were ground in a wooden bowl with a wooden pestle and, in the later stages of grinding, water was added and the finer portions of platinum removed as soon as they were suspended. In this way Wollaston obtained a uniform mud or pulp. The next stage was to compress the wet mud, which was carefully packed in a tapered brass barrel of about 1 in. internal diameter. After compression, the cake was heated first on a charcoal fire to drive off moisture and grease and to give it a firmer degree of cohesion, and finally heated in a wind furnace to a very high temperature. The ingot was forged while hot and afterwards either rolled down or drawn into wire.

The following figures quoted by Wollaston illustrate the gradual bonding of the particles as the process proceeds :

Specific gravity of cake of metal mud = 4·3
„ „ after pressing = 10
„ „ after wind furnace = 17–17·7
„ „ after forging = 21·25
„ „ of drawn rods = 21·4

The process described above is, in main essentials, still used in this country. A purer grade of metal is undoubtedly produced by modern chemical methods, and the fine powder is now compressed dry instead of in the wet state.[1] The dry powder is subjected to a pressure of 5 tons/in.^{2} in an iron mould. The pressed ingot so obtained is heated gradually to a temperature of 1500° C. and then forged.

It will be convenient here to make a few general remarks about this process, and to compare it with the melting and casting process to be described later. The powder method obviates gas contamination and the picking up of impurities from refractories such as occur during melting, and it is, therefore, an important process where it is necessary to maintain the metal in the highest state of purity. It is not so convenient, however, as oxy-hydrogen blowpipe melting for general work, nor is the process suitable for dealing with scrap. For the production of alloys, also, the fusion method is more convenient.

A very thorough forging of sponge ingots above 1000° C. is necessary in order to get rid of porosity.[14] If this is not done the resultant sheet shows blisters. To give such a thorough forging, bars of large cross-section are necessary. If an attempt is made to produce too large a bar, the friction at the side of the mould becomes important, and the bar so produced is of varying density and either warps or fractures when heated or shows shrinkage holes at the least dense points, resulting in large blisters or double stock. The amount of metal, therefore, which can be accommodated in one ingot is restricted and is less than the amount which can be dealt with by melting methods.

It is said [1] that the sponge ingots, provided that they have been made from pure platinum handled in a proper manner, and have been sufficiently annealed, are physically and metallurgically superior to the usual unalloyed melted metal, and can be drawn or rolled perfectly satisfactorily. Under ordinary commercial working conditions the melted metal is found to be slightly harder than the pressed metal. The Brinell hardness figure (10 mm. ball : 500 kg. load) for annealed pressed sheet is 38–42, whereas for annealed cast sheet it is 40–44.

Blowpipe Melting and Casting.

In this process an oxy-hydrogen or oxy-coal-gas blowpipe is used for melting (the freezing point of platinum is 1773° C.). The nozzle of the blowpipe is made of platinum or platinum–iridium alloy, and the blowpipe may be water-cooled. The design of furnace is the familiar one suggested by Deville and Debray [13] shown in Fig. 1. It consists of two well-fitting lime blocks pressed within a supporting casing of sheet iron. The top is bored centrally to take the nozzle of the blowpipe while the bottom is scooped out to form a hearth. A slanting groove is made in the bottom half for the exit of the products of combustion during melting and is subsequently used for casting. The furnace is arranged to tilt in such a way that the position of the lip *D* does not alter, by having the lip in line with the two hinges *LL*. This is necessary because the dazzling whiteness of the stream of molten platinum makes it impossible to see the mould. The shape of the furnace can be easily modified to a rectangular or elliptical section if it is required to use more than one blowpipe for large quantities of metal.

Using the furnace shown in Fig. 1, Deville and Debray melted 11·6 kg. of platinum in 42 minutes, by means of oxygen and coal-gas. The consumption of oxygen was 1200 litres, and the loss of weight in metal (after allowing for a mechanical loss) was approximately 0·5 per cent. which corresponded closely to the amount of impurity present in the platinum.

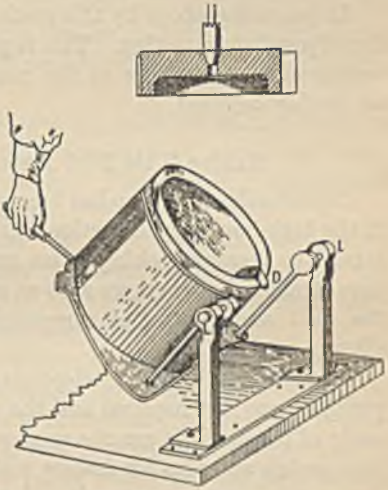

Fig. 1.—Deville and Debray's Furnace for Melting and Casting Platinum.

During melting, volatile metals were removed and other impurities such as silicon were oxidized and absorbed by the lime hearth. There is always this refining action during melting on lime, and the metal is kept molten until the refining action is completed. If highly pure metal is being melted, the gas consumption is less, and about 60 litres of oxygen are required for each kg. of platinum. Overheating of the metal should be avoided, since there is a sensible volatilization at very high temperatures. The metal is usually cast into a graphite mould. Care is taken not to have the mould too hot, since platinum readily takes up carbon, rendering the metal very brittle. Silica moulds may also be used,[14] particularly if a high gas content is suspected, since the slow cooling enables some gas to be liberated. The slow rate of cooling leads to the formation of large grains and more care is needed in working the ingot.

The process described above is still used to a considerable extent, and charges of up to 600 oz. troy (18·6 kg.) can be dealt with at one time. The blowpipe flame is kept slightly oxidizing to remove impurities and to prevent the platinum becoming contaminated with calcium, which would be produced at the very high temperature under reducing conditions. Under the usual working conditions very little calcium finds its way into the melt, and only traces can be found in the finished metal. The need for highly pure lime is apparent, and for melting the highest purity platinum by this method Heraeus has used calcium oxide made by igniting marble.[15]

Other types of refractory can be used for making small melts, but particular care must be taken in the case of magnesium oxide and alumina to keep the conditions oxidizing. These and other refractories will be discussed in the next section.

In preparing alloys by this method the added metals may be introduced just before casting. This is particularly desirable if the alloying constituents are volatile at the melting point of platinum or if they are readily oxidized.

Melting in the High-Frequency Induction Furnace.

Considerable attention has been given during recent years to melting in the high-frequency induction furnace. This process is commercially attractive because melting losses are low. In addition, there are the usual technical advantages such as ease of control of atmosphere above the melt and control of composition coupled with good mixing of alloys.

The choice of refractory depends on a number of factors such as the purity of product required and the conditions of melting.[16] Crucibles made of fused thoria are the most satisfactory for melting very highly pure metals and also for dealing with the highest melting point alloys. For general work, magnesia, alumina, zirconia, zirconium silicate, and lime are satisfactory. In the case of these latter materials very little contamination occurs if melting is done under oxidizing conditions, but under reducing conditions or *in vacuo* appreciable quantities of impurities may be picked up.

Some time ago Reeve[17] published a very interesting account of the melting and casting of platinum *in vacuo.* He used an alundum crucible lined with zirconia, and melted the platinum under a vacuum of 0·1–0·01 mm. of mercury. The mould made of graphite or nickel, was situated in a side arm of the apparatus just above the level of the top of the crucible, and the metal was cast *in vacuo* by tilting the furnace. Reeve found that ingots produced by this method were extremely sound and free from cavities. As an example, he mentioned that ingots of 0·5 in. in diameter and weighing 500 grm. could readily be drawn to 0·003 in.-diameter wire in one continuous length without breaking.

Arc melting is unsuitable for the platinum metals because of the ease with which carbon is picked up, and for the same reason the Arsem type of furnace cannot be used. Attempts to use the atomic hydrogen torch have also been unsatisfactory, no workable piece of metal having been produced by this method.[14]

Rolling and Drawing.

The pure metal is both soft and ductile, and ingots can be rolled down cold. It is usual, however, to commence by working hot at about 800° C., a rapid reduction being possible. The alloys also are worked hot, but the reductions are smaller. During this treatment the surface picks up iron, but this is readily removed by boiling hydrochloric acid.

Cold-working of sheet is carried out by 5–10 per cent. reductions in thickness per pass, the total reduction between annealings being determined by the nature of the material. The annealing temperature also varies with the nature of the alloy.

The temperatures recommended for short 5-minute anneals by Wise and Eash[18] are: chemically pure platinum 900°–1000° C.; 5 per cent. iridium alloy 1100°–1200° C.; 10 per cent. rhodium alloy 1100°–1200° C.; 20 per cent. iridium alloy 1200°–1400° C.

The ordinary wire-drawing operations do not require special comment, and by careful work platinum can be bare drawn down to 0·005 in. in diameter. To obtain finer wires it is necessary to resort to Wollaston's method.[19] Wollaston took a wire of 0·01 in. diameter fixed it centrally in a cylindrical mould $\frac{1}{3}$ in. in diameter, and cast molten silver round it. The ingot and core were then treated as a single rod and drawn down to the required size, when the silver could be removed by nitric acid. In this way Wollaston produced wires down to 0·00003 in. in diameter. The fine wire is not usually in one continuous length if the diameter is reduced beyond 0·0001 in.

Miscellaneous Operations.

Platinum sheet can be formed to various shapes by the usual cold-forming operations such as spinning, stamping, &c. Seamless tubing is made by forming a circular blank into a cup and then drawing this on a mandrel through dies to the required finished dimensions.

The pure metal is difficult to work on a lathe or punch press since the metal tends to drag. The iridium alloys are better in this respect.

The metal is joined either by welding or soldering. Hammer welding is possible at quite low temperatures. Pure gold is a very satisfactory solder, but for platinum jewellery where white solders are necessary a number of white alloys, containing palladium, gold and smaller amounts of platinum, silver, and copper, are used.

PALLADIUM.

Palladium is a very malleable and ductile metal and can be readily fused, cast, and mechanically worked by the methods already described for platinum.

Wollaston, the discoverer of palladium, was the first to describe a method for converting sponge into a malleable piece of metal.[2] In principle the method consisted of making a low melting point fusible mass by the addition of sulphur, just as arsenic was used in the case of platinum. The sulphur was roasted off in a series of stages and the ingot gradually consolidated. In the light of modern knowledge this process could not give highly ductile or highly pure metal.

With the development of the oxy-hydrogen blowpipe it became quite easy to melt palladium in quantity since the melting point is 1553° C., some 220° C. below that of platinum. Palladium is usually melted on a lime hearth and cast into graphite moulds. Various precautions are necessary to prevent gas absorption. Palladium is usually regarded as a metal with a high affinity for hydrogen, and, while this is true at low temperatures, in a state of fusion it readily dissolves oxygen. This gas is largely liberated during solidification and the metal may swell to twice its original volume. As in the case of silver, no oxide phase can be detected microscopically in the solidified metal. By suitable control of flame composition, oxygen absorption can be largely eliminated. During melting there may be an appreciable loss by volatilization, so that quite apart from other considerations the metal should not be overheated.

Palladium can be readily melted with an oxy-coal-gas flame, but there is a definite danger that sulphur contamination will occur. In this respect palladium is more sensitive than platinum. A very small content of sulphur leads to the formation of a brittle compound Pd_4S [20] which usually separates along the grain boundaries. This compound is insoluble in palladium and melts at 785° C. Even 0·02 per cent. of sulphur leads to hot-shortness and at room temperatures reduces the ductility of the metal.[21]

For melting in the high-frequency induction furnace, the refractories mentioned in the case of platinum give good service. Graphite crucibles cannot be used since carbon is so readily picked up.

Palladium and its alloys are worked by methods analogous to those described for platinum, and do not call for detailed description. The pure metal tends to work-harden rather more rapidly than platinum. The extraordinary ductility of pure palladium is demonstrated by the fact that it can be beaten out into leaf in the same way as gold.

A satisfactory annealing treatment for pure palladium consists in heating in air to 800°–900° C. for 5 minutes.[18] Annealing at temperatures above 1000° C. results in a pronounced decrease in elongation owing to the onset of marked selective grain-growth. Below 1000° C. the grain-size remains very uniform. A slight surface discolouration occurs during cooling owing to the formation of a thin palladium oxide film. If this is objected to, the metal may be heated and cooled in nitrogen.

Palladium alloyed with other metals of the platinum group, *e.g.* rhodium and ruthenium, requires a higher annealing temperature. With 5 per cent. of added metals the annealing temperature is increased to 1000°–1100° C.[18]

RHODIUM.

Deville and Debray [13] melted rhodium on a lime hearth with an oxy-hydrogen blowpipe and found its density to be 12·1. When very pure they found it malleable and ductile.

At various times rhodium has been melted, cast, and mechanically worked. For instance, Grüneisen [22] measured the density of a rod of rhodium 27 cm. long and 1·6 cm. in diameter, which had been cast by Heraeus.

Rose [23] measured the density of a piece of rhodium, made by Messrs. Johnson, Matthey and Company, which had been forged from sponge and not melted.

It is clear from the above references that rhodium may be worked starting either with sintered sponge or a cast ingot.

More recently Swanger [24] and Sivil [14] have described more systematically the problems involved in the mechanical working of melted rhodium. High-purity rhodium is essential for ease of working. The melting point of rhodium (1966° C.) is considerably higher than that of platinum (1773° C.), which makes it somewhat more difficult to melt with the oxy-hydrogen flame. The rhodium meal is compressed into pellets in a steel mould before melting, and the pellets are melted with a "hard" (oxygen-rich) flame. During melting, oxygen is absorbed in considerable quantity, and the metal tends to spit and sprout during solidification. If, however, the supply of oxygen to the torch is reduced when the metal is molten, spitting can be largely obviated, and the metal made to freeze with a fairly smooth surface.

Rhodium can be melted readily in the high-frequency induction furnace. Thorium oxide crucibles are the most satisfactory though with care zirconium oxide crucibles can be used.

Melting in air leads to the same troubles due to dissolution of oxygen as in oxy-hydrogen melting, but if the metal is frozen slowly forgeable ingots are obtained. If melted *in vacuo* (about 1 mm. of mercury pressure) a smooth silver-white surface is obtained. In the case of small vacuum-fused ingots, large shrinkage cavities make forging difficult, hence it may be necessary to remelt on a lime hearth.

It should be noted that molten rhodium has a considerable affinity for carbon, a property shared by the other metals of the group. Rhodium melted in an Acheson graphite crucible increased in weight by 1·8 per cent.[24] The button was very hard and brittle and could not be forged either hot or cold. The colour of the metal was noticeably darker than that of pure rhodium.

The forging or swaging of rhodium ingots does not present any unusual difficulties. They cannot be forged at room temperature, but become quite malleable above a red heat.

For the production of wire the ingots may be hand-forged at about 1100° C. to bars of a suitable size for swaging. The bars are heated in an oxy-coal-gas or oxy-hydrogen flame and enter the swaging dies at a temperature of about 1000° C. Wire produced by swaging above 800° C. is not ductile at room temperature, the metal having a coarse-grained, equiaxed structure. By drawing through tungsten carbide dies at gradually decreasing temperatures, a fibrous structure is developed until the metal can eventually be drawn at room temperature. In this way wire down to 0·004 in. diameter has been made.

Rhodium sheet is made by hot-rolling to a thickness of about 0·030 in. at which size it becomes sufficiently ductile for cold-rolling.[14] During the cold-work frequent annealings at high temperatures (about 1200° C.) are necessary. The annealed material hardens rapidly, and by far the greatest reduction occurs during the first pass. Foil has been produced in sheets 10 in. × 24 in. × 0·001 in.

After annealing at 1200° C., the Brinell hardness of rhodium is 101.[24] The metal does not machine readily, however. Great difficulty was experienced in drilling sight holes in specimens used for melting point determinations.

IRIDIUM.

No systematic account of the working of iridium has been given in the literature. The metal is, in normal circumstances, so rare and valuable that only the precious metal refiners have had opportunities to investigate its properties.

Early attempts to fuse iridium were unsuccessful, but from 1837 onwards it was known that a fusible product could be obtained by adding phosphorus to very hot iridium sponge.[25] This recalls the early use of arsenic in the metallurgy of platinum and of sulphur in the metallurgy of palladium. The phosphorus process was later elaborated by Holland for the manufacture of iridium alloy grains suitable for tipping fountain pens.[26] The fusible alloy contains about 7 per cent. of phosphorus, and can be cast into thin plates, which are very brittle.

Deville and Debray [13] melted iridium with an oxy-hydrogen blowpipe. The operation was not easy, and they used 200–300 litres of oxygen in melting 25 grm. of metal. They were unable to melt iridium with the oxy-coal-gas blowpipe. At room temperature the ingot broke under impact, disclosing a rather coarse, crystalline structure, but at a white heat they were able to forge it.

In a letter [25] to *The Chemical News* in 1885, Messrs. Johnson, Matthey and Company stated that for many years they had succeeded in fusing and working pure iridium into rods and wires, and in 1908 Crookes described [27] the use of pure iridium crucibles for analytical work.

Sivil [14] states that iridium can be worked in a way similar to the working of rhodium, but with greater difficulty. Cold-working is quite impossible, the material crumbling to small fragments after a very small reduction. This limited workability is attained only by iridium of high purity, the presence of minute amounts of other metals, including platinum metals, reducing the malleability to zero.

It is clear that iridium can best be worked at a white heat. As a starting point either sintered sponge or fused metal may be used. In connection with the melting of iridium it should be noted that the melting point (2454° C.) [28] is very close to the maximum temperature of the oxy-hydrogen flame. Iridium can be more readily melted with the oxy-acetylene blowpipe and, provided that care is taken to adjust the flame composition, the ingot so produced is quite malleable at a white heat. The dissolution of carbon and oxygen during melting should be avoided as in the case of the other metals of the group.

The high-frequency induction furnace was used by Henning and Wensel [28] for melting iridium during the determination of the freezing point of pure iridium. Fused thoria crucibles were used, and were found to be quite satisfactory. These authors mentioned that iridium is very difficult to machine. Tungsten carbide tipped drills were used for making a slight hole in the ingot, but even so it was very laborious work.

The annealing temperature of iridium has not been determined. In determining the lattice parameter, using filings, Owen and Yates[29] found that after 240 hrs. at 600° C. some of the lines were well enough resolved for measurement.

Very little information is available about the working of iridium-rich alloys. Heraeus[30] states that the addition of more than 10 per cent. rhodium has a beneficial effect on the working properties of iridium. Swanger[31] records the use of a 72 per cent. iridium : 28 per cent. platinum alloy crucible for the study of phase equilibria of oxide systems at 2000° C.

RUTHENIUM AND OSMIUM.

The four metals previously described all belong to the cubic system and can be worked under suitable conditions. Ruthenium and osmium possess the hexagonal structure, and very little indeed is known about their working properties. They are inherently more difficult to fabricate than those metals of the group having a cubic structure, they have higher freezing points, and possess the undesirable property of forming very volatile oxides, that of osmium being very poisonous. These factors coupled with the rareness of the metals are responsible for the present lack of knowledge concerning them.

The freezing points of the metals are not known, but the difficulty of melting the metals with a blowpipe indicates that ruthenium melts at a somewhat higher temperature than iridium, while osmium is the most infusible metal of the group. Deville and Debray[13] melted very small quantities of ruthenium with an oxy-hydrogen torch, but were unable to fuse osmium. During the melting of ruthenium there was a considerable loss of metal as ruthenium dioxide and tetroxide and on freezing it spitted like rhodium. It was very hard and brittle. Osmium sintered on heating to a temperature estimated to be equivalent to the melting point of rhodium (1966° C.), and the metal had a pronounced metallic lustre showing a bluish tinge.

On melting ruthenium in a graphite crucible in a high-frequency induction furnace, it dissolves about 1·2 per cent. of carbon, thus conforming to the general behaviour of the platinum metals.

There seems no definite reason to exclude the possibility of working these metals, and it is thought that an attempt using modern powder methods might prove successful, provided that working was done at a sufficiently high temperature. There are indications that sintered ruthenium powder is forgeable at very high temperatures.

As regards the annealing temperatures of these metals, we have the evidence of Owen, Pickup, and Roberts[32] that annealing at 800° C.

for 6 hrs. failed to remove the distortion from ruthenium, but after 4 hrs. at 1000° C. it gave quite satisfactory X-ray photographs. Osmium which had been crushed and ground in an agate mortar required 5 hrs.' annealing at 1000° C. before well-defined lines were recorded. The annealing temperatures in the accepted sense are probably above 1000° C.

Osmium filaments which were at one time used in incandescent lamps were formed from powdered osmium held together with a bonding material which was burnt out before the lamp was used. This method gave very fragile filaments.

SOME PROPERTIES AND USES.

Physical Properties.

The physical properties of the platinum metals are, as might be expected, very dependent on purity; consequently those uses of the metals which depend on specific physical properties demand products of extremely high purity.

In Germany an attempt has been made to draw up specifications for the various grades of platinum used in industry. Five grades of purity are recognized, as follows:

Platinum A. Physically pure platinum with a minimum standard of purity of 99·99 per cent. Used for thermocouples and resistance pyrometers.

Platinum B. Chemically pure platinum with a minimum standard of purity of 99·90 per cent. Used for electrodes.

Platinum C. Utensil platinum containing up to 0·3 per cent. iridium, other metals not exceeding 0·1 per cent. Minimum platinum content 99·7 per cent.

Platinum D. Technically pure platinum containing at least 99 per cent. platinum and not less than 99·5 per cent. of platinum metals.

Platinum E. Jewellery platinum containing not less than 95 per cent. platinum.

It should be noted that the highest quality of platinum is designated "physically pure" platinum, and is used where specific electrical properties are required. The purity of this grade of platinum is best determined either by a thermoelectric method or by measurement of the temperature coefficient of resistance. The thermoelectric method is stated to be more sensitive even than spectroscopic tests.[33]

At the Bureau of Standards (U.S.A.) each batch of material is tested against a special standard (Pt 27) which contains less than 1 part in 10^6 of impurity. In some cases the thermal e.m.f. against the standard Pt 27 has been found to be as much as 50 microvolts at 1200° C. when spectroscopic tests failed to show any impurity. The smallest amount of impurity which has been detected spectroscopically corresponds to a change in thermal e.m.f. at 1200° C. of about 20 microvolts. In general, small amounts of impurity make it positive thermoelectrically to pure platinum.

Dissolved gases as well as metallic impurities have a marked effect on the thermoelectric properties. Sivil[14] records the case of a sample containing dissolved oxygen whose thermal e.m.f. was reduced from 4 microvolts to 1 microvolt by heating *in vacuo*. He also states that platinum melted in the atomic hydrogen torch gave at 1200° C. an e.m.f. of 750 microvolts against a platinum standard.

The temperature coefficient of resistance between 0° and 100° C. is also a sensitive indication of purity. Physically pure platinum should have a value of the ratio $\frac{R_{100^\circ}}{R_{0^\circ}}$ of at least 1·390. The presence of 0·1 per cent. palladium will lower the value of this ratio to about 1·379 while 0·1 per cent. iron lowers it to 1·355.[34] Gerlach[15] has shown that the purest form of platinum prepared by Heraeus has a residual resistance between 4° and 1·35° A. scarcely 0·0003 of the resistance at 0° C.

In the determination of the freezing point of platinum at the National Physical Laboratory, using fused thoria crucibles, Schofield[35] measured the value of $\frac{R_{100^\circ}}{R_{0^\circ}}$ before and after the freezing point determinations. In one example given the value decreased from 1·3919 to 1·3911, showing that very little contamination occurred.

Physical methods for testing the purity of the other platinum metals are not so well developed.

Some of the more important physical properties are given in Table II, and the most reliable data given for each metal.

Platinum on account of its permanence and stability has been proved to be the ideal material for constructing standards of mass and length. For instance, in Great Britain we have to-day two legal standards of mass, the pound avoirdupois which is the mass of a certain piece of platinum marked "P.S. 1844 lb." and the kilogram which is the mass of a certain lump of platinum, preserved in Paris, called the "Kilogram des Archives." The inconsistencies of base metal standards such as brass and gun-metal were clearly shown when it became necessary

TABLE II.—*Physical Properties of the Metals of the Platinum Group.*

Property.	Platinum.	Iridium.	Osmium.	Palladium.	Rhodium.	Ruthenium.	Units.
Atomic number	78	77	76	46	45	44	
Atomic weight	195·23	193·1	191·5	106·7	102·91	101·7	0 = 16
Specific gravity	21·40	22·42	22·48	12·16	12·41	12·20	Grms. per c.c. at 20° C.
Melting point	1773·5°±1°	2454° ± 3°	Higher than ruthenium	1553° ± 2°	1966° ± 3°	Higher than iridium	° C.
Boiling point	4300°	>4800°	>5300°	2200°	>2500°	>2700°	° C.
Specific heat :							
0° C.	0·0316	...	...	0·0584	...	...	Calories per grm.
0°–100° C.	0·0319	0·032	0·031	0·0590	0·058	0·061	
Temperature coeff. of linear expansion :							
20° C.	8·9	6·5	...	11·7	...	...	$\times 10^{-6}$ per ° C.
40° C.	8·99	...	6·6	...	8·5	9·6	
Thermal conductivity : 18° C.	0·166	0·141	...	0·168	0·210	...	Calories cm.$^{-1}$ sec.$^{-1}$ temp.$^{-1}$
Specific resistance, annealed : 0° C.	9·97	5·33	9·5	10·78	4·3	14·47	ohm-cm. $\times 10^{-6}$
Temperature coeff. of resistance :							
Hard	0·003917	...	...	0·0037	...	...	0°–100° C. per ° C.
Annealed	0·003923	...	...	...	0·00457	...	
Young's modulus	16·8	51·5	...	11·3	27·5	...	Dynes per sq. cm. $\times 10^{11}$
Structure type	Face-centred cubic	Face-centred cubic	Hexagonal close-packed	Face-centred cubic	Face-centred cubic	Hexagonal close-packed	
Unit cell :							
a_0	3·9158	3·8312	2·7304	3·8824	3·7957	2·6987	Angstrom units
c_0/a_0	...	...	1·5785	...	...	1·5833	

to replace the brass standard pound lost in the Houses of Parliament fire in 1834, and since that time platinum has been used.[36]

The permanence of platinum has also been shown [37] in a remarkable way by the constancy of the B.A. Standards of resistance made of this metal, over the period 1865–1932. The temperature coefficient of resistance of the standard platinum coils is low (308×10^{-5}) compared with the value of modern high-purity platinum (392×10^{-5}), yet these coils have remained absolutely constant.

The high-temperature properties of the platinum metals are of some general interest. For most high-temperature uses it is important that they should remain either of constant weight or of constant composition, and mechanical strength is usually a secondary consideration.

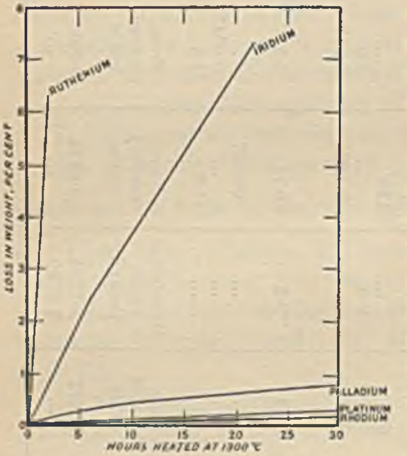

FIG. 2.—Volatility of Platinum Metals in Air at 1300° C. Results of Sir William Crookes.

Crookes [38] carried out some experiments on the loss in weight of the pure platinum metals when heated in air at 900° and 1300° C. His results for 1300° C. are shown in Fig. 2. The least loss in weight is shown by rhodium, and this is closely followed by platinum. Palladium shows somewhat higher losses, while iridium and ruthenium lose weight very rapidly. Osmium was not included, presumably because of the poisonous nature of the volatile tetroxide, but it would have given by far the highest weight loss. At 900° C. rhodium and platinum showed practically no weight loss even after prolonged heating, but palladium lost 0·18 per cent. in 30 hrs. and iridium 0·09 per cent. in 22 hrs.

Carter [39] has indicated that weight losses for wires heated electrically are greater than for wires heated externally, and that rhodium is more volatile than platinum at temperatures above 1300° C.

In analytical work the constancy in weight of platinum crucibles after ignition is essential, and this point has been carefully examined by the Bureau of Standards.[40, 41]

Platinum crucibles are not often made of "physically pure" metal, and there may be present small amounts of iridium and rhodium and traces of iron. Below 900° C. the loss of weight on heating in all cases is negligible, and at lower temperatures there may even be a slight gain in weight due to the iron content diffusing to the surface and oxidizing. At higher temperatures there is a definite loss in all cases as shown in Table III.

TABLE III.—*Approximate Loss in Weight mg./*100 *cm.*^{2}*/hr. for Platinum Nearly Free from Iron.*

Temperature, ° C.	Platinum containing:			
	Pure Platinum.	1% Iridium.	2·5% Iridium.	8% Rhodium.
900 or less . .	0	0	0	0
1000 . . .	0·08	0·30	0·57	0·07
1200 . . .	0·81	1·2	2·5	0·54

Above 900° C., the loss in weight for iridium-containing platinum is very much greater than that of pure platinum, and increases with the iridium content and with temperature. Rhodium-containing material shows lower weight losses than pure platinum at all temperatures above 900° C. These observations indicate the desirability of using platinum free from all metals other than rhodium. The addition of rhodium is beneficial in that it lowers weight losses and moreover gives a more robust material. For general laboratory use the Bureau of Standards recommends a rhodium content of 3–3·5 per cent. A further example may be taken from the use of the 10 per cent. rhodium–platinum alloy gauzes for the catalytic oxidation of ammonia, where weight losses are again lower than for the pure platinum gauzes.

In thermocouple work constancy of composition is important and the above remarks indicate why the platinum–rhodium alloys are superior to the platinum–iridium alloys.

The losses in weight of the platinum metals (other than palladium) on heating in air are probably due to the formation of volatile oxides. The evidence in the case of osmium, ruthenium, and iridium is quite definite, but it has often been doubted that the loss in weight of platinum and rhodium is due to the formation of volatile oxides. In the case of these two latter metals there is a negligible loss *in vacuo* or in hydrogen and nitrogen, and in an oxygen atmosphere the loss is proportional to the partial pressure of oxygen. This seems to be decisive evidence against a true volatilization loss, and in favour of the view that volatile oxides are formed. Palladium shows a definite weight loss *in vacuo* and in the case of this metal true volatilization probably occurs.

The use of platinum for the resistance windings of high-temperature laboratory furnaces is well known. Pure platinum has some disadvantages, but it has been found that the alloy 80 per cent. platinum : 20 per cent. rhodium is much more satisfactory.[31] This alloy has a higher melting point than platinum, a higher specific resistance, lower temperature coefficient of resistance, lower density, lower rate of volatilization, and less tendency to become brittle due to crystal growth.

Other physical properties of the metals have led to important uses, some of which will be mentioned briefly. The high reflectivity and silvery-white appearance of rhodium coupled with its nobility has led to the use of thin rhodium electrodeposits for the protection against tarnish of sterling silver ware, reflectors, and a multitude of trinkets made by the jewellery trade. The high density of platinum and platinum–iridium alloys coupled with high corrosion-resistance and good workability makes them suitable materials for constructing radium needles and tubes for the medical profession. Finally, the similar thermal expansion coefficients of platinum and glass led to the widespread use of platinum as a lead-in material.

Mechanical Properties.

The mechanical properties of the two very ductile metals of the group, platinum and palladium, are known fairly completely, but information about the other four metals is incomplete. Such data as is available is presented in Table IV.

TABLE IV.—*Mechanical Properties of Platinum Metals.*

	Platinum.	Iridium.	Osmium.	Palladium.	Rhodium.	Ruthenium.	Units.
Ultimate strength :							
Hard * . .	16·0	...	...	20·9	...	...	Tons/in.^{2}
Annealed . .	9·8–10·7	...	...	13·4	...	...	0·05 in. wire
Proportional limit :							
Hard * . .	12·0	...	...	14·2	...	...	Tons/in.^{2}
Annealed . .	2·4–4·5	...	...	2·2	...	...	0·05 in. wire
Elongation :							
Hard * . .	2·5	...	...	1·5	...	...	Per cent. in 2 in.
Annealed . .	21–34	...	...	39–41	...	...	0·05 in. wire
Reduction of area :							
Hard * . .	95	...	...	91·5	...	...	Per cent.
Annealed . .	92	...	...	89–92	...	...	0·05 in. wire
Erichsen ductility :							
Hard . .	7·8	...	...	7·6	...	...	mm.
Annealed . .	12·2	...	...	12·0	...	...	
Hardness :							
Cast . .	50	172	350	52	101	220	H 2/30/120 except Osmium which is a Vickers number.
Hard . .	97	...	...	109	...	...	
Annealed . .	47	...	...	49	101	...	

* 50 per cent. reduction after annealing.

Attention is drawn to the great hardness of osmium and ruthenium.

The most important platinum alloys are those used for the manufacture of fine jewellery. Owing to the difficulties of assay of platinum alloys, it has not yet been found possible to evolve a scheme for hall-marking platinum jewellery, and at the present time most manufacturers adhere to a 950 standard which has been agreed to by all the important European countries. Iridium counts as platinum in this 950 standard. Base metals may be present in amounts up to 5 per cent. and two commonly used alloys contain 3 per cent. and 4·5 per cent. of copper, respectively. These two alloys have adequate hardness and strength for most purposes, and have good working properties. The use of copper for hardening platinum follows the long-established trade custom of hardening the two precious metals gold and silver. In the case of platinum the use of base metals is quite unnecessary, since the quality of platinum goods could best be maintained by the use of alloys hardened solely with the other platinum metals such as iridium, rhodium, and ruthenium. These alloys are superior in several respects to the copper-containing alloys. The highest-quality platinum jewellery is made from 5 per cent. and 10 per cent. iridio-platinum. Other very high-grade alloys can be made with the addition of 5 per cent. rhodium plus ruthenium, the ruthenium content being varied according to the hardness required.

A general idea of the properties of the various platinum alloys can be obtained from Table V, which records the Brinell hardness values of the fully-annealed materials.

TABLE V.—*Brinell Hardness of Annealed Platinum Alloys.*

	Weight Percentage of Alloying Metal.			
	5 Per Cent.	10 Per Cent.	15 Per Cent.	20 Per Cent.
Iridium	80	105	140	175
Rhodium	80	85	88	91
Ruthenium	105	158	Alloy unworkable	Alloy unworkable
Palladium	65	70	73	75
Copper	110	135	142	145

More detailed information concerning certain important alloys is given in Table VI.

A similar range of palladium alloys may be prepared with similar strength characteristics. Iridium, rhodium, and ruthenium harden palladium to a rather less extent than they harden platinum for equivalent additions. Palladium alloys were largely used for jewellery purposes during the Great War when platinum was scarce. In more normal times this use has largely disappeared, though on account of appearance and working properties they are much superior to "white gold" alloys.

TABLE VI.—*Mechanical Properties of Platinum Alloys Cold-Drawn (50 Per Cent. Reduction) and after Annealing.*[18]

Material.	Condition of Alloy.	Proportional Limit. Tons/in.^{2}.	Ultimate Strength. Tons/in.^{2}.	Elongation, Per Cent. on 2 in.	Reduction of Area, Per Cent.
5% Ir : 95% Pt	Hard	23·9	30·8	2·0	92
	Annealed	8·0–10·3	17·4–18·5	22–32	95
10% Ir : 90% Pt	Hard	24·2	36·8	2·5	94
	Annealed	13·4–16·1	23·7–24·6	25–27	95
20% Ir : 80% Pt	Hard	44·95	62·6	2·5	85
	Annealed	26·4–27·7	41·5–45·5	20–21	89
10% Rh : 90% Pt	Hard	24·8	37·6	3·0	90
	Annealed	7·6–9·8	21·0–21·9	25–37	94
4% Ru : 1% Rh : 95% Pt	Hard	22·6	38·0	3·5	87
	Annealed	8·0–12·5	26·8–27·7	19–33	93
5% Ni : 95% Pt	Hard	31·2	46·0	2·0	84
	Annealed	14·7	29·0	23·5	93
3% Cu : 95% Pt	Hard	21·6	36·1	2·5	84
	Annealed	7·6–9·8	23·7–25·9	26–34	91
4·5% Cu : 95·5% Pt	Hard	24·2	40·9	2·5	64
	Annealed	9·4–11·2	27·7–30·4	24–28	86

After jewellery the next most important group of alloys are those used in dentistry, and here platinum and palladium are alloyed with the metals of the coinage group. A sub-division of the alloys into wrought and casting alloys is convenient. The wrought alloys are used in the form of circular blanks for swaged plates and in the form of wire and thin bands for correcting malformations of the mouth. Two of the most useful alloys for swaged plates are "dental alloy" of the composition platinum 30 : silver 70 per cent. and the alloy palladium 50 : silver 50 per cent. The high-strength wires and bands used for correcting malformations of the mouth are of complex and varied composition and may contain up to 30 per cent. of platinum and/or palladium, the remainder being gold, silver, and copper. These alloys are very responsive to heat-treatment, as shown by the comprehensive work of Wise, Crowell, and Eash.[42, 43] The transformations responsible for hardening are similar to those occurring in the systems gold–copper, palladium–copper, and platinum–copper in the neighbourhood of the 50 atomic per cent. alloys. In the fully heat-treated condition such alloys may show ultimate strength values of 65–80 tons/in.^{2}.

Dental casting alloys should not have a melting point greater than

1050° C., hence the amount of platinum and/or palladium which may be added is restricted. Alloys in the 18 carat range may contain up to 12–15 per cent. platinum and/or palladium, but cheaper alloys of approximately 9 carat quality may contain up to 25 per cent. of palladium. The addition of the platinum metals increases the response to heat-treatment, and the alloys are white in colour and are, therefore, inconspicuous in the mouth. Most of the casting alloys can be hardened by simple heat-treatment, and in this state regularly develop an ultimate strength [44] of 45–50 tons/in.^{2}.

Various other special platinum metal containing alloys are fabricated to meet the special needs of industry. The alloy platinum 95 : nickel 5 per cent. is particularly suitable for the filaments used in amplifying tubes in communication systems. A large variety of platinum metal contact alloys are used where conditions are severe or where great reliability is required. Aeroplane and automobile magneto contacts, for instance, are made of 15–25 per cent. iridio-platinum. File-hard alloys containing relatively large amounts of the " by-metals " are used on relays where contact pressures are very low. The alloy palladium 60 : copper 40 per cent. is finding many uses among which may be mentioned telegraph relays. A brief reference should also be made to the very hard alloys containing varying proportions of iridium, osmium, and ruthenium for fountain pen points.

Chemical Properties.

The catalytic and corrosion-resistance properties of the platinum metals lead to their extensive use in the chemical industries.

As regards catalytic reactions brief mention might be made of the use of gauzes of the alloy rhodium 10 : platinum 90 per cent. for the oxidation of ammonia in the production of nitric acid, and the use of finely divided platinum on a suitable carrier for the contact process of sulphuric acid manufacture.

The corrosion-resistance of the platinum metals is made use of in chemical processes where the conditions are severe. As examples there may be mentioned spinnerets used in the artificial silk industry and anodes used for the manufacture of per-salts and oxidizing agents.

ACKNOWLEDGMENTS.

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REFERENCES.

[1] D. McDonald, *Chem. and Ind.*, 1931, **9**, 1031–1041.
[2] W. H. Wollaston, *Phil. Trans. Roy. Soc.*, 1829, **119**, 1.
[3] Anon., *Engineering*, 1930, **130**, 349–351, 422–425, 454–457.
[4] C. Langer and C. Johnson, *Trans. Canad. Inst. Min. Met.*, 1927, **30**, 903–908.
[5] R. L. Peck, *Mining World*, 1930, **1**, 632.
[6] A. R. Powell and E. C. Deering, Brit. Patent 316,063.
[7] T. Scheffer, *Handl. Akad. Stockholm*, 1751, **14**, 275.
[8] —— Achard, *Mem. Akad. Wiss. Berlin*, **1779**.
[9] R. Knight, *Phil. Mag.*, 1800, **6**, 1.
[10] A. Tilloch, *Phil. Mag.*, 1805, **21**, 188.
[11] R. Hare, *J. Franklin Inst.*, 1847, [iii], **14**, 128.
[12] —— Macquer and —— Baumé, *Mém. Acad. Sci. Paris*, **1758**, 119.
[13] H. St.-C. Deville and H. Debray, *Ann. Chim. Physique*, 1859, [iii], **56**, 385.
[14] C. S. Sivil, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, **1931**, 246.
[15] W. Gerlach and E. Riedl, *Physikal. Z.*, 1933, **34**, 516 (Addition by Feussner of Heraeus).
[16] W. H. Swanger and F. R. Caldwell, *Bur. Stand. J. Research*, 1931, **6**, 1131.
[17] H. T. Reeve, *Metals and Alloys*, 1931, **2**, 184.
[18] E. M. Wise and J. T. Eash, *Trans. Amer. Inst. Min. Met. Eng.*, 1935, **117**, 313.
[19] W. H. Wollaston, *Phil. Trans. Roy. Soc.*, 1813, **103**, 114.
[20] F. Weibke and J. Laar, *Z. anorg. Chem.*, 1935, **224**, 49.
[21] A. Jedele, *Z. Metallkunde*, 1935, **27**, 271.
[22] E. Grüneisen, *Ann. Physik*, 1907, [iv], **22**, 811.
[23] Sir T. K. Rose, *J. Inst. Metals*, 1925, **33**, 109.
[24] W. H. Swanger, *Bur. Stand. J. Research*, 1929, **3**, 1029.
[25] Messrs. Johnson Matthey, *Chem. News*, 1885, **51**, 71.
[26] N. W. Perry, *Chem. News*, 1885, **51**, 1–5, 19–21, 31–33.
[27] Sir W. Crookes, *Proc. Roy. Soc.*, 1908, [A], **80**, 833.
[28] F. Henning and H. T. Wensel, *Bur. Stand. J. Research*, 1933, **10**, 809.
[29] E. A. Owen and E. L. Yates, *Phil. Mag.*, 1933, [vii], **15**, 472.
[30] W. C. Heraeus, G.m.b.H., German Patent No. 561,121.
[31] W. H. Swanger, A.S.T.M. and A.S.M.E. Symposium on the Effect of Temperature on Metals, **1931**, p. 610.
[32] E. A. Owen, L. Pickup, and I. O. Roberts, *Z. Krist.*, 1935, (A), **91**, 70.
[33] F. R. Caldwell, *Bur. Stand. J. Research*, 1933, **10**, 373.
[34] W. Goedecke, *Festschrift zum fünfzigjährigen Bestehen der Platinschmelze G. Siebert G.m.b.H. Hanau*, **1931**, 72.
[35] F. H. Schofield, *Proc. Roy. Soc.*, 1934, [A], **146**, 792.
[36] Sir R. T. Glazebrook, *Proc. Phys. Soc. (Lond.)*, 1931, **43**, 412.
[37] Sir R. T. Glazebrook and L. Hartshorn, *Phil. Mag.*, 1932, [vii], **14**, 666.
[38] Sir W. Crookes, *Proc. Roy. Soc.*, 1911–1912, [A], **86**, 461.
[39] F. E. Carter. See discussion on paper Ref. No. 31 by W. H. Swanger.
[40] G. K. Burgess and P. D. Sale, *U.S. Bur. Stand. Sci. Paper* No. 254, 1915.
[41] G. K. Burgess and R. G. Waltenburg, *U.S. Bur. Stand. Sci. Paper* No. **280**, 1916.
[42] E. M. Wise, W. S. Crowell, and J. T. Eash, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 363.
[43] E. M. Wise and J. T. Eash, *Trans. Amer. Inst. Min. Met. Eng.*, 1933, **104**, 276.
[44] A. R. Raper and E. C. Rhodes, *Brit. Dental J.*, 1935, **58**, 349.

DISCUSSION.

(*Condensed.*)

The President: This paper marks a slight departure from our usual traditions, inasmuch as normally we regard the Institute's proceedings as a vehicle for the conveyance of the results of original research work. However, from time to time we have departed from that idea in order to include what we consider valuable reviews of work on technical and industrial operations. The present paper belongs to that class; it gathers together what the Publication Committee deem to be a valuable collection of data in a convenient form.

M. J. Dhavernas * (Member): Some of the work done by the Centre d'Information du Nickel in connection with the application of palladium in the form of thin beaten leaves may be of interest to members. The leaves or foils have been affixed to leather and various fabrics and have been used in bookbinding. Palladium does not tarnish like silver and has a "warmer" colour than platinum. Palladium "leaf," hot stamped on fabrics, has also given quite interesting results, and really beautiful designs have been obtained. Palladium "gilt" picture frames have also been tried and found very good. For making outside signs the success of palladium has not been complete. In some cases a slight tarnish has developed, probably due to the sulphurous fumes in the atmosphere. No doubt other applications of beaten palladium "leaf" will be found and developed. The tonnage involved is, of course, small and will never reach a high figure.

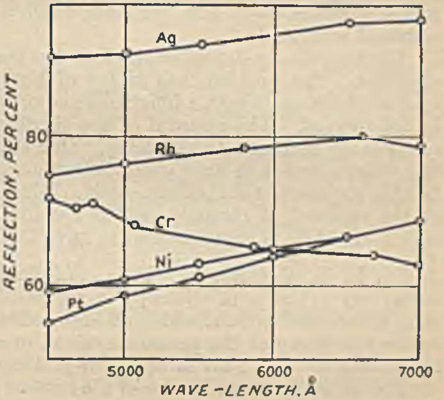

Fig. A. (After Grube and Kesting.)

Dr. W. H. Heraeus † (Member): Mr. Atkinson has mentioned in his paper the various properties of the platinum group metals. With the great importance attained by rhodium since the increased production of the International Nickel Company from their Canadian mines, there has arisen an urgent need for finding new uses for the metal. It has been found that, in addition to its outstanding chemical properties, rhodium has also valuable physical properties; thus, it has an extraordinarily high reflective power in the visible region, and recent work has shown that it can be electrolytically deposited on mirror surfaces. Fig. A shows the reflective power of various metals for light of different wave-lengths; the values vary as follows:

	Per cent.
Silver	93–98
Rhodium	75–80
Platinum	55–68
Nickel	58–68
Chromium	72–63 (decreasing with increasing wave-length)

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This discovery has resulted in wide applications of electrolytically-coated rhodium mirrors in technology, since they not only have a high reflective power but also are highly resistant to oxidation. The curves in the figure are taken from the article by Grube and Kesting.*

Dr. M. BALLAY † (Member): I had the pleasure a year ago of visiting the precious metals refinery at Acton, under the guidance of the authors of the present paper. For a metallurgist accustomed to less noble metals the impression is that of an enormous laboratory, utilizing laboratory apparatus and methods. One wonders if it is really a metallurgical works until one sees the safe that contains the metals, and then one recalls the definition that metallurgy is the art of transforming ores into bank-notes, and that this definition is not concerned with the volume of metal produced but with its value. Regarded from that point of view, there can be no doubt that Acton is undoubtedly an important metallurgical centre.

Palladium, which is cheaper than platinum or rhodium, is not entirely resistant to corrosion, but behaves well in certain atmospheres; palladium "leaf" has been used for outdoor signs and has stood up well. French workers in precious metals have succeeded quite satisfactorily in the delicate work of producing palladium "leaf." They have experienced no difficulty in making leaves weighing 10–20 grm. per 1000, which is of the order of thickness usually obtained with gold.

Electrolytically-deposited rhodium has been used to prevent the tarnishing of silver. The problem has arisen of how to remove the rhodium in the case of pieces dealt with a long time ago or where there has been some failure in the process. The removal of the rhodium is very difficult. Rhodium is remarkably resistant to corrosion. One cannot have everything, however; one cannot expect to have good corrosion-resistance and at the same time to be able to remove the rhodium easily. The authors have studied the problem of the removal of rhodium, which has limited its electrolytic applications, and it would be of great interest to have their conclusions.

Dr. L. H. CALLENDAR,‡ B.Sc., A.R.C.S. (Member): Have the authors found any evidence of allotropy in the platinum metals? By analogy with iron, nickel, and cobalt, which all show allotropic modifications and are also in the 8th group of the periodic system, one might expect to find allotropic modifications of at least some of the platinum metals.

The authors refer to the use of the highest purity platinum (99·99 per cent.) for resistance pyrometers. Instruments using platinum of considerably lower purity have been used with perfect satisfaction. Occasional checking of the constants of such instruments over a period of 40 years has only shown extremely minute changes.

Since the platinum thermometer has now been adopted as one of the chief international standards of temperature (an accuracy of $\frac{1}{1000}$° C. being easily attained at, say, 500° C.), and since the work of metallurgists is so largely dependent on the accurate measurement of temperature, a note of reminiscence about the origin of the platinum thermometer may be of interest.

Just 50 years ago my father, the late Professor H. L. Callendar, established the relation between the temperature scale and the electrical resistance of platinum.§ He was working by himself at Cambridge on his Fellow-

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* G. Grube and E. Kesting, *Z. Elektrochem.*, 1933, **39**, 948.

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

§ H. L. Callendar, *Phil. Trans. Roy. Soc.*, **1887**, p. 165; H. Le Chatelier, "The Measurement of High Temperatures," **1912**.

ship thesis, and in those days they had not the same facilities as we have now. He made the whole of his difficult gas thermometry apparatus himself, and after 6 months' work had it broken by a cleaner. He re-made it, at the same time inventing a new simple type of gas thermometer for comparisons with platinum, considerably more accurate than Regnault's international standard instrument of that time. All this work, requiring the highest precision and accuracy, had to be carried out on a window sill in a passage between two rooms, and apparently it was properly done, for in spite of innumerable re-tests, his figures have stood practically unchallenged after 50 years.

A well-known advantage of platinum is that it can be sealed into glass, and in comparing the platinum with his improved standard gas thermometer, my father adopted the then unique plan of sealing his platinum spiral inside the bulb of his gas thermometer, thus getting a perfect comparison between the two.

There is a property of platinum that does not seem too generally known outside the industry, namely, the danger of using it in conjunction with silicon. I myself at one time had the misfortune to melt up three crucibles and a basin before I found out that it was due to the silicon; the makers here rather mislead us, suggesting a minute trace of copper as the cause of all the trouble.

Sir ROBERT MOND,* M.A., LL.D., F.R.S.E. (Member): The remarks of Dr. Callendar, whose father I had the honour and privilege to know, remind me of one of my early experiences with platinum thermopiles, when I was pleased to be able to beat the late Sir Robert Austen by being the first to establish platinum thermometers in works. I had to make them myself, and something like 12 ft. long to get them where I wanted them in the furnaces. I used nickel tubes and churchwarden pipe-stems for insulation, and I had to work delicate galvanometers with pumps working in the basement. However, I succeeded in making them, and they worked quite satisfactorily. I calibrated them once a month at 100° and 400° C. Nowadays platinum–iridium and platinum–rhodium couples have become a commonplace in measurement, and that that is so is due largely to the work of Heraeus in Germany and of Callendar at Cambridge.

[Sir Robert's contribution to the discussion concluded with some interesting personal recollections of the foundation and growth in Great Britain of the precious-metal refining industry.]

CORRESPONDENCE.

THE AUTHORS (*in reply*): Both M. Dhavernas and Dr. Ballay have given interesting information about palladium leaf. We are glad to acknowledge here the pioneer work of M. Dhavernas and his associates in developing the technique of beating palladium to the form of leaf and for developing its applications.

We are also indebted to Dr. Heraeus for his interesting remarks about the high reflectivity of rhodium and for directing attention to the applications of rhodium in Germany. Similar developments have taken place in the U.S.A. and in Great Britain, so that the uses of rhodium are now of world-wide importance.

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* Director, International Nickel Company of Canada, Ltd.

We agree with Dr. Ballay that the stripping of defective rhodium deposits is difficult. One method of which we have had experience is to immerse the article in a mixture of molten potassium and sodium cyanides; if the article is made the anode and a current passed, the removal of the rhodium is accelerated. In this way rhodium plating can be removed from silver articles without any significant attack of the silver.* It is obvious, however, that the process is only suitable for operation by experts and there is still need for a simple and effective process which can be carried out in any plating shop.

The information given by Dr. Callendar on the development of the platinum resistance thermometer by his father was most interesting; personal notes of this type are very valuable when they refer to an invention which has been of such outstanding benefit to the science of metallurgy. In a similar way we are indebted to Sir Robert Mond for his interesting reminiscences of the early use of the instrument in works' practice.

Dr. Callendar raised the question of the allotropy of the platinum metals. This subject should perhaps have been dealt with in the paper and we thank him for directing attention to the omission. Jaeger and collaborators † have published accurate series of specific heat determinations at high temperatures for each of the metals of the platinum group. They ascertained that whereas the metals iron, cobalt, and nickel show many irregularities in the specific heat–temperature curves owing to allotropic changes occurring in them the metals osmium, iridium, and platinum give specific heat–temperature curves that are practically straight lines giving no indications of transformations. The series ruthenium–rhodium–palladium show a transitional state between the two foregoing extreme cases. Ruthenium shows true static allotropy which in may respects is similar to that shown by iron. The specific heat–temperature curves of rhodium and palladium show maxima which are indicative of dynamic allotropy. Other physical properties determined over suitable temperature intervals show discontinuities at the temperatures indicated by the specific heat determinations of Jaeger and collaborators. The full evidence cannot, however, be considered in detail here.

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* Further details are given in British Patent No. 419,819.

† *Proc. K. Akad. Wet. Amsterdam*, **1927, 1930, 1931, 1932.**

THE COMPLEX INTERDEPENDENCE OF THE PROPERTIES OF ALLOYS AND THE INDUSTRIAL CONDITIONS OF THEIR MANUFACTURE, TESTING, AND USE.* 742

By Marquis R. de FLEURY,† Member, and Dr. H. PORTIER.‡

Synopsis.

Indirect factors influencing the properties of light alloys in service are classified and some methods of recognizing and controlling them are described.

Introduction.

(By R. de Fleury.)

The present study summarizes the experience of many years, directing attention to the unsuspected and troublesome factors which intervene at every stage between the production and utilization of an alloy. After a preliminary qualitative study [1] I have persisted in attempts to discover the laws governing the various factors, and to evaluate their influence. Work for the Air Ministry (of France) has given me the opportunity to apply and verify my results in this sphere of application. The bearing of these problems on the safety of aircraft is sufficient to show their importance. The following presentation may seem complicated, but it is the complication of the subject itself which is to blame, rather than its analysis. In the latter I have had the invaluable assistance of M. Portier.

I.—General.

(By the Authors.)

All metallurgists in contact with manufacture are aware of the many apparently unrelated factors which are brought to light during experiments with new alloys, new processes, or new tests. In addition to the problems involved in the pursuit of improved properties, in meeting more rigid tests, in the perfecting of manufacturing technique, or imposed by the design and dimensions of the article, either in the foundry or in use, there are the more general but less evident troubles

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which intervene unexpectedly, in a manner at once more deceiving to the founder and more dangerous to the user, since they are difficult to trace and are often aggravated by apparently logical remedies. In the interpretation of an incident of either fabrication or functioning, both direct and indirect factors should be considered; better still, they should be foreseen by the Management from a continual analysis of the facts of production.

METHOD OF CLASSIFYING FACTORS.

Observations made by one of the authors,[2] over many years, led him to classify the various factors even before defining them, according to Table I.

The direct factors are revealed by existing knowledge and experience. It is the less apparent factors that are mainly to be considered, for it is impossible to foresee what may be the indirect repercussions of a remedy applied as the result of an error in diagnosis. It is wrong to classify remedies in the same way as the factors to which they correspond, since, for example, a remedy for a direct factor (1–C) can have disastrous consequences in introducing a new indirect (2–C) or even unrecognized factor (3–C). In the closed cycle comprising the various stages in the life of an article, from its entry to the foundry as raw material to its return as scrap, a number of factors intervene, which appear to be unrelated, but which are actually so interdependent that a simple modification of one can upset or re-establish the equilibrium of the whole cycle.

TABLE I.

Influence of the Factors.	Elucidation of the Factors.		
	1. Direct (Immediate Interpretation Obvious to the Senses).	2. Indirect (Requiring the Interpretation of Observed Facts).	3. Temporarily Unrecognized (Brought Out by Hypothesis and Experiment).
A. Apparent (*i.e.* more or less deceptive) .	1–A	2–A	3–A
B. Occasional (dependent on a particular circumstance) . .	1–B	2–B	3–B
C. Fundamental . .	1–C	2–C	3–C

In the paper which follows this interdependence is studied in the particular case of light-alloy castings, although the problem is the same for all metals.[3]

II.—INFLUENCE ON THE PROPERTIES OF ALLOYS OF INDIRECT FACTORS DURING MELTING.

Experience shows that, in the best-directed foundries, the quality of the product is subject to inexplicable fluctuations which often disappear of their own accord. They are due to the intervention of indirect factors, the influence of which is small but cumulative, such as the increase in the amount of impurities in the metal by repeated remelting, and the consequent depreciation. The amount of such depreciation can be measured by the change in a given property, such as castability, elastic limit, &c., or more simply by the increase in the number of rejects. It increases with the "net output ratio," M (*i.e.* the ratio of the weight of metal charged in the furnace to the weight of good castings leaving the works). This differs from the "gross output ratio," m (the ratio of the weight of metal charged to the total weight of castings). Then if r is the proportion of scrap recharged at each melt

$$\frac{1}{M} = \frac{1}{m}(1 - r) \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

At each charge the weight of good castings is replaced by an addition of new metal equal to $\frac{1}{M}$ and the depreciation takes place on the complement, A, of the preceding melt.

If α is the elementary coefficient of depreciation for each melt, the depreciation, T, after n melts is given by the following expression, which forms a convergent series:

$$T_n = \frac{\alpha A[1 - A^n(1 - \alpha^n)]}{1 - A(1 - \alpha)} \quad . \quad . \quad . \quad . \quad . \quad (b)$$

and, after an infinite number of remelts:

$$T_\infty = \frac{\alpha A}{1 - A(1 - \alpha)}$$

or, in terms of M

$$T_\infty = \alpha(M - 1) + 1 \quad . \quad . \quad . \quad . \quad . \quad (c)$$

The depreciation is thus proportional, partly to the coefficient of depreciation, which depends mainly on direct factors (which are under control and should be favourable) and, partly, to M, which varies with the more or less insidious action of external factors, of which the influence is often unrecognized, and for which the *true* remedies often differ greatly from the *immediate* remedies.

III.—INTERDEPENDENCE OF GENERAL EXTERNAL FACTORS AND THE PROPERTIES OF ALLOYS.

Organization of Production.

If a factory be considered the current manufacture of which has a mean output of M_2, and it be supposed that important orders have to be met, for which the true output ratio, M_1 is greater than M_2 on account of foundry demands or increase in scrap percentage; a mean output ratio M' results, which is given by : [4, 5]

$$M' = \lambda M_1 + (1 - \lambda)M_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

where λ is the percentage of the new manufacture, *e.g.* a delicate type of aluminium aero-engine cylinder block involving a high scrap percentage ($M_1 = 4$) is introduced into a current production whose output ratio has been reduced to 1·5 (M_2). Then the mean output ratio is given by equation *d* as 2·75. This increase is clearly due to the mixing of the two manufactures, and it would be useless to apply direct remedies for the loss in efficiency of the original manufacture, which had not previously given trouble. The fundamental remedy lies in the reorganization of the production on the following lines: The equilibrium of the two manufactures can be not only re-established, but even improved by casting "in echelon," *i.e.* a certain number of melts are made for the current work, and the remainder for the new work, the scrap, however, being pooled. The new manufacture will have a virtual output ratio M_1', lower than M_1, the weight of castings produced at each melt remaining equal to $\frac{1}{M_1}$. The difference, therefore, must be absorbed by the remainder of the production, each melt of which will produce a weight of castings proportional to $\frac{1}{M_2}$ and equal to $\left(\frac{1}{M_1'} - \frac{1}{M_1}\right)\frac{1}{M_2}$.

Hence $\quad \lambda\left(\frac{1}{M_1'} - \frac{1}{M_1}\right)\frac{1}{M_2}$ must be equal to $\frac{1}{M_1}(1 - \lambda)$

or

$$\frac{M_1}{M_1'} = 1 + M_2 \cdot \frac{1 - \lambda}{\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad (e)$$

The equation (*e*) gives a value of 1·60 for M_1' in the case of the examples chosen. It shows, too, that if the proportion of the new manufacture is not too great, or if its output ratio, M_1, does not exceed a certain value, the virtual output ratio can equal unity; that is to say, all the excess metal can be used up by the original manufacture without appreciable degradation.

Influence of Specialization.

Certain firms, for economic reasons, specialize in the mass-production of a particular article. Such production is in a precarious state of stability. In the manufacture of automobile cylinder blocks the normal scrap percentage is about 12 per cent., but it periodically reaches 24 per cent., above which it is prohibitive. The reason is the depreciation of the metal with successive re-meltings by an amount which increases with the ever-increasing percentage of scrap reintroduced. The same thing is seen in aircraft work, and aluminium and magnesium castings generally, for which the output ratio is high and purity of the raw materials is important. Some firms wisely sell their scrap at low price to founders of less important castings; others shut their eyes to the problem, renewing stock and changing personnel when crises occur. It should be added that when the financial direction of a firm re-establishes its technical equilibrium by using new metal and putting excess scrap into stock, it can falsify completely the balance sheet of the firm by neglecting to allow for the depreciated quality of the scrap. Financial administrators are inclined to disclaim responsibility for the technical repercussions of their own directions.

Such are the dangers of specialization, to avoid which it is necessary to supplement the principal manufacture of high output ratio by a secondary manufacture having a lower output ratio—for example, the casting of magnesium alloy wheels for aircraft ($M_1 = 4$) together with wheels for trucks in the same material ($M_2 = 1{\cdot}5$).[6]

Influence of External Specifications.

An increase in purity does not necessarily improve quality and may, indeed, reduce it, as was the case with Duralumin during the War, when restriction of the amount of scrap to be used caused a decline in the properties of the metal by reducing the excess of silicon necessary for the formation of Mg_2Si.

A tightening of the acceptance test on the finished product, by increasing the proportion of rejects, raises the factor M, and accelerates the depreciation T.

The Effect of the Scrap Market.

The development of aircraft work requiring a high proportion of virgin metal and having, moreover, a high output ratio, the breaking up of old cars and aeroplanes, and many other sources, have created large floating stocks of scrap, the market value of which has decreased, owing to lack of demand. Later applications, such as the light alloy cylinder head, have given rise to competition, the principal cause of which is the use of such scrap by certain makers. The dangers involved need no emphasis; 10 years ago the use of aluminium for cylinder heads was jeopardized by lack of consistent soundness. In the case of pistons, also, the much superior high-silicon alloys have been replaced to some extent by very cheap alloys, which owing to progress in design give a certain amount of satisfaction to the non-discriminating buyer. The existence of large floating stocks of scrap would thus appear to prejudice the development of serious applications unless research is carried out by producers to permit the use of secondary metal without bringing it into discredit.

The Question of National Defence.

In order to assure a peace-time production, to guarantee adequate capacity for the needs of war, it is necessary to create civil outlets and to organize and distribute the production on a national plan. In the important case of magnesium alloys, for example, in Germany the problem has been attacked by insisting on the use of the material for the wheels of public vehicles.

IV.—FOUNDRY FACTORS.

In the case of a pure metal or eutectic, the shrinkage is localized in internal cavities which do not usually communicate with the surface: with alloys having a solidification interval the phenomena are more complicated, and cause a succession of defects very different in appearance, but having the same cause. In both cases the problem of the foundry is to assure complete feeding of the still liquid portions of the casting from external sources. This is effected mainly by risers or denseners. The former are liable to reduce the cooling rate seriously, and to make higher casting temperatures necessary, thus reducing the mechanical properties of the alloy. Moreover, they obviously increase the output ratio, and, as a remedy for cavities, may have immediate success, whilst forming the root cause of troubles to come. It is always possible to replace a riser by a suitably placed runner, and it is equally possible to use chills, so reducing the output ratio, M.

Top pouring is to be recommended, since it eliminates at least one riser, but careful technique is required to avoid entrainment of oxide.

It is difficult to distinguish between cavities due to gas and those due to shrinkage, since they can have the same appearance, and are subject to the same laws of progress, division, and localization. In effect the imprisoned gas follows the free path of the remaining liquid metal, exactly as the shrink; they are both stopped in the same way

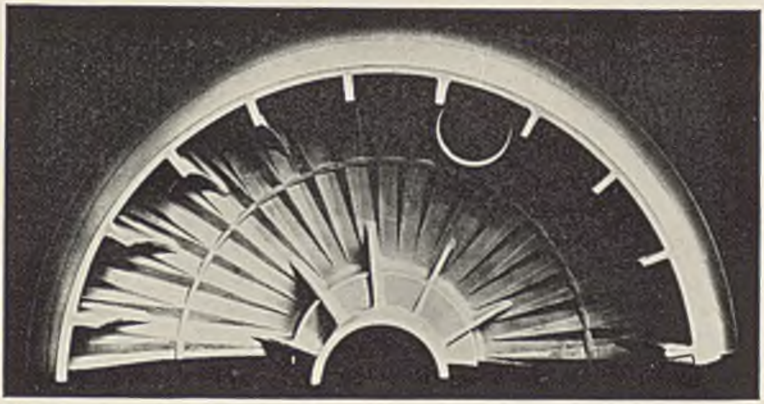

FIG. 1.—Cast Aeroplane Wheel, the Web of which is Composed of Pyramids on a Very Thin Plate, so as to Ensure Adequate Feeding, and to Control and Reduce Internal Stresses.

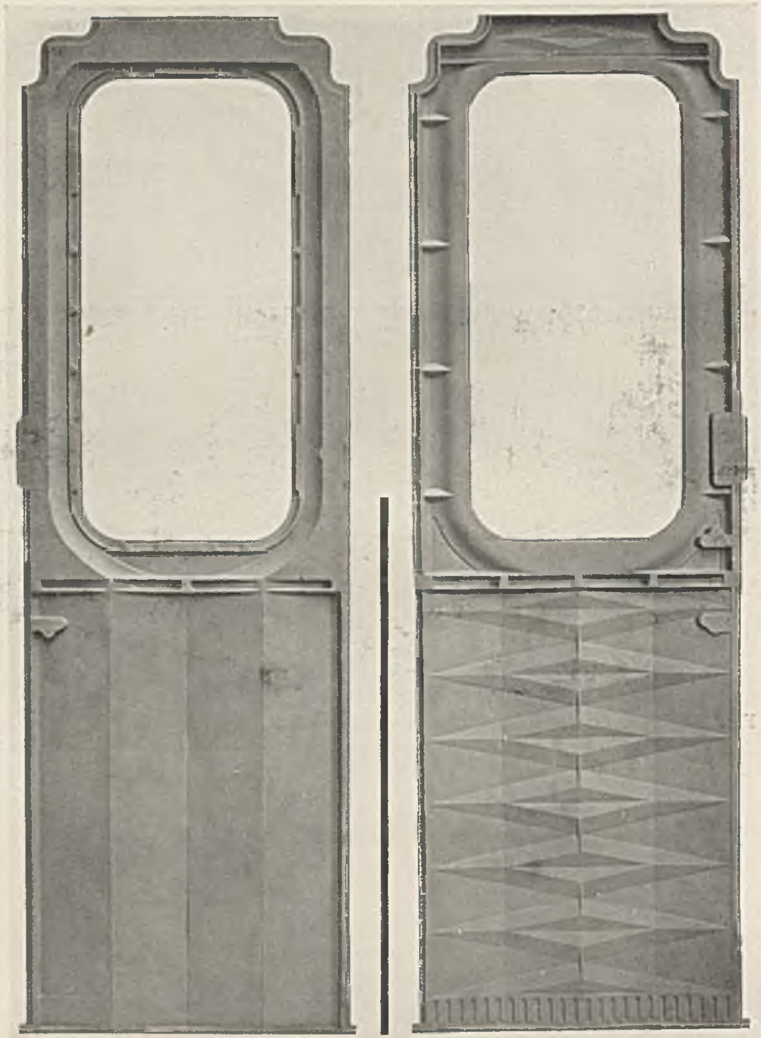

FIG. 2.—Cast Railway Door, the Panel of which is Composed of Pyramids on a Very Thin Plate, in Order to Reduce Founding Difficulties and Increase Rigidity.

and at the same points, when the metal becomes too viscous. Although the permeability of the sand affects the gas-hole and not the shrinkage cavity, yet the remedies for the latter are usually suitable for the former.

Iron crucibles are a possible cause of trouble in the foundry, as increase of iron content of the metal not only affects the mechanical properties but also increases the solidification interval.

The physical and chemical quality of the moulding sand also introduces many indirect factors, and such unusual occurrences as the pick-up of soot from a neighbouring railway may lead to bad castings.

The question of design is perhaps best approached by imagining the casting to be divided into a large number of thermally differing zones, each of which is considered as a separate problem. A characteristic example is a magnesium alloy aircraft wheel, with heavy rim and thin web. If the latter is made of uniform thickness this cannot be less than 5–6 mm. on account of feeding and internal stress difficulties. It is, therefore, divided into a large number of radial pyramids—see Fig. 1 (Plate VIII)—giving a thickness, in the thinnest parts, of only 1·5–2 mm. and an average thickness of less than 4 mm. The thick parts feed the thin parts and split up the internal stresses. A similar construction is seen in the railway door of Fig. 2 (Plate IX), the average thickness of the panel being less than 3·25 mm.[7]

V.—THE RELATION OF THE USE OF ALLOYS TO THEIR PROPERTIES.

The Size-Factor.

As has been seen, a feeding head, in suppressing shrinkage, may cause a cavity to appear elsewhere, and castings of more than a certain size, or difficulty, will suffer from a vicious circle of defects, the remedy for one (apparent, direct factor, 1–A) constituting an occasional, temporarily unrecognized factor, 3–B, in the appearance of another. If extreme measures have to be taken for a given casting, the factor of safety (in use) may be reduced by hidden defects. Safety in large castings is more likely to result from using alloys with a small solidification interval, which involves redesigning to allow for poorer mechanical properties, *e.g.* the large monobloc castings in Alpax for marine work, which cannot be safely made in other alloys.

When Alpax was first used in France for cylinder blocks considerable difficulties with porous barrels were experienced, for which the quality of the metal was held responsible (apparent, direct factor, 1–A). The real cause of the trouble was the design (fundamental factor, 3–C), and German founders, using the same alloy, had no trouble, because they designed their blocks to take inserted barrels.

Large monobloc castings for severe duty cannot be made in high-strength alloys having a large solidification interval without prohibitive risks and difficulties. For these alloys monobloc design must be abandoned. Alpax, on the other hand, is unsuitable for designs which require the assembly of a large number of small units, on account of its poor resistance to high local stresses, particularly at right angles to the assembly bolts.

Thermodynamic Factors.

Breakdowns of motors are sometimes attributed to faulty material, when the basic cause is to be found in one of the numerous thermodynamic factors of its functioning.[8] Systematic piston seizure, for example, has at times been traced to the use of inferior fuel. Again, corrosion of magnesium-alloy petrol tanks by additions of tetraethyl lead to the fuel, resulted in decomposition of this anti-detonant, so that, until a chemical remedy was found, the metal of the tank was accused of reducing the possible compression ratio.

On the other hand, the thermodynamic factors are, themselves, affected by the appearance of new alloys. The use of beryllium–copper alloys of high thermal conductivity, for exhaust valves, has enabled these to work at lower temperature, and so increased the life of the engine.

Influence of Modulus of Elasticity.

The strength and elastic limit of light alloys has been increased, whilst the modulus of elasticity has remained almost unchanged. The secondary factor of deformation consequently governs the factor of safety to an increasing extent. For a casting of given design there is a particular value of the elastic limit of the material, which it is useless to exceed.[9]

The importance of the modulus of elasticity was shown in the case of aero engines, having their cylinders in line. These were subject to systematic breaking of crank-shafts, due to deformation of the aluminium-alloy crank-cases. When the latter were made more rigid the trouble ceased, but it reappeared when they were cast from the same patterns in magnesium alloy of different modulus of elasticity.

Effects of Use.

In many constructions the flexibility and natural period of vibration [10] vary with time. Particularly in the case of assembled units, where stress concentrations occur at the joints, the fatigue limit of the material is all important. It must be emphasized that it is not only the parts transmitting power which are subject to fatigue, but also the whole supporting structure—especially when this is not of monobloc design.

CONCLUSIONS.

Some actual examples are given of a number of external factors which, by their subtle and often unsuspected interdependence, have been able to upset the manufacture and functioning of a machine. There are many others.

Metallurgists are warned against the unconsidered application of new alloys, and engineers against hasty condemnation of the materials with which they are supplied. In spite of careful forethought metallurgists and engineers will encounter unsuitable applications which will throw a prematurely advertised material into disfavour. This is the explanation of the amazing set-backs to be remembered in the history of the most logical new developments.

REFERENCES.

[1] R. de Fleury, "Les facteurs de sécurité méconnus," *Congr. Internat. Sécurité Aérienne*, 1930, **2**, 113.

[2] R. de Fleury, *Congr. Internat. Sécurité Aérienne*, 1930, **2**, 113–119; *Congr. Fonderie Paris*, **1931**; *Bull. Assoc. Tech. Fonderie*, 1931, **5**, 127–133.

[3] R. de Fleury, *Congr. Internat. Sécurité Aérienne*, 1930, **2**, 29–34, 113–119; *Rev. Mét.*, 1931, **28**, 610, 616; *Congr. Fonderie Paris*, **1932**; *Bull. Assoc. Tech. Fonderie*, 1932, **6**, 235–243.

[4] R. de Fleury, *Bull. Assoc. Tech. Fonderie*, 1932, **6**, 236.

[5] R. de Fleury, *Compt. rend.*, 1932, **194**, 1739; *Bull. Assoc. Tech. Fonderie*, 1932, **6**, 235.

[6] R. de Fleury, *Publ. Tech. Sci. Ministère de l'Air*, 1935, **(75)**, 110.

[7] M. Lancrenon, *Rev. gén. Chemins de Fer*, **1932**, July.

[8] R. de Fleury, *Congr. Internat. Sécurité Aérienne*, 1930, **2**, 43–119.

[9] R. de Fleury, *Bull. Soc. d'Encour.*, 1921, **130**, 875; *Rev. Mét.*, 1923, **20**, 541; *Compt. rend.*, 1923, **177**, 592; *Bull. Soc. Ing. civils*, **1925**, Oct.–Nov.; *Internat. Air Congr. London*, **1923**.

[10] P. le Rolland and P. Sorin, *Publ. Sci. Tech. Ministère de l'Air*, 1934, **(47)**.

DISCUSSION.

(*Condensed.*)

DR. C. H. DESCH,[*] F.R.S. (Vice-President): This paper and the Autumn Lecture by Professor Chevenard of the previous day constitute a new phase in the proceedings of our Institute, being an account of the application of scientific principles to the internal organization of an industry. On most of the points raised, it is our industrial members whom we are anxious to hear. I wish to deal only with one aspect which I think is new to the Institute, and that is the influence of re-worked metal and of scrap on the conduct of metallurgical processes. That is a problem which is necessarily becoming more and more insistent as the production of any metal or metallurgical product increases.

A century ago, the production of steel was only a minute fraction of that of pig iron. As the industry increased, the proportion continuously changed,

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until in 1914 the production of steel was nearly equal to that of pig iron. Since 1918 the curves have crossed, and now the production of steel exceeds, and exceeds in an increasing ratio, the production of pig iron, because the quantity of scrap used is so enormous. Metal which has once been used returns into industry, and in the ordinary open-hearth process a charge, for example, of 60 per cent. scrap and 40 per cent. pig is quite a usual one.

Similar conditions are bound to arise in the case of other metals. The quantity of scrap, old metal re-worked, must continually increase; and that, as the authors clearly show, introduces problems of some importance into the conduct of metallurgical processes. Here is a question which will have to be faced very carefully. In view of the increasing purity of some of the metals, which, as indicated in the paper by M. Gauthier, is now showing itself to be of such vast importance, this gradual accumulation of impurities in the course of re-working will open up new problems of refinement.

Professor A. PORTEVIN * (Member): M. de Fleury has allowed himself to be carried away by the spirit of generalization when he extends to all metallurgical smelting operations the consequences of cumulative alterations by continuous remelting of scrap which have caused him so many troubles in the aluminium foundry. In ordinary practice the melting of aluminium is accompanied by an irreversible oxidation reaction between the metal and the atmosphere which results in changes in the properties of the castings; but if the metal is protected from the action of the atmosphere, if the nature of the latter is modified to prevent oxidation, or, better still, if the metal is covered with a slag which reacts irreversibly with the oxide formed, then this gradual degradation on repeated melting disappears and the foundry operations can be carried out with the continuous re-use of scrap. Again, certain industries, such as those making brass for screw-cutting or basic electric furnace steel, are entirely based on *exclusive* feeding of the manufacture with scrap, without any progressive diminution in the quality of the metal taking place; on the contrary, the finished metal from the foundry is of much superior quality to the unsorted scrap which forms the furnace charge.

Mr. H. J. MAYBREY,† B.A. (Member): As an industrial member of this Institute, a foundryman, I find that in the aluminium business the scrap question is becoming a very difficult one. The only solution that I can see for dealing with heterogeneous material is the making of secondary ingots prior to delivery.

Dr. P. G. BASTIEN ‡ (Member): The deterioration of the metal as a result of repeated remelting might be due to oxidation or to the absorption of nitrogen from the air when in the liquid state. It is particularly important in the case of metals having great chemical affinity, such as aluminium and magnesium.

We have had the opportunity to study § the influence of five successive remeltings of an extra-light alloy of magnesium containing 6 per cent. aluminium, and it has been shown that there is a rapid decrease in the castability of the alloy and that its mechanical properties, particularly its resistance to impact, declined. It would be dangerous to exaggerate this question of deterioration, however, because the metallurgy of a particular metal cannot

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‡ Répetiteur a l'École Centrale des Arts et Manufactures, Paris.

§ P. Bastien, *Bull. Tech. Min. Aéronaut*, 1933, (20); *Rev. Mét.*, 1934, **31**, 324–329.

be considered to be established until the material is capable of being refined just prior to casting. Thus, aluminium can be deoxidized and purified before casting either with the aid of a suitable flux or even by filtration, as has been shown by Professor Chaudron. Similarly, the alloys of magnesium are now purified before casting with the aid of a flux consisting essentially of alkaline metals and alkaline earths, which in a well-conducted works, will reduce deterioration to small proportions.

MARQUIS DE FLEURY (*in reply*) : Works must have means for utilizing their secondary products in a judiciously chosen complementary manner. A works which limits itself to the exclusive production of high-grade material may not be commercially successful for long.

CORRESPONDENCE.

MR. J. R. GREEN,[*] B.Sc. (Member) : I should like to express my great appreciation of this paper, and to say that I hope more of a similarly analytical kind will appear in our *Journal*.

It should be pointed out, however, that not all metals are so depreciated by remelting as those considered by the authors and some of the speakers : with the tin–lead alloys, in which I am interested, remelting, under suitable and easily-controlled conditions, is very beneficial, and is in fact an essential part of the manufacturing process.

Professor A. M. PORTEVIN [†] (Member) : The classification of factors adopted by M. de Fleury is, above all, of a personal and psychological order, since the "immediate" factors (col. 1) are those which come to mind first of all, the "indirect" (col. 2) those which need reflection, and the "temporarily unrecognized" (col. 3) those which are not thought of; again "apparent" (*A*) in opposition to "fundamental" (*B*) implies an estimation of the importance of the factors and an *a priori* judgment on their rôle. In other words, all this depends on the knowledge, the character, the judgment, and the intelligence of the person responsible for investigating the factors of the problem in hand. Actually, the most frequent and the most human variables which interfere with this classification of the factors are :

(1) Ignorance, general or personal, of the factors taking part and of their relative importance, or indolence of mind, which comes to the same thing.

(2) Routine, or inversely the method and publicity which mentions in the general orders certain factors or certain properties.

(3) Experience, which remembers analogous examples or judges them.

(4) Intuition, which frequently is only an unconscious reasoning making appeal, without appearing to, to acquired knowledge or experience.

(5) *Amour propre* and the fear of responsibility, which cause to be considered as immediate and fundamental factors just those which do not depend on us and the rôle of which covers up our responsibility. This is the most common state of mind which makes the mechanic or the user think only of the metal, its quality, its treatment, and its defects, and which incites the metallurgist to blame the conception, the design, the dimensions, and the execution of a mechanical piece.

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There are always two problems to be solved, namely (a) a metallurgical problem, which is the choice of the metal, and (b) a mechanical problem, which is the utilization of this metal; each problem depends on numerous factors, some of which are common to both.

(a) *Choice of metal.* This depends on a number of factors which I grouped under the following headings about 10 years ago: *

(1) Mechanical, physical, and chemical properties; determined, without exception, under the conditions of use of the metal.

(2) Possibility and ease of working: either cold (machining or stamping) or hot (forging, founding). None of these depends on properties which come into play during use.

(3) Price: this is determined by the composition of the alloy, its purity and method of fabrication, design of the article, and other treatment costs.

These three groups of factors are thus interconnected to some extent and certain of them are still only imperfectly understood.

(b) *The mechanical problem* also brings into play factors which are either imperfectly known or more or less poorly defined and difficult of measurement although known for a long time. This is the case with certain properties which are being investigated at the present moment, namely, viscosity, reactivity, endurance, corrosion under stress, &c. Again the mechanic is often ignorant of the distribution and real value of internal influences, such as photoelasticity and analogous processes, of the rôle of various methods of assembly, of discontinuities, of self-vibrations, &c., under stresses. All these factors have lain hidden for a long time, but they can no longer be ignored or not taken into account.

It is known that the production of clean castings involves a considerable number of factors and phenomena, the most important of which I have enumerated and classified in Tables I and II in my article on "Metallographie et Fonderie." †

From these it will be seen that any foundry property or phenomenon (π) whatever (pipe, crack, blow-hole, segregation, &c.) is a complete property depending on a great number of variables, some (x, y, z) common and others (ξ, η, ζ) particular or specific, *i.e.*

$$\pi = f(x, y, z \ . \ . \ . \ \xi, \eta, \zeta \ . \ . \ .)$$

Two properties or phenomena π^1 and π^2 both depend on x, y, z and can also depend on one or more of the factors ξ, η, ζ common to different extents, but not common to all the foundry properties. Some of these factors act equally on the properties of the castings in use. These common factors are the source of the interactions or interdependences of Messrs. de Fleury and Portier. Since, on the other hand, one cannot, *a priori*, envisage the general effect of all these factors, nor establish at the moment an order of importance for all cases and for all types of castings, only a small number of them are brought to mind at first, depending on the psychological and human variables previously mentioned; these are the immediate or apparent factors of M. de Fleury. Experience often proves that the most important factors, called fundamental by M. de Fleury, are among those which are neglected, that is, temporarily forgotten.

Finally, of the phenomena accompanying the solidification of metals, there are those which are produced during fusion, notably changes in the chemical composition, by which is meant every modification of the original

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* "Dix Ans d'Efforts scientifiques et industriels," **1926**, 276 (Paris: Chimie et Industrie).

† *Bull. Assoc. Tech. Fonderie*, 1932, **6**, (1), 19.

composition of the charge, whether produced by the addition of other elements which act like the constituents of the alloy or by the absorption of foreign constituents, such as oxygen or other gases. These modifications produce changes in the properties, often unfavourable, which the authors consider only as depreciation or " degradation " of the metal and for which they give an expression of recurrence for a succession of n re-fusions which the metal undergoes in foundry practice. This expression is established on the hypothesis that the changes which occur are the same in each fusion, or, in other words, increase linearly with n, which, of course, is not the case of the reactions which occur tend towards a chemical equilibrium, as, for example, the absorption of hydrogen by the metal. On the other hand, the expression assumes that no efforts are made to diminish or inhibit the changes producing deterioration or to make them " negative," as, for example, by interposing a refining operation.

Marquis de Fleury (*in reply*) : I recall that the aim of our paper was to demonstrate the too little recognized generality of the part played by very complex and unsuspected interactions in the stability of the equilibrium of any industrial manufacturing process.

To do this we took for granted the direct factors and intentionally passed them over in our paper. Their great number, enumerated by Professor Portevin and by Monsieur Bastien, serves only to emphasize the complexity of possible combined interactions, and that strengthens our conclusions.

Obviously progress in transformation processes can modify the nature, the importance, and even the direction of the action of certain more or less isolated direct factors in a manufacturing process.

The processes of the interactions, however, modified by progress to a greater or less extent, continue to be general laws of industrial stability. Insufficient attention is given to these laws of stability, not only in factories, but even in technical instruction.

As a first example, a secondary fusion foundry is never equipped for refining operations, like a true metallurgical factory. A growing precision of the composition and characteristics of alloys is now the rule; and this daily confronts refineries with those new metallurgical problems of which Dr. Desch speaks.

As a second example, when, in consequence of progress in metallurgy, a cause of deterioration is brought to light, and subsequently removed by appropriate fluxes, there still remain other causes of deterioration, of a minor degree, but acting none the less surely, in time, and forming obstacles to the new degree of precision required by the progress achieved. Magnesium at present appears to be somewhat improved by fluxes in the course of the successive refusions. Yet nevertheless it deteriorates progressively by absorption of silicon impurities from the foundry sand.

As a third example, mechanical industry itself does not escape the rule of deterioration. Equipment destined for high precision work loses its capacity for precision by normal wear and tear. The frequent and costly replacement of plant is as strictly necessary as precision itself, without any possible amortization, in a factory specializing in products with a very narrow tolerance.

In the three examples cited above, it is evident that the conjunction with a manufacture of high precision of a complementary manufacture of less precision, capable of using the deteriorated material or plant, is absolutely necessary to ensure the stability of the equilibrium of the industrial quality of the products, and to insure at the same time the stability of the commercial equilibrium of the enterprise.

We must not lose sight of the fact that it is progress itself which tends to make the equilibrium always more precarious, because every advance appears to the head of the firm as a basis of new exigencies in the market and as a basis of a new limitation of possibilities. That is to say that the question of the industrial stability of a manufacture presents itself with a degree of acuteness which will always be greater to-morrow than it was yesterday.

It was to this that we wished to direct attention, emphasizing the preponderating influence on the properties of metallurgical products of the parallel organization of laboratory research, of new commercial prospects, of markets and even, very often, of the creation of the latter, rationally combined.

From this point of view we regret that the Institute of Metals was obliged to publish only a *résumé* of our original paper; although this was extremely clear, it was necessary to eliminate, for the sake of brevity, a large number of concrete examples.

VEINING AND SUB-BOUNDARY STRUCTURES IN METALS.*

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By L. NORTHCOTT,† Ph.D., M.Sc., MEMBER.

SYNOPSIS.

A network structure, termed veining, which occurs within the crystals has been studied in several pure metals and in many alloys of copper, and methods for its production are discussed. The structure is shown to be due to the precipitation from solid solution, in a network form, of the oxide of the metal during cooling. The influence of alloying additions on veining in copper has been examined and the effect of heat-treatment and recrystallization on veining correlated with changes in hardness. Similar structures referred to as sub-boundary structures have been observed in a number of other alloys. These structures are due to the precipitation, also during cooling, of a constituent of the alloy.

(1) INTRODUCTION.

VEINING structures have been considered in the past mostly in connection with fairly pure irons or low-carbon steels. The structure takes the form of a network, usually irregular, inside the α-iron crystals and has been termed α-veining or the sub-boundary structure. In a recent investigation,[1] it was concluded that the structure is due to the precipitation of iron oxide during cooling and that the solid solubility of the oxide in iron decreases with decrease in temperature, a conclusion which has been confirmed by analytical methods.[2-4] In the same paper,[1] examples were given of veining in copper and nickel, and with both these metals it was also concluded that veining results from the precipitation of the oxide of the metal during cooling. The decrease in the solid solubility of copper oxide in copper with decrease in temperature has since been confirmed by chemical analysis.[5]

The investigation of veining structures has now been extended to non-ferrous metals and alloys generally, and the results are described in this paper.

(2) PRODUCTION OF VEINING OR VEINING-FREE METALS.

As the earlier investigation [1] had shown the dependence of veining, in the case of iron, nickel, and copper, on the oxidation of the metal,

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methods of increasing the oxide content were selected for the purpose of obtaining material in which veining might be present. The methods adopted were: (*a*) Melting the metal in an oxidizing atmosphere. In some instances it has been found sufficient to melt the material without using a flux or reducing agent. With lower melting point metals, the practice commonly adopted was to pour the melt from one crucible to another several times in air; alternatively air has been blown through the melt, using a silica tube to introduce the air well below the surface of the metal; (*b*) Annealing the metal in air; (*c*) Heating the metal in contact with its oxide. In this case the oxide is packed either around the polished metal or in a hole drilled in it.

In all cases it has been found necessary to arrange for a slow rate of cooling.

A comparison sample of many of the metals was prepared by passing hydrogen through the melts and solidifying in an atmosphere of hydrogen. The intention was to obtain material free from oxide.

(3) VEINING IN PURE METALS.

All the metals examined were of the highest purity commercially available. Of the metals which had been oxidized according to one or more of the methods described above, veining has been observed in cadmium, zinc, antimony, magnesium, aluminium, silver, copper, nickel, and iron.

Veining has not been observed, in the present investigation, in either tin or lead. The structures observed in the individual metals (taken in the order of their melting points) are briefly described below. A reference to recommended etching reagents and methods will be found in the Appendix (pp. 252–253).

Cadmium.—A typical structure is shown in Fig. 1 (Plate X). The two crystals in the photograph are easily distinguished by the difference in orientation of the twins. It will be noted that the direction of the veins does not appear to be affected by the twins. No veining was observed in the original cadmium or in the hydrogen-treated sample.

Zinc.—Two qualities of zinc were examined containing 99·99+ per cent. and approximately 99·98 per cent. zinc, respectively. Neither sample showed veining in the condition as received or after the hydrogen treatment, but much veining was observed after treating the melt with air. The microstructure of zinc is similar to that of cadmium, and it was also observed with zinc that twinning did not appear to cause any discontinuity in the veins.

Magnesium.—A sample of 99·95+ per cent. magnesium showed no veining as received, whereas the air-treated material showed veining.

The appearance of both veining and crystal structure of magnesium, Fig. 2 (Plate X), was similar to that in the case of cadmium.

Aluminium.—Veining, which was not observed in the original sample, was found in the air-treated sample, and was still observed after treating this with hydrogen. Hydrogen treatment of the melt for ½ hr. was sufficient to remove veining from most metals, but was found to have no effect on the structure in aluminium.

Copper.—The commercial varieties of cast or wrought copper examined all showed oxide present in the usual globular form but not as veining. Such copper remelted without charcoal or flux showed an excess of the copper–copper oxide eutectic and no veining. When excessive oxidation of the melt was prevented, however, and the metal slowly cooled, veining was present. Several samples of copper were obtained showing veining; all consisted of large crystals, up to 1 cm. in diameter, due to the slow solidification, and the veining was both coarse and well-defined. Typical structures are illustrated in Figs. 3 and 4 (Plate X). The actual appearance of veining, especially in copper, depends very much on the conditions of polishing and etching as well as on the magnification and focussing. The veins may either appear light against a dark background or dark against a light background. Occasionally it has been necessary to photograph the structure slightly out of focus in order to obtain sufficient contrast for reproduction. At low magnifications the veins appear as continuous lines, but usually the discontinuous nature of the veins can be shown in copper at quite moderate magnifications. In addition to the dotted appearance of the veins at higher magnifications, the apparent absence of any connection between veining and dendritic structure will be noticed. When treated in the liquid state with hydrogen for a sufficient length of time, veining was removed (see Fig. 5, Plate X).

Nickel.—Veining was induced in pure nickel by annealing the metal in air for many hours, as described in a previous paper.[1] The depth of penetration was considerably less with nickel than with those metals described previously.

Iron.—Good examples of veining have frequently been observed in different samples of wrought irons and in steel (Figs. 6 and 7, Plates X and XI), but not in electrolytic iron as deposited. No difficulty was experienced in inducing veining in the latter either by annealing in air or in contact with iron oxide at a high temperature. The study of the veining in iron and steel has been described in some detail in the previous paper.[1]

Silver.—Silver is considered last, as the veining in this metal is of a different type from that described above. Two qualities of silver were examined, the first was 99·9+ per cent. pure and the second, which was obtained through the courtesy of Mr. D. McDonald of Messrs. Johnson, Matthey & Company, Ltd., was of 99·99 per cent. purity. No veining was observed in samples prepared by bubbling hydrogen through the melt and allowing solidification to take place in an atmosphere of hydrogen, but veining was present after the silver had been poured to and fro in air, then slowly cooled in the furnace (Fig. 8, Plate XI). Veining in silver may be considered as a special type on account of the fact that although silver oxide Ag_2O exists, it decomposes at temperatures in the neighbourhood of 300° C., although the dissociation temperature is known to increase with increase in pressure. Further reference to the structures in silver will be made later in the paper.

Of the pure metals examined, tin, lead, and antimony failed to show veining. Some difficulty was expected with the first two metals in view of the comparatively small range of temperature between their melting points and atmospheric temperature; their extreme softness and the facility with which they recrystallize only added to difficulties in examination. Greater uncertainty was felt about antimony; several samples were prepared by oxidizing the melts, but the oxide occurred too readily in globular form similar to the oxide eutectic in copper. The addition of an alloying element was, therefore, made for the purpose of deoxidizing, on the lines described below for copper. Antimony, unlike copper, forms only a few alloys in which one phase alone occurs over any appreciable range in composition at the antimony end of the diagram. An alloy was prepared containing 2 per cent. tin, and this resulted in the suppression of excess globular oxide and the formation of a discontinuous veining network somewhat similar to that observed in silver. When the rate of cooling was increased by air cooling from 590° C. a sample of dimensions approximately 2 in. × 1 in. × ½ in., the network structure was more pronounced. It is probable, therefore, that pure antimony would also show veining if the state of oxidation were more closely controlled than it had been in the present work.

(4) VEINING IN ALLOYS.

An investigation was made to determine the effect of a second constituent on the formation of veining. Copper was selected as the basis metal in view of its industrial importance and the comparative ease with which it was possible to develop veining in suitably prepared samples. The general procedure adopted was to melt 4–6 lb. of electrolytic copper under charcoal, add the required amount of the second element, pour the alloy to and fro in air about six times, using a second pre-heated crucible, and then to allow solidification to take place in the crucible in the furnace. The ingot was sectioned along its axis and the axial face examined for veining. Particulars of the alloys prepared are given in Table I.

TABLE I.—*Copper Alloys Prepared by Air-Treating the Melt.*

Added Element.	Percentage of Addition.	Constitution.	Veining?
Zinc	5	α-solid solution	pronounced coarse veining
	10	α	ditto
	15	α	less pronounced veining
	30	α	slight veining
	39	$\alpha\ (+\ \beta)$	very slight veining
	40	$\alpha + \beta$	trace of veining in β
	48	β	chiefly random deposit, some network
	50	$\beta\ (+\ \gamma)$	veining present
	61	γ	possibly ditto
Tin	2	α	pronounced coarse veining
	5	α	much veining
	6	$\alpha\ (+\ \delta)$	ditto
	7	$\alpha + \delta$	ditto
	10	$\alpha + \delta$	slight veining
Phosphorus	0·2	$\alpha\ (+\ Cu_3P)$	veining present
	0·55	$\alpha + Cu_3P$	P network present
	0·5	$\alpha + Cu_3P$	veining and P network present
Silicon	0·5	α	much veining present
	4	$\alpha + \gamma$	slight veining
	5	$\alpha + \gamma$	very slight veining
Aluminium	2	α	veining present
	6	α	ditto
	8	α	ditto
Arsenic	2	α	veining present

The effect on veining of the various additions to copper may separately be described briefly as follows:

Copper–Zinc Alloys.—Additions of small quantities of zinc to copper resulted in veining which was more pronounced than in copper alone, as is shown in the 5 per cent. zinc alloy in Fig. 9 (Plate XI). Comparatively light etching developed the structure chiefly in the interdendritic areas, but continued polishing and etching showed veining to exist throughout the crystals. The veins appeared as fairly coarse lines, especially after deep etching, but a light treatment and examination at higher magnifications (see reference to Fig 10 below) showed the discontinuous nature of the veins. The addition of zinc eliminated the coarse globules of Cu_2O which are a common feature of most commercial coppers. Increasing the zinc content of the α-solid solution had little effect other than to make the structure less coarse and much less easily developed in the dendritic axes of the crystals (Figs. 10 and 11 (Plate XI), 70 : 30 brass) but veining could still be observed. In the 60 : 40 alloy, consisting of approximately equal proportions of the α- and β-solid solutions, a possible trace of veining was observed in the β-solid solution only. In the next sample, containing sufficient zinc to ensure an all β-alloy, the distribution of the deposit was random (similar to that in Fig. 21, Plate XIII) and was developed equally throughout the crystals as the freezing range was insufficient to cause much "coring." Another sample prepared by allowing the crucible containing the melt to cool in air showed a somewhat similar structure, except that there was some evidence of a network formed by a linking up of the separate particles (Fig. 12, Plate XI). A more complete network structure was obtained as described later by cooling a small sample rapidly in air. With sufficient zinc to saturate the β-solid solution and to ensure the presence of a small quantity of γ, veining was again observed, similar to, but not so pronounced as, that shown in Fig. 16, Plate XII. The alloy consisting solely of the compound Cu_5Zn_8, which is the principal constituent of the γ-solid solution, was exceptionally difficult to prepare for micro-examination, but there was again a definite suggestion of veining.

Copper–Tin Alloys.—When small additions of tin were made to copper, pronounced veining of the type found in the low-zinc brasses was again observed. Further additions of tin appeared to reduce the quantity and also to refine the veining, and greater difficulty was experienced in developing it. Veining was present, however, even in alloys containing the δ-solid solution and Fig. 13 (Plate XII) shows a bronze containing sufficient tin to ensure the presence of the δ-constituent, which appears as small lakes. The lines of the network in this photograph appear singularly continuous, and it was only by examination under very high magnifications that the discontinuity became apparent. This is shown in Fig. 14 (Plate XII), at a magnification of × 2500 obtained by the use of the objective of N.A. 1·60 developed by H. Wrighton [6] for high-power work. With this objective all the veins were easily resolved; there appeared to be no connecting lines between the individual particles constituting the veins. In the 10 per cent. tin alloy the veining was most prominent in the dendritic areas of the crystals.

Copper–Phosphorus Alloys.—The first two alloys, containing 0·2 and 0·55 per cent. phosphorus, respectively, were prepared by adding the required amount of phosphor–copper (15 per cent. phosphorus) to the copper melted under a thin layer of charcoal, and allowing it to cool down slowly in the furnace without pouring to and fro in air. Veining was observed in the 0·2 per cent. phosphorus alloy, of a type similar to, although not so pronounced as, that found in the original copper, but no oxide veining was observed in the 0·55 per cent. phosphorus alloy. In this there were several isolated particles of free phosphide, and in addition a secondary deposit of phosphide indicative of veining was observed. The latter structure was somewhat irregular and was confined to the interdendritic areas adjacent to the major phosphide deposits. The addition of 0·55 per cent. phosphorus appeared to have been sufficient to deoxidize the copper completely. The third alloy containing 0·5 per cent. phosphorus was poured to and fro in air six times before being allowed to cool, and the structure was for the most part similar to that of the second alloy containing 0·55 per cent. phosphorus. Several crystals in the third alloy, however, showed both veining and the phosphide network, the former in the middle, dendritic areas and the latter in the interdendritic, phosphide-rich areas of the crystals. The rate of cooling was not the best for the production of veining in a good network form (Fig. 15, Plate XII).

Copper–Aluminium Alloys.—The veining in the 2 per cent. aluminium alloy was similar to that observed in the low alloy brasses and bronzes. Veining in the 8 per cent. alloy was finer (Fig. 16, Plate XII) and more general throughout the crystals, and required prolonged etching to develop the structure as may be seen from the coarse nature of the grain boundary. Subsequently, long annealing at a temperature just below the solidus failed to remove the structure which, therefore, should not be mistaken for dendritic segregation.

Copper–Silicon Alloys.—The 0·5 per cent. silicon alloy showed veining similar to that in the low-zinc or low-tin copper alloys. Increasing the silicon content to 4 per cent. introduced the γ-constituent and considerably increased the difficulty of developing veining, but veining was definitely present although it was confined to the dendritic areas. This feature is of interest in view of the general tendency for impurities to concentrate in the interdendritic spaces, and would appear to be due to the smaller solubility of the oxide in the silicon-rich portions of the cored α-solid solution.

Copper–Arsenic Alloy.—Veining was present in an alloy to which 2 per cent. of arsenic had been added, and was similar in appearance to that in the low-tin alloy except that it was less pronounced.

Nickel–Copper Alloys.—In addition to the specially prepared alloys described above, veining has been observed in other alloys. As two of these have been employed in some of the heat-treatment experiments, brief descriptions may be made here. One alloy, ECN, was a cupro–

nickel containing 70 per cent. nickel and 0·6 per cent. graphite, the remainder being copper; the samples examined were cut from a chill-cast ingot of dimensions 36 in. × 3 in. × 2 in. The structure of the alloy as received is shown in Fig. 17 (Plate XII); in addition to abundant veining, coring and graphite deposits were also in evidence. The dimensions of the veining network were much smaller than in the majority of the other non-ferrous alloys examined. The other alloy, LAQ, containing 20 per cent. nickel, was also received in the " as cast " condition; the structure was pronouncedly dendritic but no veining was observed. Slow cooling from 1020° C. resulted in abundant veining.

General Effect of Alloy Additions on Veining.

It is worth recording that whereas the addition of a small quantity of an alloying element to copper facilitates the development of veining in suitably oxidized specimens, large additions have the reverse effect. The actual percentage of the added element required to show these effects is different for the different elements, and will presumably depend on (*a*) the range of composition of the particular α-solid solution; (*b*) the deoxidizing power of the added element, and (*c*) the solubility in the alloy of the oxide which is formed. Much care was required in preparing for micro-examination most of the alloys containing appreciable alloy additions. So pronounced is the difficulty of developing the veining structures in some alloys, that in a few, for example the 70 : 30, ($\beta + \gamma$), and γ-brasses, and the higher silicon alloys in particular, it had almost been decided that no veining was present, but etching and light polishing were repeated for a large number of times, and eventually the structure was developed. Fortunately, when veining is present, it is often possible to detect some suggestion of the structure in comparatively early stages of preparation.

The present study has shown the definite lack of homogeneity of oxide content in the cored structures of the majority of the cast alloys. Although in a few instances the veining is evenly distributed throughout each crystal, the alloying addition usually tends to concentrate or even confine the veining in certain portions of the crystal presumably owing to differential solidification which leads to variations in concentration of the alloying element across the crystal. This in turn controls the distribution of the oxide, since the solubility of the oxide is affected by the concentration of the solid solution. In addition, where the alloying element is strongly deoxidizing, the deoxidation will be greatest where the alloying element is most concentrated. Thus, in the low alloy copper alloys, veining occurs mostly in the interdendritic areas, but it occurs in the dendritic areas in some of the high-alloy copper alloys and in intermediate positions in the intermediate types of alloys. The position of the veining in any one crystal is affected by two opposing influences: (*a*) the tendency for oxide-rich material to concentrate in the interdendritic spaces according to the natural law of differential solidification, and (*b*) the reduced solubility of the oxide in the alloy-rich portions which also occur in the interdendritic spaces owing to differential solidification.

Of the deoxidizing agents which have been considered, it is clear that phosphorus is the only one which when present in slight excess is capable of completely removing oxide from the metal, and this is presumably due to its being volatile at the temperature of the melt.

The facility with which veining may be produced in those alloys containing only a small alloying addition is at least partly due to the deoxidizing effect of the addition in removing excess oxide from the melt. Oxide contents greater than that required to saturate the α-solid solution at the temperature corresponding to its maximum oxide content result, during the final stages of solidification, in precipitation of comparatively coarse particles, usually in the form of a eutectic. Further precipitation of material during cooling in the solid state is liable to result in deposition on that already present, so that little evidence of veining may be shown.

(5) HEAT-TREATMENT EXPERIMENTS.

Effect of Annealing Temperature on Veining.

The effect of temperature was determined by annealing samples of the copper (LJY) and cupro-nickel (ECN) at temperatures from 250° to 1000° C. for 2 hrs. and then quenching. Similar effects were noticed in the two materials. Two-hour treatments caused little change in the appearance of the veining until 600° C. was reached, when it was apparent that solution and coalescence of the veining particles were taking place. These processes increased with increasing temperature until complete disappearance of the veining occurred. No veining could be detected after quenching from 900° C. in the case of the copper and 1000° C. in the case of the cupro-nickel. The disappearance of veining took place first in the dendrites, especially in the case of the cupro-nickel, with the result that the dendritic structure, arising from differential solidification, appeared to be more prominent after annealing at the intermediate temperatures than it was originally. The coalescence and partial solution of the veining constituent after treatment of the copper at 800° C. are shown in Fig. 18 (Plate XII) and of the cupro-nickel at 750° C. in Fig. 19 (Plate XIII). A comparison of Fig. 19 with Fig. 17 shows the intensifying effect of solution and partial precipitation on the casting structure. Heating to still higher temperatures caused the solution of the veining constituent from the interdendritic spaces, with the result that the dendritic structure again became less pronounced as it was originally. It was also noticed, especially in the case of the copper sample, that the veining persisted in some crystals more than others; after treatment at 800° C., for example, a few crystals appeared free from veining, whereas the veining in other crystals was still prominent although the type and quantity were different from the original structure.

The hardness of both materials was determined by the Vickers diamond pyramid after the different heat-treatments; the results are given in Table II.

TABLE II.—*Effect of Heat-Treatment on Hardness (Vickers Diamond Pyramid).*

Annealing and Quenching Temperature, ° C.	Hardness Value.	
	Copper (LJY).	Cupro-Nickel (ECN).
...	60	140
250	63	140
500	52	142
600	48	141
750	42	116
800	36	107
900	39	122
1000	40	127

These figures confirm the results of the microscopical examination: coalescence at the intermediate temperatures leads to loss of hardness, and solution at the higher temperatures has a hardening effect. The first two or three values for each material are high on account of a small amount of work-hardening to which the original materials had been subjected.

Effect of Time of Annealing.

The effect of prolonging the annealing was determined on fresh samples of the copper (LJY) and the cupro-nickel (ECN). One sample of each material was annealed for 20 hrs. at 400° C. and quenched, and another sample was given the same time at 750° C. and quenched. The treatments at 400° C. caused slight coalescence and possibly solution of the veining particles. A considerably greater change was naturally observed after the treatment at 750° C. Much solution and coalescence had occurred in both alloys, similar to that observed after 2 hrs. at 800° C. (cf. Fig. 18, Plate XII; copper after 2 hrs. at 800° C.), although there was more coalescence after the treatment for 20 hrs.

The hardness values after annealing at 400° and 750° C. were 48 and 37, respectively, for the copper, and 130 and 111 for the cupro-nickel alloy. The temperatures of the 2-hr. treatments corresponding to these figures were approximately 600° and 800° C. in the case of the copper and 680° and 780° C. in the case of the cupro-nickel. The lower temperature is apparently more affected by the duration of the annealing, the greater hardness changes observed in each alloy indicating that equilibrium is less rapidly attained.

Release of Suppressed Veining.—I.

The temperatures favouring the solution of the veining constituent have already been considered, and it has been shown that when the metal is quenched at temperatures not too far below the melting point, veining is no longer to be observed. This "suppression" of veining by severe quenching is a characteristic property of the type of veining at present under discussion. It has also been shown that heating the metal to a high temperature and cooling at a suitably slow rate results in veining once more. In view of this, two questions may be asked: (1) what happens when a quenched specimen is reheated? and (2), during slow cooling at what temperatures is the veining formed?

The effect of re-heating a quenched specimen was determined on samples of the copper (LJY). Two specimens were first quenched in water from 1000° C. after 1 hr. at that temperature and the specimens annealed for 20 hrs., one at 400° C. and the other at 750° C., and then quenched. Pronounced veining was present in the specimen treated at 400° C., as shown in Fig. 20 (Plate XIII), the meshes of the network being considerably smaller than in the original copper. Some difficulty was experienced in sharply defining many of the veining "lines," as if movement of the veining constituent had commenced in a direction away from the veins. The same specimen was re-quenched from 1000° C. and again annealed at 400° C., this time for only 2 hrs. The dimensions of the veining network were the same as after treatment for 20 hrs., but the veins were much more sharply defined.

The other specimen, quenched after 20 hrs. at 750° C., showed no veining but only a random precipitation (Fig. 21, Plate XIII), although occasional examples suggestive of line formation of the deposit could be observed. (It was noticed in this case and also in one of the β-brass samples where random precipitation took place, for the "deposit" to appear very much like etching pits. A similar effect was observed in a few other specimens, especially when very deep etching had been employed, and has also been noted by Rhines and Mathewson [5] in their study of cuprous oxide in copper.) The specimen showed the same structure when given a further treatment by quenching from 1000° C. and heating for only 2 hrs. at 750° C. A third treatment was therefore given; the specimen was quenched from 1000° C., heated at 750° C. for only 10 minutes, and then quenched. Pronounced veining was now observed similar to that in the specimen given the treatment for 2 hrs. at 400° C. It is apparent, therefore, that the random deposit previously observed after the longer 750° C. treatments does not indicate the method of precipitation at that temperature but must be due to coalescence subsequent to precipitation. The experiment at 750° C. confirms in a remarkable manner the tendency towards coalescence observed at the treatment at 400° C.

Hardness Results.

The hardness of the specimens was determined at each stage using the Vickers diamond pyramid on the surfaces prepared for micro-examination; the results are given in Table III. For comparison there are also given the results of hardness determinations on two other samples of the copper, one slowly cooled from 1000° C. at the rate of ¼° per minute and referred to later, and the other a sample hydrogen treated in the melt and then annealed in hydrogen at 1000° C. and slowly cooled, and in which veining was completely absent. Thus, although the effect of the veining constituent is slight, the hardness of the copper is definitely influenced by the form in which the veining constituent occurs.

Table III.—*Hardness of Heat-Treated Copper (Vickers Diamond Pyramid).*

Heat-Treatment.	LJY 1.	LJY 2.
Quenched from 1000° C. . .	40	40
ditto + 20 hrs. at 400° . .	45	...
ditto + 20 hrs. at 750° . .	...	39
Quenched from 1000° C. . .	39	39
ditto + 2 hrs. at 400° . .	41	...
ditto + 2 hrs. at 750° . .	...	39
ditto + 10 minutes at 750° .	...	41
¼° per minute, cooled from 1000° C.	36	
Hydrogen treated, and annealed .	30	

Release of Suppressed Veining.—II.

The determination of the temperatures at which veining is formed during cooling was made on two alloys: the 5 per cent. zinc–copper alloy and the copper–nickel alloy (LAQ) containing 20 per cent. nickel. Separate samples of each alloy were annealed at 1000° C., one pair quenched at that temperature and the remainder cooled at the rate of

2° per minute and quenched at intervals of 200° C. No veining was observed in the copper–zinc samples quenched at 1000° or 800° C. A coarse type of veining had commenced to form during cooling to 600° C. (Fig. 22, Plate XIII) although some crystals showed very little of the structure. By the time 400° C. had been reached much veining was general throughout the specimen, as in Fig. 4 (Plate X), and little difference was observed between this and the one quenched at 200° C.

The effect of the treatments on the copper–nickel alloy was rather different. No pronounced veining could be observed in any of the samples, although a possible trace occurred in those quenched at 400° C. and below. There was, however, a slight random deposit in samples quenched below 800° C., and it was concluded that the cooling rate had not been the best to develop the network structure. The specimens were therefore re-treated, using a cooling rate about four times that previously adopted. The structures then corresponded with those of the 5 per cent. zinc–copper alloys at the different temperatures; a trace of veining was observed after quenching at 800° C., and the veining increased in quantity as the quenching temperature was lowered.

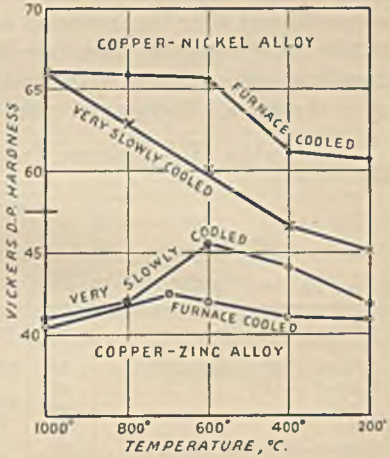


Fig. 37.

In view of this difference in structure, the samples of the 5 per cent. zinc–copper alloy were also subjected to the more rapid cooling. The only difference observed was that the veins in the more quickly cooled specimens were possibly slightly finer. The results of hardness tests are plotted in Fig. 37. The agglomerated precipitate in the copper–nickel alloy cooled at the lower rate resulted in a lower hardness figure than was obtained when the constituent occurred in a veining form. The copper–zinc alloy showed veining at both rates of cooling, and the higher hardness range of the very slowly cooled samples was presumably due to more complete precipitation.

Heat-Treatments in Hydrogen.

In a previous section it was mentioned that no veining was observed in samples prepared by bubbling hydrogen through the liquid metal and allowing to cool down in an atmosphere of hydrogen. The only exception to this was aluminium, whose oxide is known not to be reduced except at very high temperatures. Heat-treatments in hydrogen were, therefore, carried out on several metals and alloys in the solid state to determine whether and to what extent veining could be removed from materials in which it was originally present. Particulars of the treatments are summarized in Table IV.

Of the materials treated, only two types failed to show complete removal of veining from the surface of the specimen. In order to determine the depth of removal and to check that the heat-treatment alone was not responsible for the removal of veining, several specimens were sectioned after the treatment and the transverse faces examined. Before being sectioned, these specimens were given a thick electrodeposit of copper to enable the transverse faces to be examined right up to the edges. The general effect of the hydrogen treatment on the

TABLE IV.—*Hydrogen Treatments of the Solid Alloys.*

Specimen.	Treatment.		Veining Present?	
	Hours.	° C.	Before Treatment.	After Treatment.
Zinc	20	360–400	yes	no
Silver	3	900	yes	yes, as before
Copper (electrodeposited)	24	950–1000	no	no
Copper (LJY)	46	950	yes	no
Nickel	50	1000	yes	no
Iron	45	950	yes	no
Copper–zinc (5% Zn)	20	900	yes	no
ditto (10% Zn)	20	900	yes	no
Copper–tin (2% Sn)	20	900	yes	no
Copper–aluminium (2% Al)	3	1000	yes	yes, as before
Copper–silicon (0·5% Si)	23	1000	yes	yes, larger than before
The undermentioned specimens were plated and a transverse section examined after the hydrogen treatment.				
Copper (LJY)	22	900	yes	almost completely removed
Copper–zinc (5% Zn)	3	950	yes	veining removed from edge
ditto	22	900	yes	ditto
Copper–tin (2% Sn)	3	950	yes	ditto
ditto	22	900	yes	almost completely removed
Copper–nickel (70% Ni)	3	950	yes	veining removed from edge
ditto	20	950	yes	ditto
Copper–phosphorus (0·2% P)	3	950	yes	ditto
ditto	20	950	yes	ditto
Copper–aluminium (2% Al)	23	1000	yes	yes, as before
Copper–silicon (0·5% Si)	3	950	yes	ditto

structure was the same in the different specimens. Veining was present in the middle of the specimen, but there was an outer rim completely free from veining. The transition between the two fields occurred independently of the crystal boundaries. A typical structure is illustrated in Fig. 23 (Plate XIII) which shows a portion of the transverse section of the low-tin bronze up to the edge. There was little difference in the thicknesses of the veining-free layers in different alloys given the same treatment, and the rim was, in general, only slightly thicker after the longer treatments. Unsoundness aided diffusion of the hydrogen, since in one or two bronze samples which showed pin-hole unsoundness " as cast," the removal of veining was almost complete throughout the specimen.

As mentioned above, there were two prominent exceptions to the rule by which veining is removed by hydrogen at high temperatures; a third exception, a type not included in the present section, will be referred to later. The first exception is offered by alloys containing either aluminium or silicon, and is apparently due to the inability of hydrogen to reduce aluminium or silicon oxide except at temperatures considerably in excess of those used in the present work. In the alloy of copper containing 0·5 per cent. silicon, for example, veining persisted even on the surface after a treatment of 23 hrs. in hydrogen at 1000° C.; the veining in this copper–silicon sample was on a much larger scale in most of the crystals than it was originally. Presumably alloys of other materials containing oxides not reduced by hydrogen will also be unaffected by the hydrogen treatment.

Veining in Silver.

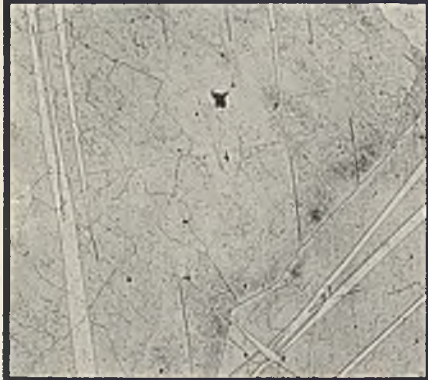
The second exception is offered by pure silver. In this, the original veining had the appearance of a succession of cavities as due to gas (Fig. 8, Plate XI),and no change was observed as a result of the hydrogen treatment. It was mentioned earlier in the paper that silver represents a special type, since its oxide decomposes at relatively low temperatures. The solubility of oxygen in molten silver has been measured by Sieverts and Hagenacker [7] and in solid silver by Steacie and Johnson.[8] It was shown that whereas silver in the liquid state (973° C.) can dissolve twenty times its volume of oxygen, the solubility in the solid state is considerably less, being 0·56 at 923° C., and decreases to a minimum of 0·087 at 400° C. Steacie and Johnson [9] consider this minimum to be due to the state in which the oxygen exists in solution, and point out that this minimum corresponds with the minimum in the heat of formation of silver oxide calculated by Keyes and Hara [10] from measurements of the dissociation pressure of oxygen in equilibrium with silver oxide.

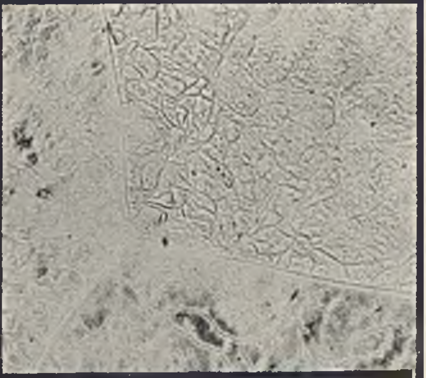
The large difference between the oxygen solubilities of liquid and solid silver is responsible for the well-known "spitting" phenomenon which is liable to occur during the solidification of silver. Sieverts and Hagenacker also calculated the changes in internal gas pressure during the solidification of silver saturated with air at 1030° C., assuming that no gas escaped, and concluded that values well exceeding 200 atm. would be obtained. Normally, of course, some gas escapes, and such a value is not likely to be reached. Partial solidification hindering the escape of gas would lead, however, to high values of internal pressure. It was calculated that under atmospheric pressure oxygen should not be liberated from the melt before 59 per cent. of the metal had solidified. This figure agrees very well with the 63 per cent. found experimentally by Allen.[11] Gas evolution then gives rise to "spitting." The porosity due to this evolution which occurs during solidification is intercrystalline or interdendritic in character and is shown as large black areas in the photomicrograph of silver, Fig. 8 (Plate XI). From their position the minute cavities indicative of veining must have occurred, however, subsequent to solidification. Although the gas pressure necessary for the formation of a bubble in solid silver will be considerably greater than that when the silver is in the liquid condition, the high internal gas pressures which can be realised and the mechanical weakness of the silver at temperatures not far removed from its melting point render this not impossible. The conditions for the appearance of gas blisters in solid metals have been considered by Allen.[11] Alternatively, partial combination between the silver and oxygen may have taken place. Allen has shown that the compound can exist at temperatures as high as 600° C. when the external pressure is sufficient to prevent dissociation. It may be concluded, however, that whether its veining constituent was initially a gas or whether it was a solid which later dissociated, silver can undoubtedly be classed amongst those metals which are capable of showing veining structures.

Quenching Experiments.

It has been shown that by increasing the temperature, the veining structure of several alloys may be made to disappear. Similar intermediate quenching experiments have not been carried out for all the other alloys in which veining was observed, but check experiments have been made by quenching several of them at temperatures not far removed from their respective solidus temperatures (except iron, which was quenched well above the upper critical temperature). All samples were maintained at the quenching temperature for not less than 1 hr. The particulars of these experiments are summarized in Table V.

PLATE X.





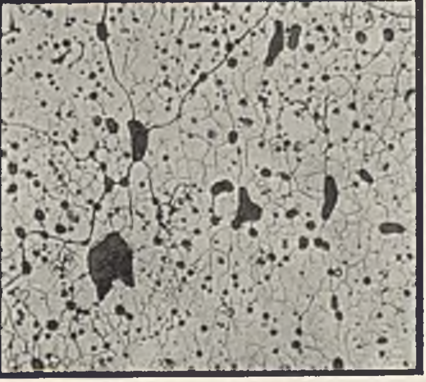


FIG. 1.—Cadmium. × 50.
FIG. 2.—Magnesium. × 50.
FIG. 3.—Copper, Dendritic Structure and Veining. × 15.
FIG. 4.—Copper. × 25.
FIG. 5.—Copper, Hydrogen Treated in the Melt, Veining Absent. × 20.
FIG. 6.—Wrought Iron. × 100.

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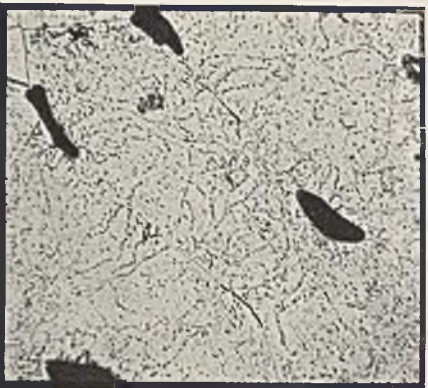

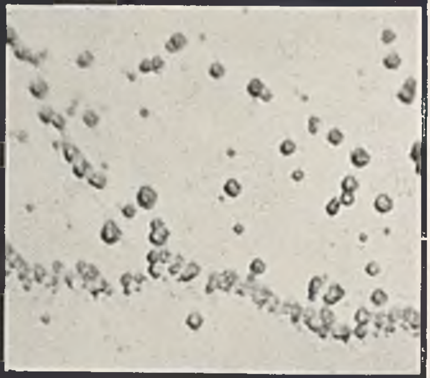

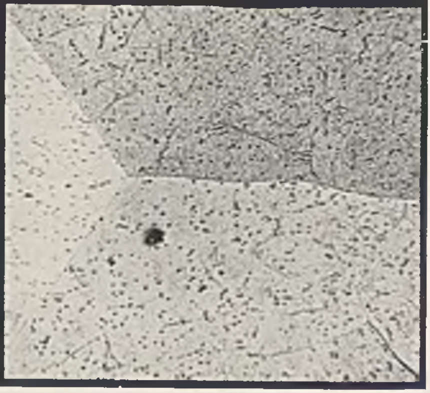

FIG. 7.—Mild Steel, 0·3% C. × 250.
FIG. 8.—Silver. × 100.
FIG. 9.—95 : 5 Copper–Zinc Alloy. × 40.
FIG. 10.—70 : 30 Brass. × 2500.
FIG. 11.—70 : 30 Brass. × 50.
FIG. 12.—52 : 48 β-Brass. × 50.

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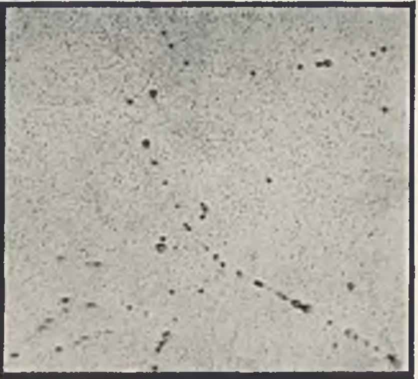

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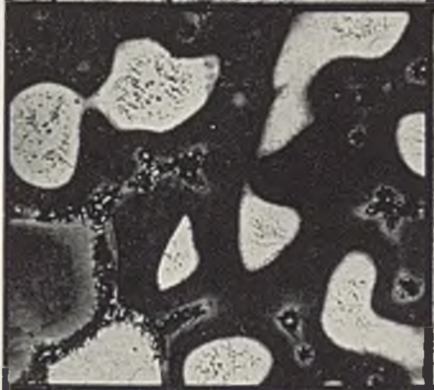

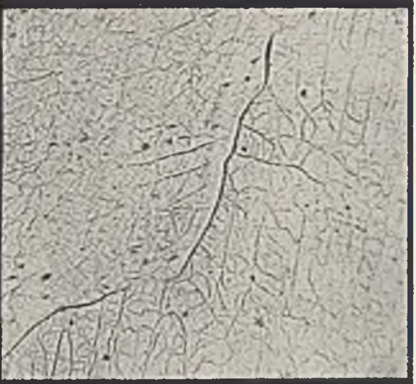

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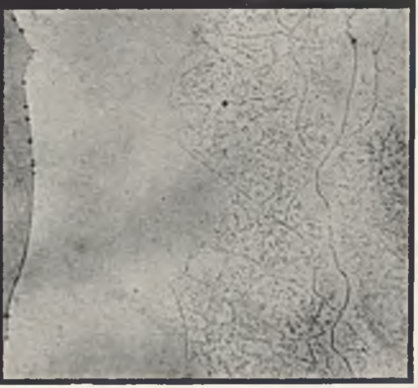

FIG. 13.—93 : 7 Copper–Tin Alloy × 100.
FIG. 14.—93 : 7 Copper–Tin Alloy. × 2500.
FIG. 15.—Copper Containing 0·5% Phosphorus. × 50.
FIG. 16.—92 : 8 Copper–Aluminium Alloy. × 50.
FIG. 17.—70 : 30 Nickel–Copper Alloy. × 100.
FIG. 18.—Copper Annealed for 2 Hrs. at 800° C. and Quenched. × 40.

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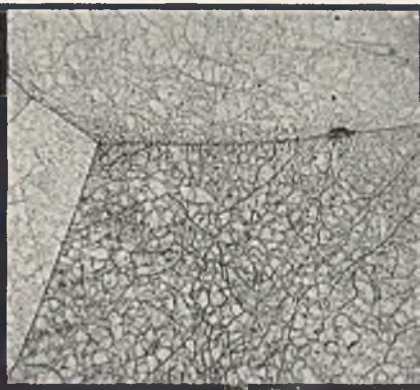

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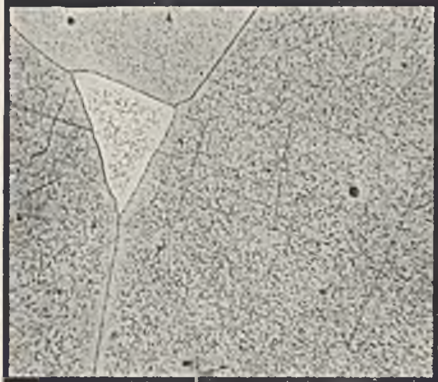

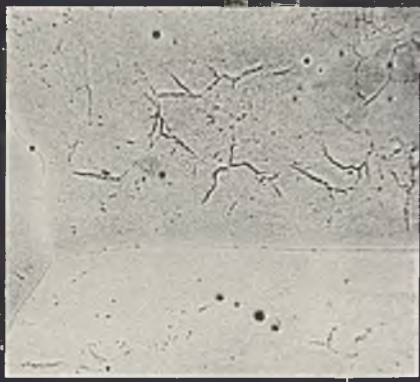

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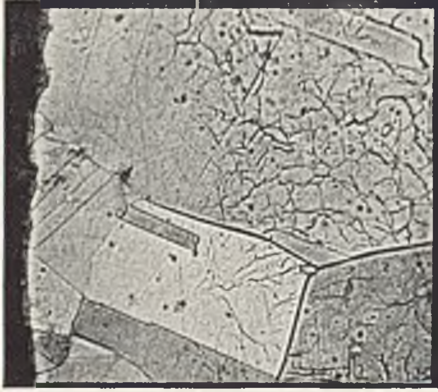


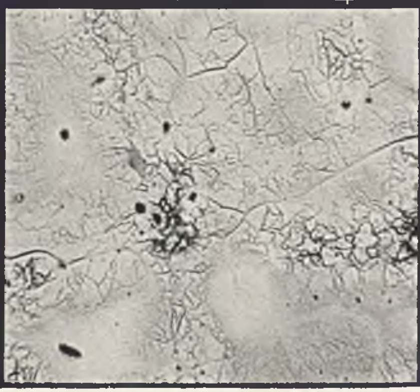
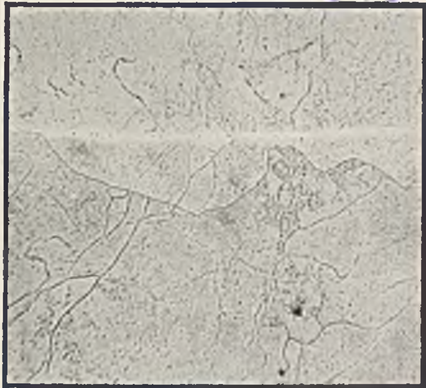


FIG. 19.—70 : 30 Nickel-Copper Alloy, Annealed for 2 Hrs. at 750° C. and Quenched. × 100.
FIG. 20.—Copper Quenched from 1000° C. and Tempered for 20 Hrs. at 400° C. × 50.
FIG. 21.—Copper Quenched from 1000° C. and Tempered for 20 Hrs. at 750° C. × 50.
FIG. 22.—95 : 5 Copper-Zinc Alloy, Slowly Cooled 1000°–600° C. and Quenched. × 50.
FIG. 23.—98 : 2 Copper-Tin Alloy, Annealed in Hydrogen at 900° C. for 22 Hrs. Transverse Section, Showing Surface Removal of Veining. × 25.
FIG. 24.—90 : 10 Copper-Tin Alloy, Annealed 3 Hrs. at 800° C. and Slowly Cooled. × 50

PLATE XIV.



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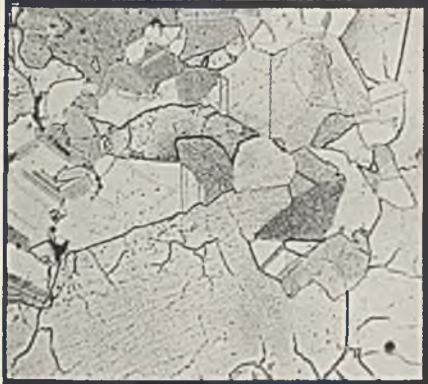

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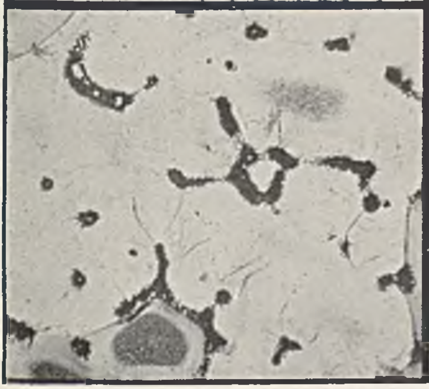

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FIG. 25.—Grain-Growth in Copper. × 50.
FIG. 26.—Veining in Recrystallized Copper. × 15.
FIG. 27.—95 : 5 Copper-Zinc Alloy, Partially Recrystallized. × 100.
FIG. 28.—Interdendritic Recrystallization in 95 : 5 Copper-Zinc Alloy. × 25.
FIG. 29.—Copper Containing 0·5% Phosphorus. × 40.
FIG. 30.—Molybdenum-Iron Alloy. × 100.

PLATE XV.

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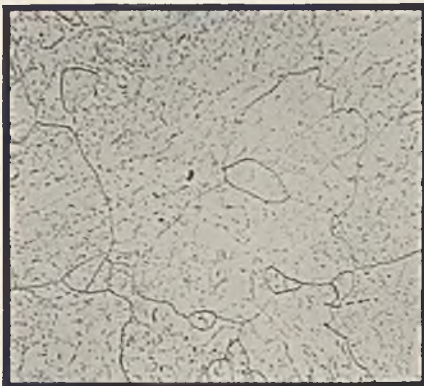

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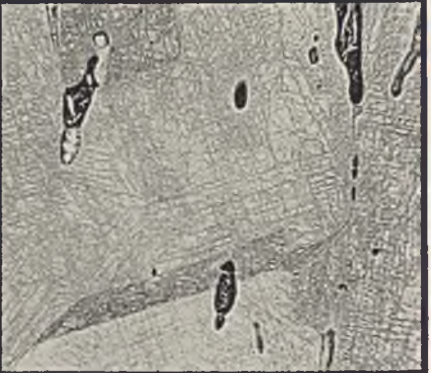

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FIG. 31.—Tantalum–Iron Alloy. × 100.
FIG. 32.—Network in Two Crystals of β-Constituent of Nickel–Iron–Aluminium–Copper Alloy. × 100.
FIG. 33.—Nickel–Iron–Aluminium–Copper Alloy, $\gamma \longrightarrow \delta$. × 250.
FIG. 34.—Air-Cooled Beryllium–Copper Alloy × 100.
FIG. 35.—Air-Cooled Beryllium–Copper Alloy. × 250.
FIG. 36.—Beryllium–Copper Alloy Air-Cooled for 1½ Minutes and Quenched. × 2500.

Table V.—*Quenching Experiments.*

Specimen.	Quenching Temperature, ° C.	Veining Present?	
		Before Treatment.	After Treatment.
Zinc	400	yes	no
Copper	1000	yes	no
Iron	1050	yes	no
Copper–tin (2% Sn)	800	yes	no
Copper–zinc (5% Zn)	950	yes	no
Copper–phosphorus (0·2% P)	950	yes	no
Copper–silicon (0·5% Si)	1000	yes	no
Copper–aluminium (2% Al)	1020	yes	no
Copper–nickel (70% Ni)	1020	yes	no

Thus, in every instance veining may be suppressed by quenching the solid alloy at a sufficiently high temperature; it may be concluded, therefore, that in these alloys also the veining constituent is more soluble at the higher temperatures. Subsequently, slow cooling resulted, once more, in the formation of veining.

Effect of Very Slow Cooling.

When veining was developed by oxidizing the melt and slowly cooling in the melting furnace, the rate of cooling of the copper alloys was of the order of 6°–2° C. per minute between the solidifying temperature and 400° C., and this rate was adopted in most of the heat-treatment experiments except when the specimens were quenched.

A sample of copper (LJY) and of fairly pure iron were annealed for 20 minutes at 1000° C. and then cooled at the rate of only ¼° per minute. Typical veining occurred in both samples before the heat-treatment, but only in the iron sample afterwards. There was a random distribution of particles in the copper sample and practically no trace of a network structure. The appearance was similar to that of the copper annealed for several hours at 750° C. and quenched (Fig. 21, Plate XIII), as described previously, and was undoubtedly due to the annealing effect exerted by the extremely slow cooling. In the iron sample the veining constituent showed some evidence of coalescence, but the metal was presumably too rigid to permit the degree of movement found in the copper.

A nickel–copper alloy containing 5 per cent. nickel, when cooled in the furnace at the rate of 1°–2° per minute from 1000° C. also showed a random distribution; cooling the same sample in air caused some alignment of the particles into the form of a network. Similar results were obtained with the higher phosphorus alloys.

Heat-Treatment of β-Brass.

The first β-brass (copper 52, zinc 48 per cent.) prepared showed a random distribution of particles, and only slight evidence of a network occurred when the melt was air-cooled. Cooling small samples in a tube furnace from about 820° C. at different rates failed to develop veining, but a tendency towards line formation was observed after air-cooling (Fig. 12, Plate XI). An increase in the proportion of veining was obtained by cooling in an air blast or better still by cooling in contact with two cold copper blocks.

Effect of Annealing.

A number of the alloys in which the dendritic structure was pronounced were annealed for short periods at high temperatures and cooled in the furnace to remove the "coring" and to determine the influence on veining. Veining was more easily developed after annealing. In the 10 per cent. tin–bronze annealed for 3 hrs. at 800° C., for example, there was abundant veining, which was more pronounced in the dendritic axes than elsewhere (Fig. 24, Plate XIII), and this resulted in the dendritic structure being actually more pronounced after annealing than before. The dendritic axes of the cored α-solid solution in the copper–tin alloys are normally etched more rapidly than the tin-rich interdendritic material, and this differential etching effect was accentuated by the duplex character of the dendrites in the annealed material owing to the separation of the veining constituent.

(6) THE EFFECT OF WORK AND RECRYSTALLIZATION ON VEINING.

Cold-Work.

Samples of a number of materials were given various degrees of cold-rolling, and sections were examined to determine whether any relationship existed between veining and strain marks. In addition, small flat tensile test-pieces were prepared from a few of the alloys and various degrees of strain applied. The test-pieces were polished and etched before straining. In most instances the slip-lines were not affected by veining, but examples were observed where a slip-line appeared to be arrested at the veins or where a small kink occurred in the slip-line as it crossed a vein. Such a kink or slight directional change may have been due, however, to the presence of a "furrow" or slight difference in level of the surface at the position of the veining line, and the only conclusion which could be reached from these experiments was that if the veining had any influence at all on the slip-lines, there was very slight evidence of it at the low magnifications at which the structures were most prominent in the samples examined.

Recrystallization Experiments.

Low-Temperature Recrystallization.—Recrystallization of a metal which does not undergo an allotropic change may be achieved either by hot-work or by cold-work followed by annealing. Control over recrystallization may be obtained by adjusting the degree of cold-work and the temperature to which the material is heated. Annealing an unworked specimen of the copper (LJY) for a short time at 500° C. has been shown to have no observable effect on the veining. In the present experiments the thickness of the specimen was reduced 10 per cent. by cold-rolling, and this was followed by annealing at 500° C. for 20 minutes. This treatment resulted in slight grain-growth, which took place by an undulating movement of the boundaries of one crystal into its neighbour. A typical example, Fig. 25 (Plate XIV), shows the old boundary, demarcated by isolated globules of copper oxide and by the abrupt ending of the veins, and also the new boundary of which the wavy form characterizes grain-growth as opposed to recrystallization, which is usually shown by straight or step-like boundaries of twins or new crystals. The lightly etched crystal in the photograph is extending into the dark crystal; scratch tests confirmed the continuity of the light crystal. The veining present in both crystals remained in the position in which it occurred before annealing, with the result that the new grain-boundary cuts across several of the veins.

High-Temperature Recrystallization.—The effect of recrystallization at high temperatures was determined on another sample of the same copper. Solution of the veining constituent has previously been shown to occur in this copper at temperatures in excess of 900° C., and veining may be produced again by slow cooling. A fresh sample was, therefore, reduced in thickness 20 per cent. by cold-rolling, annealed at 1000° C. for 1 hr., by which time it was considered recrystallization would be reasonably stabilized, and then slowly cooled at the rate of 2° per minute. Complete recrystallization had taken place and the high annealing temperature had resulted in fair-sized crystals about $\frac{1}{8}$ in. or more in width. Examination for veining showed that each of the new crystals had its own system of veining. This is well illustrated in Fig. 26 (Plate XIV), from which it will be seen that the networks in the different crystals are independent and do not extend beyond the boundaries of their own crystals. Apart from the twinning which signifies this type of recrystallization, the structure is similar in all respects to that found in the original copper slowly cooled from the melt. Similar results were obtained with many of the copper alloys.

Intermediate Stages in Recrystallization.—A tapered sample of the 5 per cent. zinc–copper alloy, in which there was abundant veining, was prepared and cold-rolled until it was flat, so that a specimen was obtained in which the internal strain varied over a wide range in different parts of the specimen. Pieces cut from this were then annealed at from 300° to 600° C. As would be expected, the crystal structure varied across the specimens, the portion which had had most cold reduction consisted of wholly recrystallized material, and that which had had least work was unchanged.

At first, especially when examined at low magnification, there appeared to be no veining in the recrystallized areas although veining was still abundant in the unrecrystallized material, but further preparation and examination at higher powers showed remains of veining principally as isolated particles more or less in line formation as if due either to coalescence or to the solution of the smaller particles constituting the veins. The effect on the sample annealed at 500° C. for 1 hr. is shown in Fig. 27 (Plate XIV). Another feature which was observed was the tendency for a twinning plane in the new crystals to spread from the position where a veining line touched the crystal. It is not possible to say whether this has any significance or whether it is merely a coincidence, but many examples were noticed.

The structure of the sample annealed at 450° C. changed gradually from the fully recrystallized at one end to the unchanged original crystals at the other, with mixtures of the two structures in varying proportions at intermediate positions. It appeared that recrystallization first took place in the interdendritic areas as shown in Fig. 28 (Plate XIV). This was unexpected as the impurities, including oxide, are concentrated in such areas, and impurities are known to increase the recrystallization temperature. The crystals were too small to permit sampling for analysis from the dendritic and interdendritic areas as has been done with large steel crystals,[12] but the quantity of impurities (excluding zinc and oxide) in the interdendritic areas must be extremely small since the alloy was prepared from electrolytic copper and 99·99+ per cent. zinc. The following explanation is put forward. Since the adjacent dendritic and interdendritic areas may be assumed to have undergone the same degree of rolling, the less pure interdendritic material will have work-hardened slightly more than the purer dendritic areas, and this increased work-hardening had the usual effect of reducing the recrystallization temperature. In order to check this view, Vickers diamond pyramid hardness tests were carried out on the different areas using a load of 5 kg. to obtain a small impression, and the results are given in Table VI. Most of the impressions were made on two adjacent crystals (*a* and *b*) which were conveniently each nearly 1 cm. in length and in which slight recrystallization had occurred at one end only.

TABLE VI.—*Variation of Hardness within the Crystals.*

Crystal Examined.	Position in the Crystal.	Vickers Diamond Pyramid Hardness.
Crystal *a*, unrecrystallized	dendritic areas	94·6, 96·5, 94·0
	interdendritic areas	99·0, 100·0
Crystal *a*, partial recrystallization	interdendritic areas, slight recrystallization increasing in quantity with decreasing hardness	77·5, 73·2, 68·8
Crystal *b*, unrecrystallized	dendritic areas	91·7, 93·4, 93·4
	interdendritic areas	98·4, 99·7, 100·0
Crystal *b*, partial recrystallization	as in *a* above	82·6, 71·2
Fully recrystallized area at end of specimen, hardness varying with size of new crystals.		49·7–53·3

The hardness of the alloy is thus different in different parts of the same crystal, and the initiation of recrystallization in the interdendritic areas would appear to be due to their increased work-hardening. The true hardness differences are most probably greater than the figures indicate since some overlapping of the impression with the different areas occurred. The effect of such overlapping is seen in the hardness determination made on the partially recrystallized areas, the higher values corresponding with overlapping of the impression beyond the new crystals.

(7) SUB-BOUNDARY STRUCTURES DUE TO AN ALLOYING CONSTITUENT.

During the examination of a wide variety of alloys, structures have occasionally been observed which show some resemblance to veining but which have obviously not been due to the precipitation of oxides. It is not proposed to consider this type of structure in detail, but a few examples are given to show the difference between this structure and veining. Simply to distinguish between the two structures in the present discussion, the one not due to oxides will be termed the sub-boundary structure as it appeared less characteristic of "veins." The origin of both structures is the same, namely, the precipitation from solution, during cooling, of a substance which is less soluble at lower temperatures. It has been found that the network structure is likely to be more pronounced when the composition is such that there is no excess of the solute at elevated temperatures in the solid state.

An example of a network structure due to an intentional constituent of the alloy has already been mentioned in the discussion of the copper–phosphorus alloys. Veining was observed in the alloy containing a small quantity (0·2 per cent.) of phosphorus. With larger additions, however, the veining was displaced by a similar structure (Fig. 29, Plate XIV) which was associated with free phosphide and which evidently resulted from precipitation of copper phosphide from solid solution.

Several examples of sub-boundary structures have been observed in alloy steels. One type is represented by steels in which a closed γ-loop is formed. When the composition is such that the alloy during cooling does not cross this loop, that is it remains in the α state throughout, sub-boundary structures may be observed if the alloying constituent forms a compound with iron in which its solid solubility decreases with decrease in temperature, and this solubility boundary is crossed by the alloy in cooling to atmospheric temperature. Examples of this type may be found in the alloys of iron with vanadium, molybdenum, tungsten, or chromium. The precipitation of the iron–molybdenum compound in line or network form is shown in Fig. 30 (Plate XIV). In this type of alloy, each crystal contained its own system of sub-boundaries, *i.e.* the network did not cross the crystal boundaries. There are other alloy steels, however, in which it is possible to select a composition where the sub-boundary constituent is thrown out of solution in a network form from the γ-modification of iron, which subsequently undergoes the allotropic change to α-iron at a lower temperature. In this instance, the sub-boundary network is independent of the finally occurring α-iron crystal boundaries. A good example of this is shown in Fig. 31 (Plate XV) of the 2·2 per cent. tantalum–iron alloy, in which the compound Fe_2Ta starts to separate at a temperature nearly 200° C. above the γ–α change point. This particular sample had been annealed in hydrogen at 1220° C. for 1 hr. and cooled in the furnace.

An interesting example of sub-boundary structures in a non-ferrous alloy has been observed in a series of complex aluminium–" bronzes " containing appreciable quantities of nickel and iron. Under certain conditions of cooling from a high temperature, a compound which is probably rich in iron separates from the β-solid solution in a network form as shown in Fig. 32 (Plate XV); the coarse black mark is a quenching crack pointing along the crystal boundary, and it will be seen that each crystal has its own network system. With a higher aluminium content, the stable phase at high temperatures is the γ-solid solution which undergoes a change to δ-solid solution on cooling, but the temperature at which this change occurs is below that at which the constituent is deposited from solution. The sub-boundary constituent remains undisturbed by the phase change as is shown by Fig. 33 (Plate XV), which illustrates an intermediate stage in the breakdown of $\gamma \longrightarrow \delta$ with the " lines " of the network continued across the γ–δ boundary.

Another alloy in which sub-boundary structures may be developed is that of copper containing a little over 2 per cent. beryllium. Cooling in the furnace from 820° C. resulted in isolated deposits of the γ-constituent. By cooling in air small samples about ¼ in. × 1 in. square, the second phase occurred in the form of a small network as shown in Figs. 34 and 35 (Plate XV).

Attempts to obtain similar structures by tempering quenched samples were not successful. Specimens tempered for 1 hr. at 200°–600° C. all showed a " martensitic " structure, although at 600° C. there was evidence of some coalescence, and this was more pronounced after tempering at 700° C. when partial re-solution had occurred. In order to examine the structure of the network at an early stage in its formation, samples were quenched at different intervals during air-cooling. There were only isolated deposits in the sample quenched after 25 seconds, but samples cooled for longer periods showed a network structure which

TABLE VII.—*Effect of Heat-Treatment on Structure and Hardness of* 2·2 *Per Cent. Beryllium–Copper Alloy* (*Vickers Diamond Pyramid*).

Heat-Treatment.	Structure.	Hardness.
Forged and fully heat-treated, as received	$\alpha + (\alpha + \gamma) +$ martensitic structure in α	406
Furnace-cooled from 800° C. at 1° per minute	$\alpha + (\alpha + \gamma) +$ random distribution of γ	144
Air-cooled from 800° C. in about 12 minutes	$\alpha + (\alpha + \gamma) +$ network of γ in α	178
Air-cooled from 820° C. for 25 seconds and quenched	$\alpha + (\alpha + \gamma) +$ isolated needles of γ forming a broken network	113
Air-cooled from 820° C. for 1½ minutes and quenched	$\alpha + (\alpha + \gamma) +$ small fine network of γ in α	142
Air-cooled from 820° C. for 3 minutes and quenched	ditto, slightly thicker network and some isolated particles	164
Air-cooled from 820° C. for 5 minutes and quenched	ditto, network coarser and more isolated particles	184
Quenched after 1 hr. at 840° C.	$\alpha + \beta$	118
Ditto and tempered for 1 hr. at 200° C. and quenched	$\alpha + \beta$ (decomposing) + faint martensitic structure in α	164
Quenched and tempered at 300° C.	ditto, martensitic structure more pronounced	342
Quenched and tempered at 400° C.	ditto	389
Quenched and tempered at 500° C.	ditto	234
Quenched and tempered at 600° C.	ditto	166
Quenched and tempered at 700° C.	ditto + isolated particles of β	128
Quenched and tempered at 800° C.	$\alpha + \beta$	120

was finest in that quenched at a barely visible red heat after cooling for 1½ minutes in air; this structure is shown in Fig. 36 (Plate XV). In order to correlate structure with mechanical properties, hardness determinations were made on the different samples; the results are summarized in Table VII.

The " martensitic " structure thus covers a wide range of hardness, and although there were certain differences in this structure in the samples of different hardness, this aspect was not explored. The network structure corresponded with only moderate hardness values, but such samples were slightly, though definitely, harder than those in which the second phase showed a random distribution.

The main difference between veining and sub-boundary structures as considered in the present paper is that whereas veining is normally removed by a long hydrogen treatment at high temperatures, the sub-boundary structure remains unaffected. The sub-boundary structures also usually consist more obviously of discreet particles; the individual particles constituting the veining structure, on the other hand, are usually only resolved under quite high magnifications. A third difference, only occasionally noticed, is that whereas there is no great difficulty in suppressing veining by quenching from high temperatures, in a few of the alloy steels for example, the sub-boundary structure tended to persist after quenching, apparently on account of the inability of the solid solution to remain highly supersaturated.

(8) Discussion of Results.

Before considering the significance of veining in metals, the results obtained will be summarized and an explanation offered as to the cause of veining. In the first instance the discussion will not include those structures of the type referred to as sub-boundaries which represent an intentional constituent of the alloy.

Veining has been shown to be developed in several pure metals and alloys as a result of slow cooling after the metal or alloy has undergone an oxidizing treatment, either by deliberately oxidizing the melt or by annealing the solid at a high temperature in air or in the presence of its oxide. Conversely, treating the liquid metal with hydrogen or annealing the solid metal at high temperature for a sufficient length of time in an atmosphere of hydrogen results in a material free from veining,* although veining has been observed under similar conditions

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* One exception to this action is given by aluminium as mentioned on p. 227. The temperature of the experiment was well below the temperature above which Al_2O_3 is reduced by hydrogen. No reducing experiments were made with magnesium which is known to form a chemical compound with hydrogen.

of treatment when an oxidizing atmosphere has been employed. This type of veining is intimately associated therefore with the oxygen or oxide content of the material. Secondly, microscopical examination of the veins at a sufficiently high magnification shows that the veining lines are discontinuous and appear to be made up of a series of small particles of a constituent, which, from the previous conclusion, must consist of an oxide of the metal concerned. Thirdly, since severe quenching from a temperature slightly below the melting point prevents the formation of veining, whereas slow cooling develops it, the solubility of the veining constituent in the metal is evidently greater at elevated than at atmospheric temperatures.

The remaining results, namely, (*a*) the effects of low-temperature recrystallization where the veining is left undisturbed by the formation of new crystals (or the growth of the original crystals) at temperatures below the solution temperature of the veining constituent; (*b*) the formation of a fresh system of veining with the recrystallization and growth of new crystals during the high-temperature annealing after cold-work; (*c*) the ability to differentiate between veining and strain-lines after cold-work; (*d*) the action of a powerful deoxidizing agent such as phosphorus in reducing or even eliminating veining; (*e*) the effect of the form in which the veining constituent is present on the hardness of the metal; (*f*) the coalescence of the particles during long annealing at intermediate temperatures; and (*g*) the effect of work in aiding the solution of the veining constituent at intermediate temperatures; these results are all consistent with the view that veining is due to the presence of metallic oxides whose solubility in the metal increases with increase in temperature.

One of the results shown by the present work is that many metals dissolve, especially at high temperatures, small quantities of their own oxides. The action is not limited to pure metals but also occurs with many alloys. Further, although the addition of a deoxidizing agent changes the composition of the oxide, it does not necessarily completely remove the oxide from the alloy. The beneficial influence of deoxidizing agents, therefore, depends on the properties of the oxide formed, and particularly of that in excess of the quantity which can exist in solid solution. It is also evident, from the small quantity of the veining constituent present and from the chemical purity of the metal even when much veining is shown, that the quantitative solubility is very small indeed.

It is of interest to consider the position of veining structures relative to twinning. Twinning may be classed either as stress twinning which is due to release of stress at atmospheric or moderate temperatures, or annealing twinning, which, although also associated with stress, does not develop until the temperature is increased sufficiently to permit recrystallization and, commonly, grain-growth. In the case of stress twinning, the veining as would be expected, passes through the twinned crystals unchanged. On the other hand, twin crystals formed by annealing at high temperatures were observed more often than not to have their own system of veining, although examples were observed where a vein crossed the twin plane. A study of the relationship between veining and twins would probably yield some information as to the temperature of twin formation and growth.

The results of the present investigation confirm those of the previous investigation on veining in iron [1] in which it was concluded that veining was due to the precipitation of iron oxide during cooling and that the solid solubility of the oxide in iron decreases with decrease in temperature. The results also explain the irregularities found in single crystals of copper by W. H. George,[13] who stated that the appearance of the structure (the same as that described in the present paper) suggested that the crystal had broken down into a large number of small ones.

It may be enquired why it is that although the majority of alloy systems contain one or more phase boundaries representing a decreased solubility of a constituent with decrease in temperature, sub-boundary structures are not more frequently observed. There are probably two reasons for this. First, it appears to be necessary to have only a certain small critical amount of the sub-boundary constituent. If much more is present there is too strong a tendency towards either a fine shower precipitate or else a massive one where the constituent is deposited on the initial particles as mentioned previously. Secondly, the rate of cooling is of some importance. In the present work, network structures have been most prominent when cooling has been slow, although an excessively slow cooling may result in too much coalescence to show any network. The optimum cooling rates differ for the different alloys, and it has been shown that whereas furnace cooling which corresponds to a rate of from 6° to 2° C. per minute is satisfactory for many alloys, others such as the β-brass and beryllium–copper require to be air-cooled at as high a rate as 300°–100° C. per minute in order to prevent coalescence.

Although the conditions favouring the precipitation of oxides or other compounds in a network form have been considered, no reason has been adduced as to *why* the deposits should assume a network form. This aspect of the subject and the possible relation between veining and mosaic structures of metals are discussed elsewhere.

SUMMARY.

(1) A network structure, termed veining, which occurs within the crystals has been studied in several pure metals and in many alloys of copper.

(2) Veining has been shown to be due to the precipitation from solid solution, in a network form, of the oxide of the metal during cooling.

(3) Many metals in the solid state can dissolve small quantities of their own oxides.

(4) The solid solubility of a metallic oxide in the metal is very small and decreases with decrease in temperature.

(5) Alloys are also capable of dissolving only small quantities of an oxide; the oxide which is formed depends on the character of the added element.

(6) Structures somewhat similar in appearance to veining and referred to as sub-boundary structures have been observed in a number of alloys, and are due to the precipitation during cooling, not of oxide, but of a compound of the metals concerned.

(7) Veining can be removed by a hydrogen treatment at high temperatures, in the solid or in the liquid state, provided that the oxide which is responsible for the veining can be reduced by hydrogen.

(8) The formation of veining structures can be suppressed by quenching the alloy from a sufficiently high temperature in the solid state.

(9) Veining can be released in a quenched specimen by slow cooling from the quenching temperature or by annealing at a suitable intermediate temperature.

(10) The addition of a small quantity of an alloying element of the deoxidizing type to copper was found to facilitate the development of veining. Large additions had the reverse effect.

(11) Solution of the veining constituent in material recrystallized at intermediate temperatures is aided by preliminary deformation.

(12) When an alloy having a pronounced dendritic structure is rolled and then annealed, recrystallization is initiated in the interdendritic areas.

(13) The hardness of the alloy has been shown to be affected by the form in which the oxide occurs, a network form corresponding with higher hardness.

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REFERENCES.

[1] L. Northcott, *J. Iron Steel Inst.*, 1932, **126**, 267.
[2] H. Esser, *Z. anorg. Chem.*, 1931, **202**, 73.
[3] N. A. Ziegler, *Trans. Amer. Soc. Steel Treat.*, 1932, **20**, 73.
[4] K. Schönert, *Z. anorg. Chem.*, 1926, **154**, 220.
[5] F. N. Rhines and C. H. Mathewson, *Trans. Amer. Inst. Min. Met. Eng.*, 1934, **111**, 337.
[6] H. Wrighton, *J. Roy. Microscop. Soc.*, 1933, **53**, 328.
[7] A. Sieverts and J. Hagenacker, *Z. physikal. Chem.*, 1909, **68**, 115.
[8] E. W. R. Steacie and F. M. G. Johnson, *Proc. Roy. Soc.*, 1926, [A], **112**, 542.
[9] E. W. R. Steacie and F. M. G. Johnson, *Proc. Roy. Soc.*, 1928, [A], **117**, 674.
[10] F. G. Keyes and H. Hara, *J. Amer. Chem. Soc.*, 1922, **44**, 479.
[11] N. P. Allen, *J. Inst. Metals*, 1932, **49**, 317.
[12] L. Northcott, *J. Iron Steel Inst.*, 1934, **129**, 151.
[13] W. H. George, *Nature*, 1935, **136**, 392.

APPENDIX.

PREPARATION OF SPECIMENS FOR MICROEXAMINATION.

Polishing.

Standard methods of metallographic polishing have been followed, a liquid metal polish being used on a soft cloth for the final hand polishing. Repeated polishing and etching have nearly always been necessary, as the presence of many scratches seriously interferes with the development of veining.

Etching Reagents.

As some etching reagents develop the veining structure more easily than others, those found most suitable are indicated below. Except with certain "easy" alloys, prolonged etching is usually necessary, and re-polishing with metal polish must be resorted to as soon as the etching-pit structure is developed.

Copper.—10 per cent. ammonium persulphate in 50 per cent. ammonium hydroxide very satisfactory. Diluting the solution reduces the tendency towards etching-pit formation but the veining structure is then left in poor contrast. Ferric chloride (10 grm. $FeCl_3$, 30 c.c. hydrochloric acid, 120 c.c. water) gives poor results and veining is not developed by nitric acid, caustic potash, or ammonia solution.

Cadmium.—1 per cent. nitric acid in alcohol followed by ammoniacal ammonium persulphate followed by a light etch with dilute alcoholic ferric chloride to clear the surface. This triple etching proved more satisfactory that a single etch.

Aluminium.—Dilute hydrofluoric acid in water.

Zinc.—10 per cent. sulphuric acid containing one or two crystals of chromic acid is very good; 5 per cent. nitric acid in alcohol is fairly good.

Silver.—10 per cent. sulphuric acid containing one or two crystals of chromic acid is good; nitric acid and ammonium persulphate are unsatisfactory.

Magnesium.—5 per cent. nitric acid in alcohol.

Antimony.—30 per cent. hydrochloric acid containing about 5 per cent. hydrogen peroxide.

Nickel.—Aqua regia.

Iron.—5 per cent. nitric acid in alcohol.

Mild Steel.—Alternate etching with ½ strength Stead's reagent and picric acid.

Stainless Steels.—10 per cent. ammonium persulphate in 10 per cent. hydrochloric acid. The acid concentration can be increased if the action is found too slow.

Alloy α-Steels.—Prolonged etching in 5 per cent. nitric acid in alcohol.

High-Nickel Copper–Nickel Alloys.—Ferric chloride as described for copper.

Low-Nickel Copper–Nickel Alloys.—10 per cent. ammonium persulphate in 20 per cent. ammonium hydroxide or ferric chloride.

Copper–Zinc Alloys.—Ammonium persulphate solution as for copper was found most satisfactory. The ferric chloride solution required prolonged etching and developed the dendritic structure excessively.

Copper–Tin Alloys.—Ammonium persulphate as above. For the high-tin alloys, acid persulphate solution (10 per cent. ammonium persulphate in 30 per cent. sulphuric acid) is preferable.

Copper–Aluminium Alloys.—Prolonged etching with the acid persulphate solution.

Copper–Silicon.—Ammoniacal ammonium persulphate as for copper–zinc, followed by washing in very dilute hydrofluoric acid solution. Acid persulphate is satisfactory for alloys containing up to about 1 per cent. silicon.

Copper–Beryllium.—Dilute alcoholic ferric chloride solution or 5 per cent. alcoholic nitric acid.

Copper–Phosphorus and Copper–Arsenic.—Ammoniacal persulphate followed by a light etch with acid persulphate to clear. Acid persulphate solution slightly less satisfactory.

False Networks.

It may be as well to point out that examples have been observed of a network structure due to cracks in a surface oxide film formed during or after etching with ammoniacal persulphate solution. Some alloys, *e.g.* the alloys of copper containing aluminium, silicon, or tin, are more prone than others to film formation. The film is easily removed by washing with dilute hydrofluoric acid or a strongly acid solution of persulphate. A simple test is to examine the specimen at low magnification at the same time trying to remove the "network" with a needle or sharp knife; a film is easily detected.

DISCUSSION.

(*Condensed.*)

Dr. C. J. Smithells,[*] M.C. (Member of Council): The author makes out a very good case for believing that the sub-boundaries shown in his illustrations are due to the precipitation of oxide particles, but I am not satisfied that this is the whole story. In the first place, his distinction between sub-boundaries and veins is very arbitrary. He distinguishes between them chiefly according to whether they are removed by hydrogen or not and the size of the particles in them. This is rather like saying that veins are sub-boundaries containing oxide particles; and, since there are many other cases of sub-boundaries in which this does not occur, the distinction does not help us to understand the nature of them any better. In 1927, Rooksby and I[†] showed that the orientation of the sub-grains was uniform inside each crystal; therefore, unless there is something in the boundary, it may not be visible on etching.

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[†] *Nature*, 1927, **120**, 226.

There are many conditions under which the main grains or crystals of a metal are in fact broken up into small fragments of practically the same orientation, which are not readily observed. The recent work of Smekal and Zwicky gives evidence of this, and the best summary of the evidence for the mosaic or broken-up structure is in a monograph written by Dr. Hume-Rothery and recently published by the Institute.

Fig. A (Plate XVI) shows a typical sub-boundary structure in tungsten which was melted in hydrogen and cast. Those sub-boundaries cannot possibly be due to tungsten oxide, which is relatively volatile, but I see no reason to distinguish them from any of the author's examples. The point of general interest is, how did the oxide or other particles which make the boundaries visible, arrive at these boundaries? It is well known that oxides and other non-metallic substances can migrate in a solid metal, but there does not seem to be any really satisfactory explanation of the mechanism.

Figs. B and C (Plate XVII) show some electrodeposited chromium which when polished had originally no visible structure, but after heating in hydrogen for 10 minutes particles of chromium oxide appear, more or less in pattern with the grain boundaries. After annealing for a further hour in hydrogen at 1000° C., they have obviously increased in size and form a typical sub-boundary structure. It is clear, therefore, that these non-metallic substances can move about inside solid metal, and that is really the point of greatest interest.

In conclusion, therefore, I believe that the sub-boundaries are quite a normal structural feature. They may be the result of strain during cooling, which can be made visible only when some second constituent is concentrated in them. This is often—but not necessarily—the oxide of the metal. The point that calls for investigation is how these substances reach these boundaries when they are precipitated from solution.

Colonel N. Belaiew,* C.B. (Member): The author has studied the occurrence in metals and alloys of a network structure within the crystal grains. Thus the relation, if any, between that network and the allotropic transformation, in pure metals, or the occurrence of a deposit, in alloys, is not to be sought in the simple boundary relations, but elsewhere. Most tantalizingly, at the very end of his paper, the author mentions that the possible relation between veining and the mosaic structure will be discussed at some future date.

It might be mentioned, however, that when studying structures similar in appearance to veining, but due to the precipitation of a metal compound, one also observes a relation between such a structure and the mosaic structure. A rather striking analogy is provided in the case of Damascene steels. As in the case of veining structures, Damascene steel shows before forging, either a network or else a structure resembling that of Fig. 3 of this paper—a structure composed of apparently continuous filaments. The formation of the Damascene structure can, moreover, be suppressed by quenching and re-formed by appropriate annealing. The analogy, however, does not stop even there, and microscopical examination reveals the striking fact that the globules in the veins, as for instance those shown in Fig. 10 of the paper, are of the same order of magnitude as the shower-particles in martensite which have been studied by Lucas and myself. I venture to suggest, therefore, that the analogy between the genesis of veining structures and Damascene steel is not only apparent but real, and that a most useful line of approach to such studies is their relation to the mosaic structure.

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* Paris.

Fig. A.

FIG. B.—Electrodeposited Chromium Annealed in Hydrogen for 10 Minutes at 1000° C.

FIG. C.—As above, after Annealing for 1 Hr.

Dr. Northcott (*in reply*): In answer to Dr. Smithells, I would say that the only differentiation between veining and sub-boundary structures is that the sub-boundary is due to an intentional constituent of the alloy and not an oxide. The structures to which Dr. Smithells has referred are therefore sub-boundary structures and are similar to those given in the paper. He may be interested in some remarks by myself on mosaic structures which are already in the press.

CORRESPONDENCE.

The Author (*in further reply*): I agree with Dr. Smithells that the distinction made in the paper between veins and sub-boundaries is purely an arbitrary one; it was made simply to distinguish between sub-boundaries containing oxide particles and those containing another constituent. The statement that Dr. Smithells and Mr. Rooksby showed the orientation of the sub-grains to be uniform inside each crystal is incorrect. To quote from the reference given: "The diffraction pattern obtained is practically the same as that given by a true single crystal, but the spots are slightly more spread. This indicates that the small grains formed by the sub-boundaries have a *nearly, but not quite*, uniform orientation in each crystal." The italics are mine. These results are in accord with my own work on the subject which will shortly be published and in which the small but definite inclinations of the sub-grains to one another has been measured. The examples of network structures in tungsten and chromium given by Dr. Smithells are representative of sub-boundary structures and behave quite in accord with the examples given in the paper.

The remarks by Colonel Belaiew on the similarity between veining and structures in Damascene steels are very interesting and it is hoped to obtain a suitable sample of this type of steel for examination.

METHODS FOR THE EXAMINATION OF THERMAL EFFECTS DUE TO ORDER-DISORDER TRANSFORMATIONS.*

By C. SYKES,† Ph.D., Member, and F. W. JONES,‡ B.Sc.

Synopsis.

This paper describes an experimental method particularly suitable for the determination of thermal changes in order-disorder transformations occurring in the temperature range 100°–500° C.

I. Introduction.

In a previous paper [1] by one of the present writers, the various standard cooling curve methods for investigating the effect of transformations on the heat content of metals and alloys were considered with particular reference to transformations involving atomic arrangement within a homogeneous solid solution. It was shown that if the Bragg–Williams [2] theory of the process was sound then standard cooling curve methods were likely to give misleading results, when applied to such transformations, unless special precautions were taken. A modified cooling curve method was proposed, and this, together with a new method for the quantitative determination of specific heat, was used to investigate the transformation in β-brass. The results obtained were suitable for direct comparison with the calculated results of Bragg and Williams [3]; the agreement is such that there can be little doubt that the transformation is an atomic rearrangement process.

A large number of alloys exhibit changes in physical properties similar to those observed in β-brass, and it is reasonable to suppose that in such cases the observed changes in properties are due to atomic rearrangement. In fact, such effects may be expected in binary solid solutions whenever the constituent metals are present in a simple whole number ratio by atoms. Whether such transformations can be

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observed or not depends, as Bragg and Williams [3] have pointed out, on two factors : (1) the energy of interchange (*Vo*) * between an ordered and a disordered position (when the alloy is completely ordered) and (2) the speed of diffusion in the alloy. The energy *Vo* is related to the critical temperature *Tc* at which the rearrangement starts on cooling—4*KTc* is approximately equal to *Vo*, *K* being Boltzmann's constant. Consequently it follows that when *Vo* is small *Tc* will occur at a fairly low temperature.

The speed of diffusion in the alloy at the critical temperature *Tc* is important since it governs the rate at which the alloy attains equilibrium. Bragg and Williams consider this factor in terms of a temperature T_1 at which the time of relaxation is one second, *i.e.* the speed of diffusion is such that the alloy relaxes to equilibrium to an extent $\frac{1}{e}$ in one second.

The types of transformations likely to be observed in practice may now be considered. Where *Tc* is small and/or T_1 is large, the chances are that no transformation will be observed except at cooling rates so slow that the rate of heat evolution is too small to be detected. When *Tc* is large and T_1 small the transformation will occur independently of the cooling rate and will be completely reversible under ordinary experimental conditions : β-Brass may be quoted as an example of this type. Finally, when T_1 is nearly equal to *Tc*, the transformation will occur, but will be affected by the experimental conditions, and, in general, the course of the transformation will not be reversible : Fe_3Al, Cu_3Au, Cu_3Pd, &c., may be quoted as examples of this type. Quantitative investigations of such transformations will necessitate special procedure to eliminate effects due to the fact that the specimens will require a finite time to get into equilibrium.

Apart, however, from the possible difficulties introduced by the slow rate of diffusion other effects arise due to the ordering process itself. In β-brass which has the approximate composition CuZn by atoms, the number of positions of order is one-half the total number of atomic sites ($r = \frac{1}{2}$), whereas in Cu_3Au, for example, the number of " ordered " positions for the gold atoms is one-quarter the total number of atomic sites ($r = \frac{1}{4}$). Theory indicates that in the case of CuZn the degree of order increases continuously from the critical temperature to lower temperatures, and consequently there is an increase in the specific heat at the critical temperature but no latent heat. In the case of Cu_3Au, however, the degree of order increases from zero immediately above *Tc* to a value of approximately 0·35 immediately below, and this involves

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* The Bragg–Williams nomenclature is used throughout.

latent heat. Owing to this large discontinuity in the degree of order–temperature curve, a certain amount of hysteresis[3, 4] is to be expected at the critical temperature. Finally, other effects due to the presence or absence of nuclei[4] are to be anticipated.

It is the purpose of the present paper to describe an experimental arrangement capable of verifying in a quantitative manner the various theoretical predictions mentioned above. The experimental method used in the investigation of the β-brass transformation has been considerably improved and extended for this purpose. It is described in detail, together with a critical estimate of the accuracy of the heat measurements.

The following aspects of the order–disorder transformation are dealt with experimentally: (*a*) the specific heat–temperature curve, (*b*) the determination of the energy content–temperature curve, and (*c*) the behaviour of the alloy at the critical temperature.

II. Experimental Arrangements.

(a) *Principle.*

In order to investigate transformations of the type already discussed, it is clear that the experimental method must allow the heat measurements to be made whilst the temperature is *continuously* varied. Calorimetric measurements of heat content by quenching in water will merely give the effect of the degree of order on the normal specific heat, and specific heat measurements at constant temperature will tend to give a value which will approximate to the Dulong and Petit specific heat as the speed of diffusion in the alloy decreases.

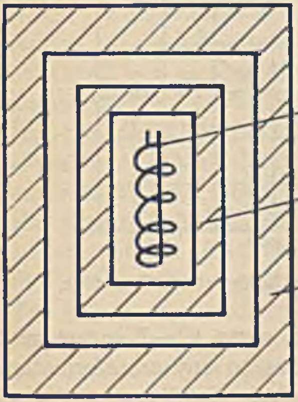


Fig. 1.

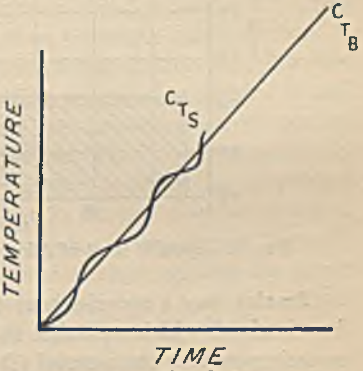


Fig. 2.

The principle used in this work is the same as that used in the investigation on β-brass. The specimen S (see Fig. 1) is mounted inside a closed copper cylinder B and thermally insulated from it. A Nichrome coil C enables the specimen to be heated independently. Now, suppose the copper cylinder B is heated at a uniform rate according to the line C_{T_B}, then by suitable manipulation of the power input to the coil C the temperature of the specimen S can be made to follow the curve C_{T_S} (Fig. 2). At the points of intersection of the two curves $T_S = T_B$, and no external heat is received by the specimen. Consequently the following equation is valid:

$$Q = MCp\left(\frac{dT_S}{dt}\right)_{T_S = T_B} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Q is power supplied to the coil; M is the mass of specimen, and Cp is the instantaneous specific heat at the temperature T_S.

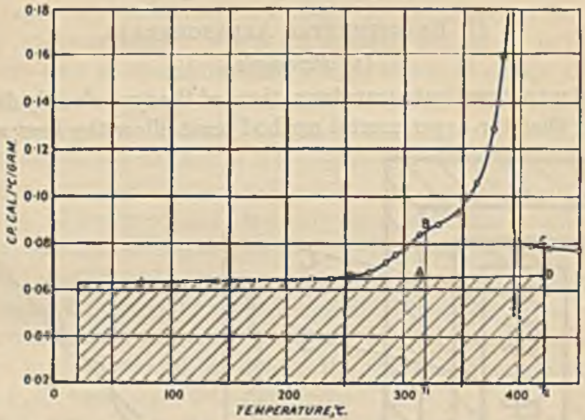


Fig. 3.—Specific Heat of Alloy Cu_3Au After Cooling at 30° C. per Hr.

In this way a specific heat–temperature curve (Cp–T curve) may be obtained which contains the effects due to any transformation superimposed on the normal (Dulong and Petit) Cp–T curve. Fig. 3 shows a specific heat–temperature curve taken on the alloy Cu_3Au after cooling from 450° C. at 30° C. per hr. Up to 200° C. approximately the Cp–T curve is substantially linear, the alloy is frozen, and the normal specific heat is observed. Above 200° C. the alloy begins to disorder and the apparent specific heat increases. At about 375° C. the specific heat increases extremely rapidly as the critical temperature is approached, and then decreases to a low value when the alloy is completely disordered.

In order to determine the energy of the transformation the curve shown in Fig. 3 may be integrated from room temperature to a temperature higher than T_C, say 420° C., where the alloy is disordered and the shaded area which is a reasonable approximation to the normal energy content of the alloy then subtracted. Since a large proportion of the heat of transformation is in the immediate vicinity of the critical temperature, an accurate knowledge of the shape of the curve in this region is required. This can be obtained if equation (1) is supplemented by corrections (*a*) for latent heat when it occurs and (*b*) for the fact that T_S may sink appreciably below T_B. Suitable methods for the determination of these corrections are available, and consequently the total energy of the transformation corresponding to any initial condition of the specimen may be determined experimentally.

If the time of relaxation is very small (β-brass) all Cp–T curves for a given specimen will be identical, and the energy of the transformation as a function of temperature may be determined directly from such a curve, *e.g.* the anomalous energy content at temperature T_1 due to the order–disorder change is given by the area *ABCD*. In the case of Cu_3Au, however, this method is not necessarily correct, since it is probable that at no temperature below T_C is the alloy in precise equilibrium whilst the experiment is in progress. A solution of this difficulty is as follows; the specimen is annealed at temperature T_1 *in situ* in the apparatus until it is in equilibrium. It is then heated to a temperature T_2 slightly above T_C, where it becomes completely disordered. Provided that the energy necessary to do this can be measured, a number of such experiments in which T_1 is varied enable the equilibrium energy–content curve to be determined. The arrangement, Fig. 1, is convenient for this purpose. A constant current is supplied to the coil C and this is switched on and off at such intervals that T_S fluctuates within $\pm$ 0·1° C. of T_B, whilst the temperature of the apparatus is raised from T_1 to T_2. The current is passed through a voltameter which enables the power input to be integrated in a very simple manner. (A Cp–T curve could be obtained and integrated. This introduces not only the problem of corrections at the critical temperature for latent heat, but also a practical difficulty of measuring Cp when $\frac{dT_B}{dt}$ is changing rapidly.) The energy content due to thermal agitation alone may be obtained from Cp–T curves by suitable extrapolation and the anomalous energy content corresponding to equilibrium conditions thus ascertained.

Finally, the apparatus can also be used in the well-known manner for the determination of specific heat at "constant temperature." The copper block and specimen are allowed to attain a steady temperature, and the rate of increase in temperature of the specimen noted for a given power input.

(b) *Apparatus.*

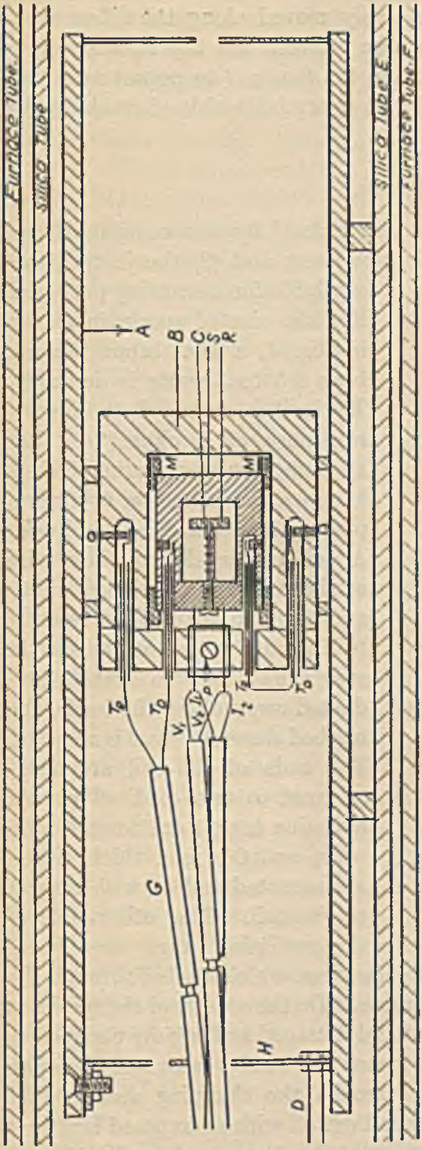
General Assembly.—Fig. 4 shows the essential features of the assembled specific heat apparatus. The specimen S and copper block B are hollow cylinders, solid at one end and closed at the other by lids. The specimen complete with heating coil C is mounted on thin mica vanes M. The lid to the copper block is in two semicircular parts, and the leads to the coil are rigidly fixed to the lower half by means of the clamp P. The block is held inside a copper container A on supports consisting of short heat-insulating pegs. Eight wires must be taken out of the container A; two for the differential thermocouple measuring the temperature difference between block and specimen T_D, two for the thermocouple measuring the temperature of the copper block (not shown), two current leads $I_1 I_2$, and two voltmeter leads $V_1 V_2$. These wires are protected from direct radiation from A by refractory tubing G.

In order to increase the sensitivity of the apparatus, the above arrangement is operated in a vacuum of 10^{-3} mm. or less. The container A is carried by a steel rod D which is firmly fixed to the steel flange O. A silica tube closed at one end encloses the container (see Fig. 5). The open end is sealed to a water-cooled steel flange O_1, and a demountable vacuum joint can be made between O and O_1 by means of Apiezon sealing compound " Q." The silica tube may be evacuated through the pipe W. The pumping equipment consists of an " 02 " oil diffusion pump, a phosphorus pentoxide trap, and a rotary oil pump.

The cold-junctions of the thermocouples are located inside the vacuum chamber. A side tube U carrying one section of an oil-sealed union is welded to the tube W. The thermocouple wires are passed through the side tube and soldered to copper wires connected to the multiple seal N. The other portion of the union Y is sealed to a glass test-tube Z, filled with Apiezon oil, and the union completed. A Dewar flask K containing ice is then mounted around the test-tube.

The leads $I_1 I_2$ and $V_1 V_2$ are connected directly to the multiple seal N, which is protected from draughts by means of a box filled with cotton wool. The metal tap L_1 enables the silica tube to be shut off for long periods under vacuum. Discharge tubes X_1 and X_2 allow the gas pressure to be observed, and facilitate the elimination of leaks. A side tube between L_1 and L_2 permits an inert gas to be admitted to the apparatus to any desired pressure.

For heating the apparatus, a tubular resistance furnace is used


Furnace Tube.
Silica Tube
Silica Tube E
Furnace Tube F
A
B
C
S
R
M
M
O
T_0
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V_1
V_2
I_1
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T_0
G
H
D

Fig. 4.

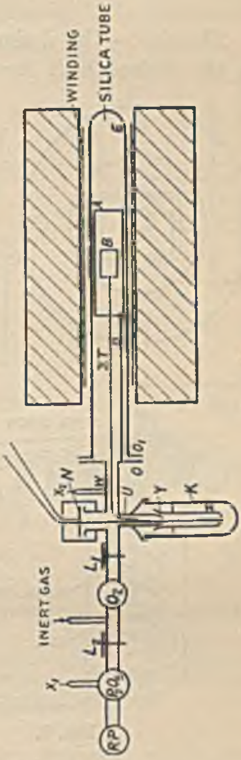
WINDING
SILICA TUBE
E
B
ST
O_1
O
N
X_2
W
U
Y
K
L_1
INERT GAS
O_2
L_2
X_1
RQ_1
RP

Fig. 5.

having a nickel–chromium winding on an Alundum tube. It is mounted on wheels and can be easily moved along the silica tube. A short length of thick rubber tube between the tap L_2 and pump " 02 " allows sufficient movement to the flange O to permit assembly of a silica tube and furnace without appreciable risk of cracking the silica tube.

(c) *Details.*

The Coil.—The design of the coil is fixed by two considerations: (1) the desired heat input to the specimen, and (2) the instruments available for measuring purposes. For the size of specimen shown in Fig. 4, a heat input ranging from 0·5 to 3 watts is desirable. The coil is arranged to have a resistance of 3 ohms., so that an ammeter maximum reading 1 amp. and a voltmeter maximum reading 3 v. could be employed. A coil of nickel–chromium wire of about 15 cm. developed length and 0·25 mm. diameter is used.

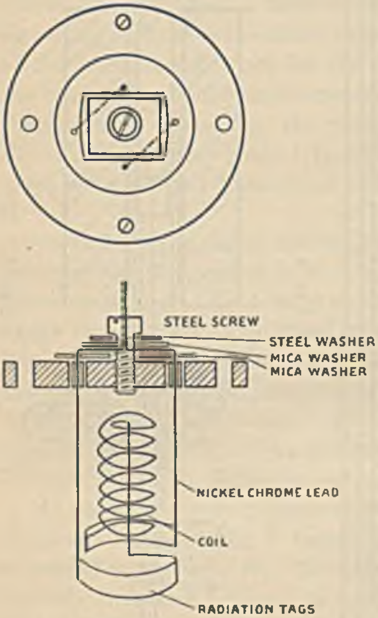

Fig. 6.

In order to mount the coil in such a way that no heat is conducted away along the leads, the method shown in Fig. 6 is adopted. The ends of the coil are hard-soldered to two oxidized copper radiation tags, 1 cm. long, 4 mm. wide, and 0·1 mm. thick, which are mounted end-on with respect to the coil. The other ends of the radiation tags are hard-soldered to 0·8 mm. nickel–chromium wires, which are led through the lid of the specimen by thin silica bushes. On the outside of the specimen these two Nichrome wires are bent and flattened and, rigidly clamped to the lid between mica washers by means of a steel washer and clamping screw. The wires after passing through the clamping arrangement are bent at right angles to the lid and cut off with an exposed length of about 3 mm. Two nickel–chromium strips, 3 mm. wide and 0·15 mm. thick, are then hard-soldered to the wires, and these pass out through the lid of the copper block and are clamped at P between mica washers.

Preparation of Specimen, Copper Container, and Copper Block.—It is tacitly assumed in the statement of the experimental method that the temperatures throughout specimen and container are uniform. Certain precautions are necessary in order to achieve this. The outer copper container is closed at both ends with copper screens. The outside surfaces are kept reasonably clean whilst the inner surfaces are coated with an adherent layer of "Aquadag."* Similarly the outer surface of the copper block is coated with "Aquadag." In this way the temperature difference between the container and block necessary to produce a given heating rate is materially reduced, and experimental conditions are more stable. The coil *C* is made from wire with black oxidized finish, and the inside of the specimen is coated also with "Aquadag." The outer surface of the specimen and inner surface of the block *B* are highly polished.

Temperature gradients between the lids and main body of both specimen and block must be made as small as possible. The adjacent surfaces on specimen and block are ground so that they are flat to within five fringes of sodium light before being held together by steel screws.

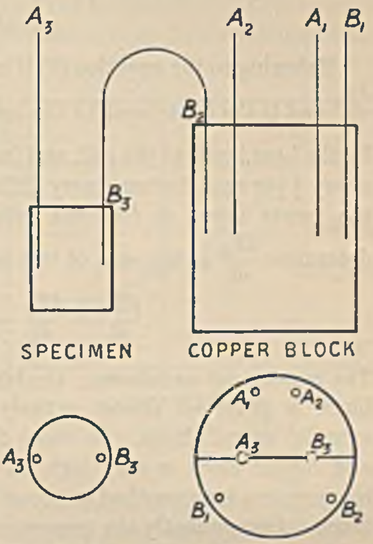

Fig. 7.—Arrangement of Thermocouple Wires.

A_1B_1 Thermocouple for Measurement of T_B. $A_2B_2B_3A_3$ Differential Couple for Measurement of (T_S-T_B).

Thermocouples.—Certain difficulties in the use of thermocouples were experienced when operating the apparatus *in vacuo*, owing to unsatisfactory contacts which gave rise to discontinuities in temperature–time curves. The usual method of passing a thermocouple down a small hole into the centre of the specimen and packing it in position is unsuitable; the convection currents due to the air normally present must conduct a large proportion of the heat received by a thermocouple.

The final arrangement for the thermocouples was as shown diagrammatically in Fig. 7. The wires were not welded—the end of each wire

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* A trade name for a preparation of colloidal graphite. This is applied to the surfaces by means of a brush. Preliminary heating of the surface to 100° C. is an advantage.

was obtained in the copper block from say 100°–450° C. In air this would, of course, present no difficulties, but *in vacuo* it is not straightforward. By trial and error the present method has been arrived at, and this is reasonably satisfactory. The furnace is rapidly heated to 280° C. (in about 10 minutes) and then maintained at this temperature by means of a Cambridge regulator which is energized by a thermocouple on the winding of the furnace. The block heats up very slowly at first, and then more rapidly until finally the heating rate approaches a maximum. At this stage (at about 100° C.) the regulator is connected to a clock so that the furnace temperature is increased continuously at 70° C./hr. From 50° to 450° C. the time required to heat the block through 0·1 mv. is then constant to within ± 7 per cent.

The coil is fed from a high-capacity storage battery. It is essential to be able to vary the current continuously, and for this purpose a special rheostat has been constructed in which the resistance wire is wound from an ebonite spool on to a nickel-plated brass spool. The current and voltage are directly measured on instruments which can be read comfortably to 0·1 per cent. of full-scale deflection.

(b) *Experimental Observations and Results.*

In order to make clear the experimental procedure a section is given of the results obtained on a copper–gold specimen of the composition corresponding to Cu_3Au as cooled at 30° C./hr. (see Tables I–III). Table I deals with the heating rate of the copper block, column 4 gives an averaged time interval which is the mean of five adjacent readings in column 3.

Table II lists the power input to the coil and its effect on the temperature difference as determined by the galvanometer deflection. A positive reading means that the specimen is hotter than the block and a negative reading indicates that it is cooler. 1° C. corresponds to 2·7 cm. deflection, so that with the exception of the region in the immediate neighbourhood of the critical temperature the temperature difference is seldom in excess of 0·3° C.

Table III gives the results as determined from the observations in Tables I and II. Columns 3 and 5 are obtained from 2 and 4 using the calibration curve of the thermocouple. Column 5 after correction from 9 gives the heating rate of the specimen, column 10.

Now
$$\frac{IV}{J} = MCp\frac{dT_S}{dt} \, . K$$

I is current in amp., V is the the voltage across the coil, $J = 4{\cdot}180$.

K varies from 0·975 to 0·970 and is a factor which takes into account corrections for finite resistance of voltmeter, voltmeter and ammeter

TABLE I.

Col.															
1. mv.	8·3	8·4	8·5	8·6	8·7	8·8	8·9	9·0	9·1	9·2	9·3	9·4	9·5	9·6	9·7
2. Time	12.40.45	42.19	43.52	45.24	46.57	48.30	50.02	51.36	53.10	54.43	56.16	57.48	59.21	13.00.53	02.25
3. Seconds/0·1 mv.	94	93	92	93	93	92	94	94	93	93	92	93	92	92	
4. Seconds/0·1 mv. Mean of 5 readings	93·0	93·0	93·0	92·6	92·8	93·2	93·2	93·2	93·2	93·0	92·6	92·4	92·4	92·6	

TABLE II.

5. Time	12.41	12.42	12.43	12.44	12.45	12.46	12.47	12.48	12.49	12.50	12.51	12.52
6. Galvo. Deflection, cm..	+0·11	+0·12	+0·15	+0·18	+0·18	+0·18	+0·18	+0·18	+0·19	+0·20	+0·19	+0·17
7. Watts.										0·588×1·322=1·072		

5. Time	12.53	12.54	12.55	12.56	12.57	12.58	12.59	13.00	13.01	13.02	13.03
6. Galvo. Deflection, cm..	+0·13	+0·11	+0·10	+0·09	+0·09	+0·04	+0·04	+0·05	+0·08	+0·08	+0·08
7. Watts.											

TABLE III.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.
Time.	Temperature of Block T_B.		Heating Rate of Block.		$(T_S - T_B)$.		$\frac{d}{dt}(T_S - T_B)$		$\frac{dT_S}{dt}$ °C./second	Q Watts.	$[M\ Cp.]$ Cal./°C.	$[M\ Cp]_R$. Cal./°C.	$M\ Cp$. Cal./°C.	Cp.
	mv.	°C.	seconds/mv.	°C./second × 10⁴.	cm	°C.	cm./minute.	°C./second × 10⁶.						
12.41	8·32	206	930	2678	+0·11	...	0·00	...	2678	1·071	9·33	9·33	8·98	0·0642
12.51	8·96	222	932	2667	+0·10	+0·1	−0·01	−6	2661	1·071	9·39	9·38	9·03	0·0645
13.01	9·60	238	925	2662	+0·08	...	+0·01	+6	2668	1·071	9·37	9·37	9·02	0·0645

corrections, &c. This equation (assuming $K = 0{\cdot}975$ throughout) gives the values of MCp in column 12, these are given a small radiation correction when $T_S \neq T_B$, giving column 13. There is a certain amount of extraneous matter, iron screws, silica quill, &c., in the specimen assembly which has a thermal capacity of 0·351 cal./° C. This is subtracted, giving column 14. These results are corrected for the slight variation of K and divided by the weight of the specimen, *viz.* 139·0 grm., giving the final column. The results are given graphically in Fig. 3. The reproducibility of experimental results in the case of specific heat measurements is about ± 3/4 per cent. at 450° C.

Figs. 9 and 10 illustrate the effect of other heat-treatments on the transformation. Fig. 9 deals with the alloy as quenched from 450° C., and Fig. 10 as cooled at 1500° C./hr. through the critical temperature.

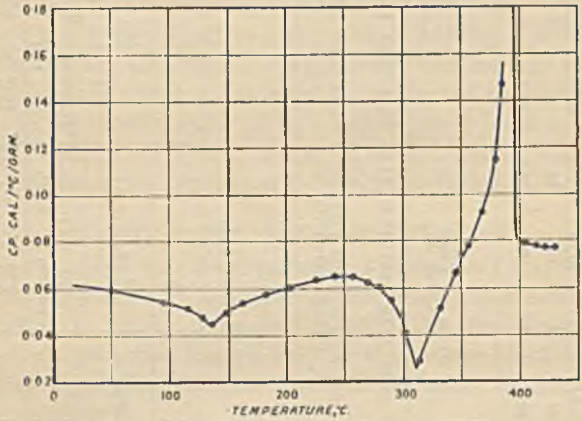

Fig. 9.—Cu_2Au as Quenched from 450° C.

Approximate energy calculations can be made from such Cp–T curves, and though they correspond to metastable states sometimes the information is important. In such cases it is preferable to integrate the power input rather than measure the area of the derived Cp–T curve, since this cannot always be obtained in sufficient detail at the critical temperature (*e.g.* a Cp–T curve including latent heat might lead to considerable inaccuracies). For this reason the authors have made it a custom always to change the power input (when it has to be changed) at the half-minute. The integration can then be carried out with reasonable accuracy. For example, if the power input to raise the specimen from 9·1 to 17·26 mv. is calculated for the 30° C./hr. experiment, the result is 2585 cal. A radiation correction should be made. This is usually small since the experimenter can arrange that the specimen stays on one side of zero roughly as long as does the other. In the particular experiment the total radiation correction is 7 cals., and this is all located at the critical temperature. In short, it is doubtful whether the calculation of this correction is worth while except at the critical temperature.

The energy contents determined in this way are in reasonable agreement with the direct energy measurements as will be shown later. The authors are of the opinion that the direct method is more reliable.

Fig. 10.—Cu_3Au Cooled Through Critical Temperature at 1500° C. per Hr.

IV. Direct Energy Content Determinations.

(a) *Method.*

In experiments of this type a mercury switch is placed in the coil circuit, and is operated by hand in such a way that the temperature of the specimen fluctuates within $\pm \frac{1}{10}$° C. of the block temperature as this is increased. Practically, this means that the image of the cross-wire on the galvanometer scale must be kept within 3 mm. of either side of the zero—a very easy thing to do. The current through the coil (which is held constant throughout the experiment) is simultaneously passed through a voltameter. The weight of copper deposited gives the total time the coil is energized. As the weight of copper deposited per amp.-hr. varies slightly with the actual physical dimensions of the voltameter, it is necessary to calibrate the particular voltameter used. Once this has been done the calibration appears to remain the same to within 0·05 per cent. over long periods. The current must be so chosen that it is sufficient to heat the specimen at 1·5° C./minute when the specific heat is a maximum. In cases where latent heat is given out this is not possible, but by a combination of maximum current (1 amp.) and reduction of heating rate it is possible to arrange that the maximum galvanometer deflection is smaller than the full-scale reading. Readings of this deflection then enable a suitable correction to be made.

At the beginning and end of an energy content run, it is important that the temperature difference between specimen and block should be zero and that the coil should contain no " stored energy." Owing to the rapid response of the thermocouples no difficulty is experienced in manipulating the switch so that as the block passes through the temperature limits the specimen is within 0·04° C. of the block temperature.

(b) *Examples.*

Specimen cooled at 30° C.*/hr.*—The current supplied to the coil was 0·800 amp., the mean voltage 2·456, and the energy was determined between 9·1 mv. and 17·26 mv. The weight of copper deposited was 1·472 grm., and 1 amp.-hr. deposits 1·178 grm.

Hence, the time the coil was energized was equal to

$$\frac{1{\cdot}472 \times 3600}{1{\cdot}178 \times 800} \text{ seconds.}$$

The number of calories supplied =

$$\frac{1{\cdot}472}{1{\cdot}178} \times \frac{3600}{800} \times \frac{800 \times 2{\cdot}456}{4{\cdot}18} \times 0{\cdot}975 = 2577$$

The radiation correction at the critical temperature was 7 cal., making a total of 2584 cal. Measurements of this magnitude usually check to within ± 0·3 per cent.

The extra energy due to the transformation is obtained as follows :

Temperature range : *i.e.* 9·1 mv. – 17·26 mv. 226° –420° C., *i.e.* 194° C.

Subtract 194 × 0·351 = 68·6 cal. for screws, &c.

This leaves 2515 cal. $\frac{2515}{139} = 18{\cdot}08$ cal./grm.

The mean normal specific heat from 226° to 420° C. is extrapolated from Fig. 3 and is 0·0652.

Energy per grm. is therefore (18·08 – 194 × 0·0652) cal. = 5·44 cal.

A result has been reached which is typical of the alloy as cooled at 30° C./hr. The initial temperature 226° C. was chosen somewhat arbitrarily, by consideration of Fig. 3, as the lower limit to the temperature at which atomic rearrangement becomes appreciable in the alloy. The value obtained is therefore not necessarily typical of equilibrium at 226° C.

This type of experiment (energy measurement) is much less tiring and involves considerably less arithmetic than the specific heat-temperature curve; on the other hand it conceals all the interesting undulations revealed by the specific heat measurements. Both types are essential in investigating complicated transformations.

Equilibrium Energy Content.—Specimen in equilibrium at 389·3° C. According to Fig. 3 (see also Fig. 12) the specific heat is very high in the neighbourhood of the critical temperature. This may be truly characteristic of the transformation at this point or due to the fact that under the experimental conditions used the specimen arrives at the critical temperature with a much higher degree of order than the equilibrium degree of order. In order to distinguish between these two possibilities the specimen was annealed just below the critical temperature for 100 hrs. This treatment according to other measurements[4] may be expected to produce an equilibrium structure throughout each individual crystal of the alloy.

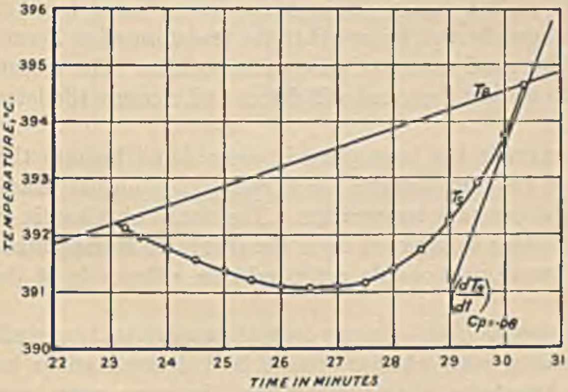

FIG. 11.—Temperature–Time Curve After Annealing Just Below Critical Temperature.

The specimen was then heated to 420° C. at about 0·3 C. per minute and the energy required was 4·21 cal./grm. Fig. 11 gives the temperature–time curves for both block and specimen. Latent heat is evolved and some overheating is observed.

The amount of latent heat may be estimated as follows. From 23·1 minutes to 30·3 minutes the energy input was constant and the total energy equivalent to 1·42 cal./grm. At 30·3 minutes when the temperature of the specimen once more reached that of the block, the heating rate of the specimen $\frac{dT_s}{dt}$ corresponded to a specific heat of 0·08. At this time, therefore, the transformation was completed. Assuming that the specific heat is 0·08 on the high temperature side of the critical temperature

$$\begin{aligned}\text{Latent heat} &= 1{\cdot}42 - (394{\cdot}6 - 392{\cdot}2) \times 0{\cdot}08 + \overset{\substack{\text{Radiation correction}\\ \downarrow}}{0{\cdot}04}\ \text{cal.}\\ &= 1{\cdot}23\ \text{cal./grm.}\end{aligned}$$

Fig. 11 and experiments of a similar character made on the same specimen confirm the prediction of the Bragg–Williams theory that latent heat should be evolved in the case of Cu_3Au. The authors feel that it would be unwise to stress this confirmation until a number of specimens melted under different conditions have been examined, since it is already well known that the transformation is considerably modified by small traces of gaseous impurities. The essential point is that the method described will detect and measure the latent heat if it exists.

This example has been given in some detail because the method appears to be quite suitable for investigating normal phase changes occurring at constant temperature. The results obtained in such cases should be easier to interpret since the energy to be measured is larger and the transformations do not persist on either side of the change point.

Mean Specific Heat.—Energy content measurements are independent of the heating rate, whereas specific heat determinations involve an accurate knowledge of this parameter. In many cases, particularly at low temperatures, the specific heat changes either slowly or linearly with temperature. Energy content experiments over 50° C. intervals may then be substituted for instantaneous specific heat determinations. This alternative is of considerable assistance at the beginning of an experiment (from room temperature to 80° C.) when the heating rate of the furnace is changing rapidly. The points marked ○ on Figs. 3, 9, and 10 were obtained in this way.

V. BEHAVIOUR OF THE ALLOY AT THE CRITICAL TEMPERATURE.

The rate of increase in specific heat in the vicinity of the critical temperature is very rapid, and it is only possible to hope to get a first approximation to the shape of the curve in this region, since the temperature gradients in the specimen may no longer be negligible. Nevertheless, such approximations are of considerable use in interpreting the behaviour of the alloy in this region.

Figs. 12, 13, and 14 give the temperature–time curves of block and specimen and also the specific heat curve for the three experiments already referred to in Figs. 3, 9, and 10.

Apart from the different heat-treatments given to the specimen, all the other experimental conditions were substantially the same, in particular the power input to the coil and the heating rate of the block.

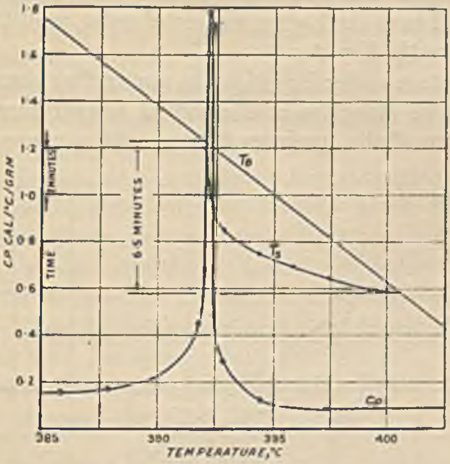

Fig. 12.—Specimen as Cooled at 30° C. per Hr. Behaviour at Critical Temperature.

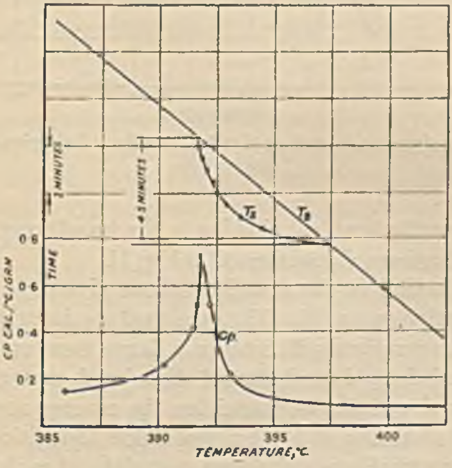

Fig. 13.—Specimen as Quenched in Water. Behaviour at Critical Temperature.

The *Cp–T* curves are quite different from one another, proving that heating rates of 1·5° C./minute do not permit the specimen to attain equilibrium at any temperature below the critical temperature.

The energies absorbed at the critical temperature are in the ratio 6·5 : 6·2 : 4·5. This is to be expected, since the specimen as cooled at 30° C./hr. would have the highest degree of order, whilst the quenched alloy would have the lowest.

As the structure under investigation approaches nearer and nearer to the equilibrium structure at the critical temperature, the temperature–time curve of the specimen flattens with a consequent increase in maximum specific heat, culminating in the transformation absorbing latent heat as has been demonstrated in Fig. 11.

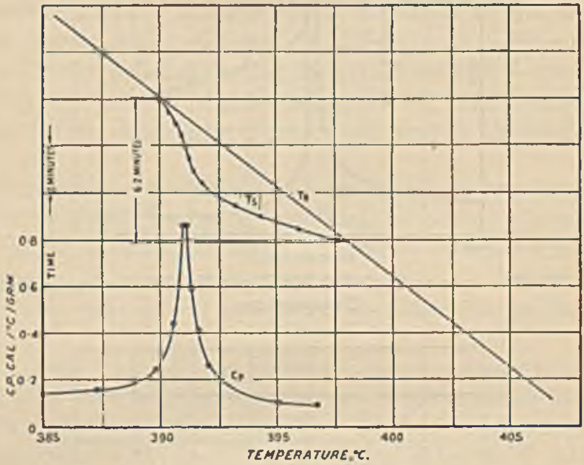

FIG. 14.—Specimen as Cooled at 1500° C. per Hr. Behaviour at Critical Temperature.

The experimental results described above give further evidence of the effect of antiphase nuclei. The quenched specimen when it reaches the critical temperature will contain a large number of very small nuclei surrounded by boundaries of disordered material. This disordered material will act as nuclei for the reverse change. In the specimen after annealing at 100 hrs. just below the critical temperature there will be practically no disordered material and each crystal will be uniformly ordered throughout. Above the critical temperature only local order exists, and the structure has an appreciably different lattice constant. A certain amount of hysteresis is to be expected, therefore, with the possibility of latent heat.

VI. ACCURACY OF THE EXPERIMENTAL RESULTS.

Specific Heat Measurements.

The maximum absolute errors involved in the measurement of power input are of the order of ± 0·2 per cent. The measurement of heating rate introduces two possible errors, one in the time interval which can be eliminated by calculating a large number of points, and the other due to inaccurate calibration of the thermocouple. It was not convenient to make a direct calibration of the thermocouple used in the copper block. A welded couple was prepared and calibrated using the fixed points of aluminium, zinc, cadmium, tin, and water. The metals were of 99·99 per cent. purity, and the values taken for the fixed points were those given by the Bureau of Standards. Intermediate readings were also taken at 50° C. intervals by comparison with a platinum resistance thermometer. The welded couple was then mounted in the copper block together with the specific heat thermocouple, and a difference curve obtained *in situ* on the apparatus. This difference curve was then used, in the manner suggested by the Bureau of Standards[5, 6] to obtain the $\frac{dV}{dT}$–T curve for the thermocouple employed in the specific heat measurements. The accuracy claimed is ± 0·4 per cent. up to 400° C. Consequently the maximum absolute error in the measurement of specific heat will be about ± 0·6 per cent.

Faulty Experimental Conditions.

It is assumed throughout that it is possible to tell exactly when block and specimen are at the same temperature, that the temperature gradients in block and specimen are negligible, and that no heat transfer takes place along the coil leads when block and specimen are at the same temperature.

The experiments carried out to determine the radiation correction enable the differential thermocouple zero e.m.f. to be found to ± 0·1° C. This corresponds to maximum uncertainty in specific heat of ± 0·2 per cent. at 400° C. The temperature difference between the lid and main portion of the block has been measured whilst the temperature of the block was increasing at the rate of 1·5° C./minute. It was found to be about 0·1° C., and any error due to this cause may be neglected. Calculation shows that the temperature differences across block and specimen are of the order of 0·02° C., so that they also may be neglected.

A considerable error may arise owing to heat transfer along the coil leads even when block and specimen are at the same temperature. The current and voltmeter leads inside the container *A* (Fig. 4) have negligible heat capacity so that they attain a temperature approximating to that of A, which may be 60° C. hotter than the block temperature. The leads $I_1 I_2$ and $V_1 V_2$ are of nickel–chromium wire to minimize conduction into the specimen; this alone only reduces the possible heat transfer to about 0·07 cal./second, which, in the absence of the clamp P, would pass into the specimen. Similarly, the heating coil may operate at a temperature up to 200° C. higher than that of the specimen. Much of the heat conducted through the ends of the coil is dissipated by the radiation tags which run in the worst circumstances at not more than 20° C. above the specimen. The clamp on the lid of the specimen reduces this temperature difference to less than 0·1° C.

The thermal resistivities of the various interfaces in the clamps are difficult to estimate, so an experiment was carried out to determine whether the proposed arrangement was satisfactory. Two Nichrome leads identical with those used inside the container A, and in the form of a U, were hard-soldered to a flattened 0·8 mm. wire representing a coil lead. A nickel wire was then soldered to the flattened wire on the unflattened side and the arrangement fitted in the clamp P. Current was then passed through the U until a thermocouple cemented to the junction at the U registered 200° C. The temperature of the wire in the clamp when steady was 0·6° C. higher than that of the lid. This experiment indicates that the clamp on the specimen will reduce the temperature difference between lead and specimen to less than 0·1° C. With regard to the incoming leads at P they are, as previously mentioned, flat Nichrome strips having about three times the contact area of the flattened 0·8 mm. wire, so that with a 60° C. difference in temperature between leads $I_1 I_2$ and $V_1 V_2$ and the block the temperature difference across the clamp is limited to about 0·06° C. Heat conduction per 1° C. temperature difference between the clamps is 3×10^{-4} cal./second, *i.e.* approximately 0·1 per cent. of the power input, so that errors due to heat transfer along the coil leads may be neglected.

The effects due to finite thermal capacity of the heating coil have so far been neglected; when the power input to the coil is changed the temperature difference between coil and specimen is also changed, and for a short time, say of the order of a minute, the power input to the specimen will be different from the input to the coil. Provided that the calculations of specific heat are restricted to readings obtained three or more minutes after the power input has been changed, no appreciable errors are involved.

Summary.

According to the above examination of the experimental arrangement a possible absolute error in specific heat determinations of ± 0·8 per cent. is to be expected. The error in the heat content measurements will be about the same. The observational errors in the case of specific heat measurements are found to lie within the limits ± 0·75 per cent. and in the heat content measurements ± 0·3 per cent.

In the investigation of the β-brass transformation the original method was checked by measuring the specific heat of pure copper and comparing the results with those due to Wust [7] obtained by the calorimeter method. Agreement to 1 per cent. was obtained but it was pointed out that the experimental results of Wust were not very convincing. Recently Jaeger [8] and his collaborators have improved the calorimetric method very considerably, and have published results on copper which are claimed to be accurate to ± 0·1 per cent.

Fig. 15 records experimental observations obtained by the present method for copper together with the results of Wust and Jaeger. The differences between the authors' results and those of Jaeger * vary from − 0·5 to about + 0·8 per cent. and are of the order that would be anticipated from the considerations set forth in this section. The most probable cause for the variation in error is to be found in the calibration curve of the nickel–chromium thermocouple. The $\frac{dV}{dT}$–T curve for this type of couple has a maximum at about 80° C. and a minimum at 180° C. These make it difficult to obtain an accurate determination of the instantaneous value of $\frac{dV}{dT}$. Provided a sufficiently sensitive potentiometer is available we think it would be preferable to use a platinum/platinum–rhodium thermocouple.

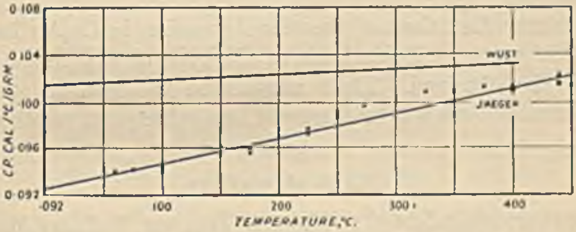

Fig. 15.—Specific Heat of Pure Copper.

A safe estimate of the absolute accuracy of the experimental results obtained by the methods described in this paper is ± 1 per cent.

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* Jaeger uses $J = 4{\cdot}188$ joules/cal. which introduces a difference of 0·2 per cent. The true differences are, therefore, − 0·7 + 0·6 per cent.

VII. THE SPECIMEN.

An ingot of copper–gold alloy of suitable dimensions was lent to the authors by The Mond Nickel Company, Ltd., of Acton. This was annealed at 825° C. for 1 hr. *in vacuo*, machined, and then re-annealed. An X-ray back-reflection photograph showed that the specimen was free from coring and lattice distortion. The chemical analysis gave 24·90 atoms per cent. gold.

VIII. CONCLUSION.

An experimental arrangement has been described, which has been specially developed for the quantitative investigation of order–disorder transformations in alloys. The apparatus possesses the advantage that it is simple to construct and easy to operate. The authors are of the opinion that it could be applied to the study of other types of solid transformation.

Various manifestations of the transformation in Cu_3Au have been used in this paper as illustrations of the type of experimental result which can be obtained. Their relation to the various theories of atomic rearrangement will be discussed in a subsequent publication.

ACKNOWLEDGMENTS.

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The authors thank Professor W. L Bragg, F.R.S., for his kind and continued interest.

REFERENCES.

[1] C. Sykes, *Proc. Roy. Soc.*, 1935, [A], **148**, 422.
[2] W. L. Bragg and E. J. Williams, *Proc. Boy. Soc.*, 1934, [A], **145**, 699.
[3] W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.*, 1935, [A], **151**, 540.
[4] C. Sykes and H. Evans, *J. Inst. Metals*, 1936, **58**, 255–280.
[5] W. F. Roeser, A. I. Dahl, and G. J. Gowens, *J. Besearch Nat. Bur. Stand.*, 1935, **14**, 239.
[6] W. F. Roeser and H. T. Wensel, *J. Research Nat. Bur. Stand.*, 1935, **14**, 247.
[7] —— Wust, *Internat. Critical Tables*, 1929, **5**, 93.
[8] F. M. Jaeger, E. Rosenbohm, and J. A. Bottema, *Proc. K. Akad. Wet. Amsterdam*, 1932, **35**, 772–779.

A FURTHER STUDY OF THE CONSTITUTION OF THE CADMIUM–TIN ALLOYS.*

By Professor D. HANSON,† D.Sc., Vice-President, and
W. T. PELL-WALPOLE,‡ B.Sc., Student Member.

Synopsis.

A further study (cf. *J. Inst. Metals*, 1935, **56**, 165) has been made of the constitution of the tin-rich cadmium–tin alloys by means of detailed thermal and microscopical analyses, and by electrical resistivity measurements.

A peritectic reaction occurs at 223° C. with a formation of a new phase, β, which undergoes eutectoid decomposition at 127° C. on cooling, producing the well-known transition at this temperature. The limits of the α and β phases have been accurately determined, and the equilibrium temperature of the eutectoid transition is shown to be 133° C.

The earlier diagrams by the authors and by Matuyama can be explained partly as representing metastable conditions which are very easily produced in these alloys, both on heating and on cooling; thus the peritectic reaction is only observed on cooling curves taken at very slow rates of cooling.

The solidus and solid solubility lines of tin in cadmium have been determined accurately, and the results are in agreement with those of Stockdale.

Introduction.

The constitution of cadmium–tin alloys has been investigated recently by the present authors [1] who confirmed that the general form of the system is eutectiferous, as shown by previous investigators. Their determination of the eutectic point agreed fairly closely with that of a very detailed investigation by Stockdale.[2] The authors showed that after annealing for 1 week at 160° C. there was no eutectic present in alloys containing 5 per cent. or less of cadmium, and that the transition at 127° C. gave a maximum thermal effect at 5 per cent. of cadmium, which was associated with the formation of a eutectoid structure at that composition.

On the evidence of certain thermal effects and the microstructures of quenched alloys, the authors presented a diagram (Fig. 1) for tin-rich alloys which agreed substantially with that previously published by Matuyama,[3] which was based on electrical conductivity measure-

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ments. This incorporated a theory that the tin-rich solid solution separates at 130° C. into conjugate solid solutions, of which the one richer in cadmium decomposes at 127° C. into a eutectoid consisting of α (tin-rich) and β (cadmium-rich). During the discussion of the authors' paper this diagram (Fig. 1) was criticized on theoretical grounds.

The authors had not determined the solidus lines of the system, their approximate positions being indicated in the diagram by broken lines. Stockdale,[4] however, in the discussion of the paper, gave results, hitherto unpublished, of his determination of the solidus lines. The α solidus fitted into the authors' diagram quite well, but the solidus of the cadmium-rich alloys differed seriously from the authors' estimation, although the microscopic work was in close agreement. The difference arose from the interpretation by the authors of certain thermal effects which were observed on these alloys.

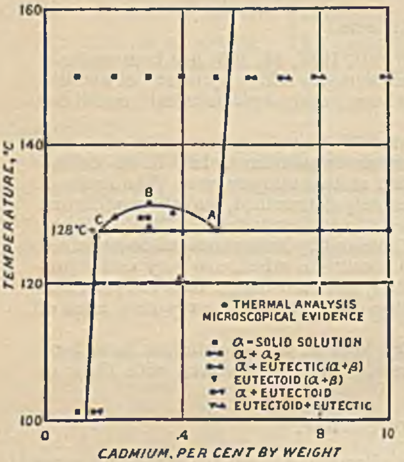


Fig. 1.

In reply to the correspondence on the paper, the authors stated that more recent work on the effect of small additions of a third metal to the cadmium–tin alloys had revealed the existence of a peritectic reaction at 223° C. in these alloys which is easily suppressed by rapid cooling. This discovery led to a more detailed investigation of the tin-rich alloys, including the determination of the solidus by micrographic methods. The solidus of the cadmium-rich alloys also has been determined in order to discover the cause of the apparent discrepancies between the previous thermal and microscopic results.

The present paper gives an account of these additional investigations and their relation to the previous work.

PART I.—TIN-RICH ALLOYS.

Preparation of the Alloys.

The alloys were prepared from Chempur tin (99·992 per cent. pure) and Tadanac cadmium (99·95 per cent. pure), as described previously.

All alloys were analyzed and the results, together with intended compositions, are shown in Table I.

TABLE I.—*Results of Thermal and Chemical Analyses.*

Alloy. Cadmium, Per Cent.	Analysis Cadmium, Per Cent.	Arrest Temperatures, ° C.							
		Unannealed Alloys.				Annealed Alloys.			
		Cooling Curves.				Cooling.	Heating.		
		1.	2.	3.	4.	1.	1.	2.	3.
0·5	0·5	230	223·2	...	...	...	...	...	226·0
1·0	1·01	228·9	223·1	...	124·5	...	...	...	223·0
1·25	1·24	...	...	...	...	126·0	140·5	162	222·0
1·5	1·50	227·7	223·2	174·0	125·5	126·5	141	167	222·0
2·0	1·97	226·2	223·0	174·0	125·5	126·5	139	165	220·0
2·5	2·47	225·3	223·0	175·2	126·0	127·0	139	160	216·0
3·0	3·00	224·2	222·8	175·5	127·7	127·0	140·0	158	213·0
3·5	3·52	223·5	...	175·8	126·5	127·0	139·0	165	208·0
4·0	3·98	222·4	...	175·8	126·4	127·2	140·0	160	204·0
4·25	4·26	...	...	...	...	127·5	140·0	160	201·0
4·5	4·52	...	...	...	...	128·0	140·0	...	197·0
4·75	4·74	...	...	...	...	127·0	140·0	...	193·0
5·0	5·01	219·8	...	176·0	125·5	127·0	140·0	...	188
5·25	5·27	...	...	...	...	127·0	139·0	...	184
5·5	5·60	...	...	...	...	127·5	140·0	...	178
5·75	5·75	...	...	176·0	125·5	127·5	140·0	...	176
6·0	6·00	217·5	...	176·0	...	126·5	140·5	...	176
8·0	8·00	214·0	...	176·2	...	127·0	140·0	...	176
10·0	10·04	209·5	...	176·0	...	127·0	140·0	...	176

THERMAL INVESTIGATIONS.

During the previous work, cooling curves were taken at a rate of cooling of 2° C. per minute, and readings were plotted at intervals of 0·05 mv. (1° C.) on a Rosenhain chronograph. This method gave no arrests between the liquidus and eutectic temperatures, but during a similar investigation of tin-rich antimony–cadmium–tin alloys, a series of arrests was found which appeared to indicate a peritectic reaction at or near to 233° C. Repeated determinations with the original binary alloys at slower rates of cooling gave very slight arrests in the case of two alloys only (1 and 2 per cent. cadmium) at 223° C. These arrests were very near to the liquidus arrest, so that undercooling, which is difficult to prevent with these alloys, could completely mask the slight thermal effects concerned.

The alloys prepared for the present investigation were of closer compositions, and a slower rate of cooling (1° C. per minute) was used. The difficulty of interpretation arising from the close proximity of the liquidus and supposed peritectic arrests on the cooling curves was overcome by taking advantage of the retarded rate of cooling which follows the commencement of the liquidus arrest. This permitted readings to be plotted at intervals of 0·4° C. instead of 1° C., thus widening the scale of the vertical ordinate on the chronograph drum. The combination of the slower rate of cooling and the more sensitive recording was completely successful, and gave a definite second arrest at 223° C. (± 0·3° C.) for compositions 0·5–3·0 per cent. cadmium. After the second arrest, the rate of cooling increased, so that it was necessary to revert to plotting at intervals of 1° C., which was maintained to the end of the curve (100° C.).

On completion of the cooling curves for a specimen, it was remelted and cast into a cylindrical chill mould of ½ in. diameter. A 30-grm. sample taken from the resulting ingot was drilled to take the bare junction of the thermocouple, annealed for 7 days at 170° C., and cooling curves were repeated over the range 165°–100° C. The specimen was contained in a Salamander pot in a larger crucible which was heated to 170° C. in an oil-bath, kept at that temperature for 30 minutes, and then allowed to cool. These conditions gave a rate of cooling of 1·5° C. per minute, and were kept constant throughout the work. This method has distinct advantages over heating in an electric furnace in that the temperature lag between the specimen and its surroundings is very much less, so that the maximum temperature to which the specimen is heated can be controlled more accurately.

Heating curves were taken for the same specimens from 100° C. to the solidus of each alloy, the rate of heating being 0·5° C. per minute.

In addition to plotting the curves on the Rosenhain chronograph, the durations of the eutectoid arrests on cooling were measured by means of a metronome, and each specimen was weighed so that the arrest time per unit weight for each alloy could be obtained.

RESULTS OF THERMAL ANALYSIS.

Some typical curves are shown in Fig. 2. The liquidus arrests are in close agreement with those previously obtained, but the investigation of alloys at closer compositions reveals a slight break in the liquidus curve at 3·7 per cent. cadmium, 223° C. The peritectic arrests occur at 223° ± 0·2° C. for alloys containing 0·5–3·5 per cent. cadmium, giving a horizontal which intersects the liquidus at the slight inflection.

The temperatures of the eutectic arrests found in the case of alloys containing more than 1 per cent. cadmium are in agreement with those in the earlier investigation, showing undercooling in alloys containing 1–5 per cent. cadmium.

Only one series of arrests was observed in solid alloys, corresponding to the well-known transition at 125°–130° C. These arrests occur at temperatures approximately 3° C. lower than were found in the earlier investigations, but the differences are probably connected with the different masses of metal and the different cooling conditions. In the case of alloys containing 2–3·5 per cent. cadmium, the arrests occur at a slightly higher temperature than the average, but no additional arrests were recorded, so that although there appears to be some peculiarity for this range of composition, there is no evidence in these results for an additional line such as that shown in the authors' previous diagram.

In confirmation of the earlier work, the slow-rate cooling curves for annealed specimens showed that the eutectoid transition occurs at 127° ± 1° C. in alloys containing 1·25 per cent. or more of cadmium. Again, there are no additional arrests at 130°–131° C. in alloys containing 2–3·5 per cent. cadmium, but with the slower rate of cooling employed there are very frequent minor disturbances of the curves between 160° and 130° C. The arrest time per grm. for each alloy is shown graphically in Fig. 3. There is a sharp maximum at 5 per cent. cadmium, confirming that this is the composition of the eutectoid. Theoretically, the curve on either side of the maximum should be linear, and the values for alloys containing 1·5–3·5 per cent. cadmium, are therefore greater than the theoretical values. These effects are discussed later in connection with the results of microscopical analyses.

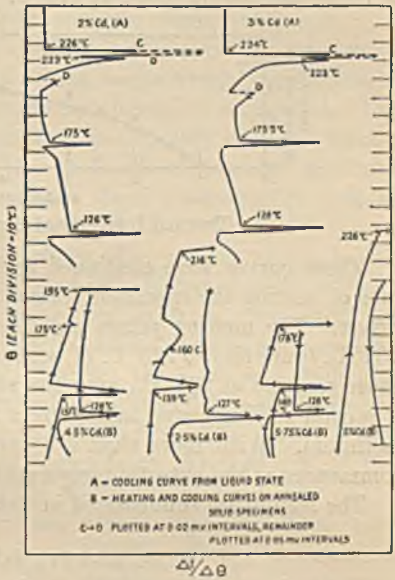


Fig. 2.—Typical Heating and Cooling Curves.

The heating curves for annealed solid specimens of alloys containing 1·25–10 per cent. cadmium, show arrests corresponding to the eutectoid transition, commencing at 138°–140° C., but these are less sharply defined than those on cooling curves, and extend over a wider range of temperature. The curves for alloys containing 1·25–4·25 per cent. cadmium show a further interruption over the range 160°–167° C.

The maximum effect occurs in the 3 per cent. cadmium alloy, and an explanation of these "arrests" is offered later. Alloys containing 3–5·5 per cent. cadmium give a very slight but sharp arrest at or near to the eutectic temperature (176° C.), but since the authors have shown previously that for equilibrium conditions the eutectic is only present with more than 5 per cent. cadmium, these minor arrests must be due to non-equilibrium conditions, and can be attributed to the lack of complete absorption of the cadmium-rich phase at the transition or during subsequent heating, causing the formation of a small amount of metastable liquid phase at 176° C.

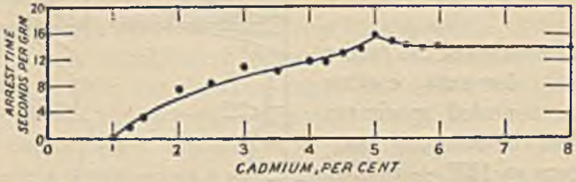


Fig. 3.—Thermal Intensity of Eutectoid Transition on Cooling.

These curves were continued until melting commenced, when the rate of heating the specimen became very slow, producing a prolonged arrest. The melting points obtained indicate a sloping solidus from 232° C. (pure tin) to 223° C. (1 per cent. cadmium), a constant temperature reaction at 223° C., over the range 1–2 per cent. cadmium, and a second solidus curve falling from 223° to 176° C. at 5·5 per cent. cadmium. With more than 5·5 per cent. cadmium, melting always commences at the eutectic temperature, 176° C.

The results are summarized in Table I.

Microscopical Analysis.

Chill-cast specimens, such as those used for the previous microstructural investigations, do not show the type of structure which is normally associated with a peritectic reaction, but this is in agreement with the present thermal investigations, which show that the reaction at 223° C. only occurs with very slow rates of cooling. In order to obtain microscopical evidence of the reaction, a series of specimens was cooled slowly in an electric furnace (under the same conditions as those used for cooling curves) from the liquid state to 160° C. and quenched in water. These specimens were prepared for examination by methods described previously, and were etched in a 2 per cent. solution of nitric acid in alcohol.

Alloys which show the arrest at 223° C. on cooling curves, all have a similar structure (Fig. 4, Plate XVIII), consisting of primary α grains (light etching) with a peritectic fringe of a darker constituent, which shows signs of incipient decomposition, and traces of eutectic. The alloys containing 4 per cent. or more of cadmium consist of the dark constituent as the primary separation with well-developed eutectic at the grain boundaries (Fig. 5, Plate XVIII). The intermediate constituent has a structure similar to that previously observed in tin-rich alloys which had been quenched after annealing at 160° C.

In order to obviate confusion it is necessary to re-name the cadmium-rich phase γ (previously called β), the intermediate phase now being called β and the tin-rich phase α as before.

Figs. 4 and 5 show clearly that the eutectic consists of $\beta + \gamma$.

To investigate the equilibrium conditions of these alloys, two series of specimens, chill-cast and slowly cooled, respectively, were annealed at 170° C. in an electric furnace under thermostatic control. The specimens were quenched and examined periodically until no further changes of structure occurred. It was found that whilst chill-cast specimens reached equilibrium after 6–7 days' annealing, it took 14 days for the slowly-cooled specimens to do so.

The structures of the annealed alloys after cooling slowly in the furnace are very similar to those described and illustrated in the authors' previous paper; thus, alloys containing up to 1 per cent. cadmium are uniform α; with 1·25–4 per cent. cadmium there is an increasing amount of eutectoid ($\alpha + \gamma$) in an α matrix; the 5 per cent. cadmium alloy is completely eutectoid, whilst with more than 5 per cent. cadmium there is an excess of γ at the grain boundaries. The proportion of eutectoid present in each alloy corresponds to the intensity of the thermal effect at 127° C., shown in Fig. 3.

During the previous investigations certain tin-rich alloys were quenched from 160° C. and also from 170° C., after a preliminary annealing for 7 days at 160° C. The structure of the 1 per cent. cadmium alloy was that of a simple homogeneous solid solution, but alloys containing 1·5–5 per cent. cadmium consisted of the α phase (light etching) with increasing proportions of dark etching areas which showed a somewhat " martensitic " structure. The 5 per cent. cadmium alloy consisted entirely of the " martensitic " structure, whilst with 6 per cent. or more of cadmium, eutectic was present around the grains. The " martensitic " areas were approximately proportionate to the amount of eutectoid in the corresponding slowly-cooled alloy, but in alloys containing up to 5 per cent. cadmium they were not separated from the light areas by definite boundaries. On this evidence, the authors considered that at 170° C., the α phase extended to 5·5 per cent. cadmium, but that quenching did not suppress the eutectoid transition entirely. An alloy containing 3 per cent. cadmium was etched in the furnace at 130° C., and quenched: this alloy consisted of two definite constituents in approximately equal amounts; the darker constituent was found to undergo decomposition at room temperature (15°–18° C.), producing a structure very similar to the eutectoid present in slowly cooled alloys.

These results were in agreement with the thermal evidence available at that time, apparently indicating that the primary tin-rich phase separates at 131° C. into conjugate solid solutions, of which the one richer in cadmium undergoes eutectoid decomposition at 127° C. The authors' diagram (Fig. 1) was very similar to the earlier one published by Matuyama,[3] which was based on electrical resistivity measurements.

The discovery of the peritectic reaction at 223° C. during the present thermal investigations, and the peritectic structures of the slowly-cooled alloys (Figs. 4 and 5) suggests another explanation of the transition at 127° C., *viz.* the eutectoid decomposition of the intermediate phase β which is produced by the peritectic reaction. If this is the true explanation, then the "martensitic" structure previously observed in quenched alloys, represents a distinct β phase, and in spite of the incipient decomposition of such a phase on quenching, a suitable etching reagent should reveal the grain boundaries. Experiments to this end were carried out, therefore, on the 5 per cent. cadmium alloy (which on quenching consists entirely of the "martensitic" structure). Several etching reagents were tried, including those used in the previous investigations. The most satisfactory results were obtained with a 5 per cent. solution of nitric acid in alcohol, which revealed the grain boundaries clearly but showed that the specimen had recrystallized on quenching, since it consisted of very coarse grains, each of which was composed of many small grains showing the "martensitic" structure (Figs. 6 and 7, Plate XVIII). The experiment was repeated several times, the specimen being quenched from 160° C. and from 170° C., into cold water (15° C.) or a freezing mixture of ice and ammonium nitrate (– 5° C.), but the same structure was obtained each time.

The recrystallization is not caused by polishing, since the specimen was prepared very carefully, and the flowed layer removed by etching and light repolishing, before quenching. Moreover, the results of mechanical tests published in the previous paper showed that this alloy as quenched from 160° to 170° C., is very much harder than the 1 per cent. cadmium alloy, which consists entirely of α, yet the latter never has a recrystallized structure provided that the specimen is prepared with reasonable care. It was concluded that the structure

PLATE XVIII.

Fig. 4.—3·5% Cd. Slowly Cooled from Melt. Primary α (light), Peritectic β (half tone), Traces of Eutectic (dark). × 50.

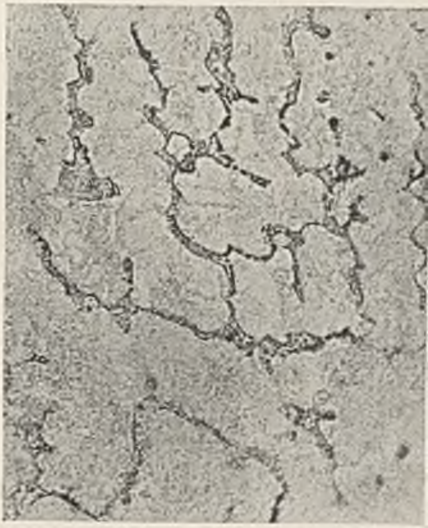


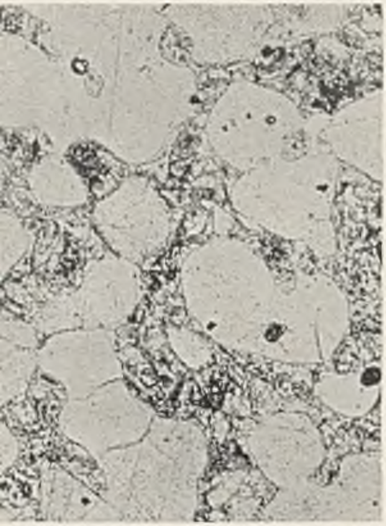
Fig. 5.—10·0% Cd. Slowly Cooled from Melt. Primary β (partially decomposed) and $(\beta + \gamma)$ Eutectic. × 200.

ig. 6.—5% Cd. Quenched at 170° C. Recrystallized β, Showing Incipient Decomposition. × 400.

Fig. 7.—Same as Fig. 6. Structure of β. × 1500.

[*To face p.* 288.

PLATE XIX.



8.—2% Cd. Quenched at 160° C. (white) + Recrystallized β (half tone). 200.

FIG. 9.—4·5% Cd. Quenched at 195° C. Recrystallized β. × 100.

G. 10.—3·5% Cd. Quenched at 205° C. Recrystallized β. × 400.

FIG. 11.—50% Cd. Quenched at 135° C. Decomposed β. × 500.

FIG. 12.—4·5% Cd. Quenched at 150° C. Traces of α (light) in Decomposing β (dark). × 400.

FIG. 13.—1·5% Cd. Quenched at 220° C. α (light) + β (dark). × 50.

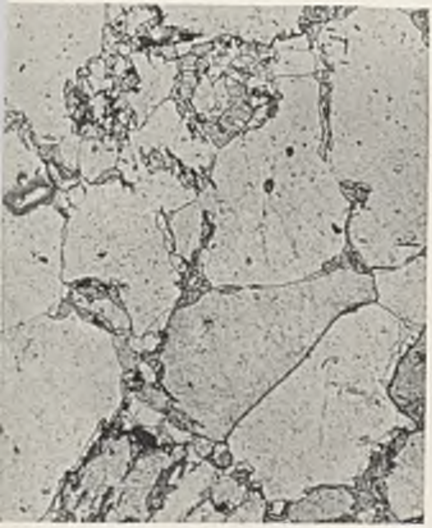


FIG. 14.—1% Cd. Quenched at 220° C. α (light) + β (dark). × 50.

FIG. 15.—5·6% Cd. Quenched at 160° C. β + Intergranular γ. × 400.

PLATE XXI.

16.—3·5% Cd. Quenched at 210° C. crystallized β + Quenched Liquid (dark). 50.

FIG. 17.—4% Cd. Heated Slowly to 140° C. Quenched Immediately. Formation of β (dark) from Eutectoid (matrix). × 100.

18.—Same as Fig. 17. α (light) + β rk) Eutectoid (half tone). × 500.

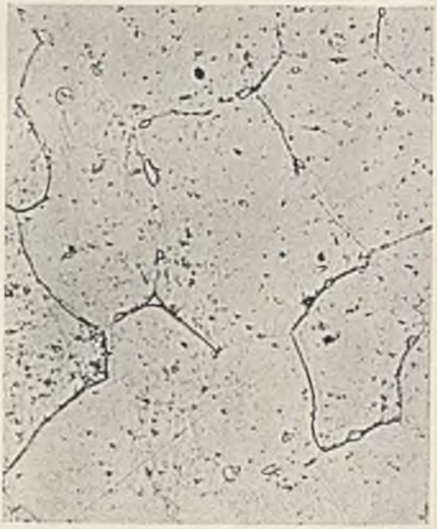


FIG. 19.—99·7% Cd. Quenched at 178° C. and Re-Prepared. Traces of Quenched Liquid in γ. × 200.

of the 5 per cent. cadmium alloy confirms the existence of an intermediate phase β, which recrystallizes and partially decomposes on quenching.

One chill-cast specimen and one slowly-cooled specimen of each alloy in the range 0·5–10 per cent. cadmium were then re-annealed for 1 day at 160° C., quenched in water, and etched in a 5 per cent. solution of nitric acid in alcohol. Alloys containing up to 1 per cent. cadmium consisted entirely of a simple homogeneous solid solution α; with 1·25–4·25 per cent. cadmium there is an increasing amount of the recrystallized suppressed β in α matrix (Fig. 8, Plate XIX); with 4·5–5·25 per cent. cadmium the alloys are entirely β (as Fig. 6), whilst with 5·5 per cent. or more of cadmium the γ phase (cadmium-rich) is present around the coarse β grains. Throughout the series the β phase is recrystallized and "martensitic," as described in the preliminary experiments on the 5 per cent. cadmium alloy, whilst the α phase is light etching and has no substructure. The only difference between the chill-cast and slowly-cooled specimens is that in all cases the grain-size of the former is much finer.

Quenching experiments were then carried out from a series of temperatures, as required, to determine the phase boundaries.

The range of composition of the β phase changes considerably with temperature but the structure is always similar (Figs. 9, 10, and 11, Plate XIX), although at higher temperatures (190°–200° C.) the "martensitic" structure becomes less pronounced, whilst quenched from temperatures below 160° C., it becomes increasingly difficult to suppress the eutectoid decomposition (Fig. 11).

With alloys containing 3·5–2 per cent. cadmium it was found that on annealing at temperatures at which they are almost entirely β (195°–220° C.), very coarse grains develop, and the quenched specimen has a "rumpled" surface, so that it must be completely re-prepared for microscopic examination. This caused considerable difficulty in obtaining the true structures, and very light polishing was essential. The structures were also more difficult to etch satisfactorily, but when developed, the β was found to differ very little from that of the higher cadmium alloys quenched from lower temperatures (Fig. 10).

In alloys which contain considerably more β than α when quenched from 140° to 200° C., the α appears as light rounded pools in the β (Fig. 12, Plate XX), but when alloys containing 1–1·5 per cent. cadmium are quenched from temperatures near to that of the peritectic reaction (215°–223° C.) the (α + β) structure is more angular and the β which forms at these temperatures tends to produce a Widmanstätten structure (Figs. 13 and 14, Plate XX).

When the γ-phase is present in quenched specimens, it always occurs around the coarse β grains (Fig. 15, Plate XX).

The limits of the peritectic reaction, and the positions of the α and the β solidus, were determined from microstructures of quenched specimens. When a specimen appeared to contain quenched liquid, it was sectioned and a face prepared at right angles to the original one; microstructurally, the quenched liquid appears as a very fine eutectic round the grain boundaries and as globules within the grains (Fig. 16, Plate XXI).

An attempt was made to determine the mode of formation of β from the eutectoid mixture of $(\alpha + \gamma)$. Specimens of alloys 4–5 per cent. cadmium were annealed at 170° C., slowly cooled at 120° C., and annealed at that temperature for 1 day so that eutectoid structure was well developed. They were then heated very slowly to 140° C. (temperature of eutectoid arrests on the heating curves) and quenched after 2 minutes at that temperature. The structures obtained from this treatment are similar in each alloy, consisting of a dark etching constituent around the grain boundaries, and as bars across the grains (Fig. 17, Plate XXI). At a higher magnification the light etching matrix has a eutectoid structure preserved (Fig. 18, Plate XXI). It appears that the β is formed in visible amounts first along the original grain boundaries, and in certain preferred positions in the matrix. It is probable, however, that the apparent residual $(\alpha + \gamma)$ eutectoid structure consists actually of three phases, $\alpha + \beta + \gamma$, the β-phase being formed by reaction as a fringe between the lamellæ of $\alpha + \gamma$. The rather indefinite merging of the light (α) and dark (γ) lamellæ in Fig. 18, as compared with the appearance of the stable eutectoid of the slowly-cooled alloy appears to confirm this possibility, but the β if present in this form is not clearly distinguished.

The equilibrium temperature of the eutectoid transition cannot be determined accurately from thermal analysis owing to the severe hysteresis which occurs, the difference between arrests of heating and cooling being 10°–13° C. The results of prolonged annealing experiments showed that the eutectoid structure $(\alpha + \gamma)$ is stable up to 133° C., since specimens quenched from this temperature contain a coarse mixture of α and γ, whilst quenching from 135° C. produces the very fine structure of β which has decomposed during quenching (Fig. 11, Plate XIX).

The results of the microscopical investigations are incorporated in Fig. 20.

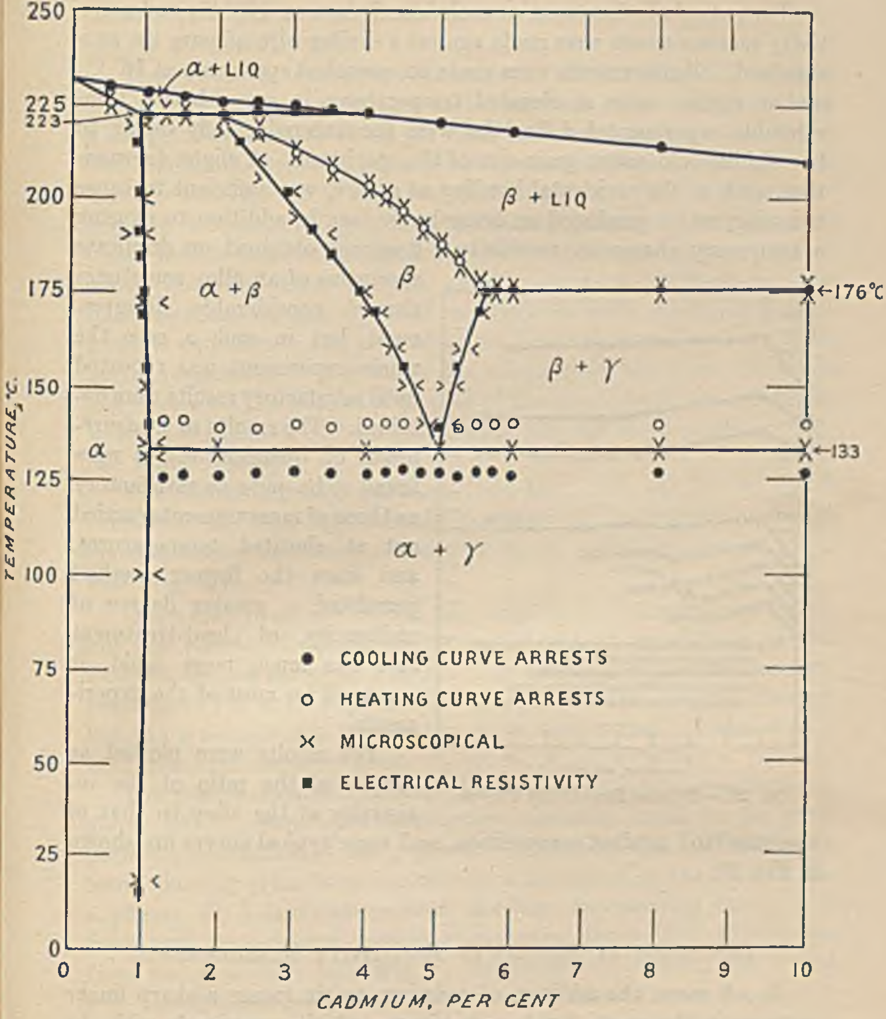


Fig. 20.—Tin-Rich End of the Cadmium–Tin System.

Electrical Resistivity Measurements.

A portion of each cooling curve alloy was cast into a cylindrical chill mould of ½ in. diameter, and specimens 1 in. long were taken from the resulting ingots, the outer skin being removed in a lathe. The specimens were then extruded at 150° C. through a 0·1 in. die under a load of 3000 kg., applied on an Avery Brinell machine.

The extruded wires were annealed for 7 days at 170° C., and resistivity measurements were made against a similar wire of pure tin as a standard. Measurements were made on quenched specimens at 18° C., and in certain cases at elevated temperatures in an oil-bath. Considerable experimental difficulties were encountered chiefly owing to low rigidity and coarse grain-size of the specimens. A slight deformation, such as the accidental bending of a wire, was sufficient to cause twinning, which produced an irregular surface in addition to causing a temporary change in resistivity. Readings obtained on duplicate specimens of an alloy sometimes showed considerable disagreement, but in such a case the whole experiment was repeated until satisfactory results were obtained. The results of measurements on quenched alloys were found to be quite as satisfactory as those of measurements carried out at elevated temperatures, and since the former method permitted a greater degree of uniformity of heat-treatment and was much more rapid, it was used for most of the experiments.

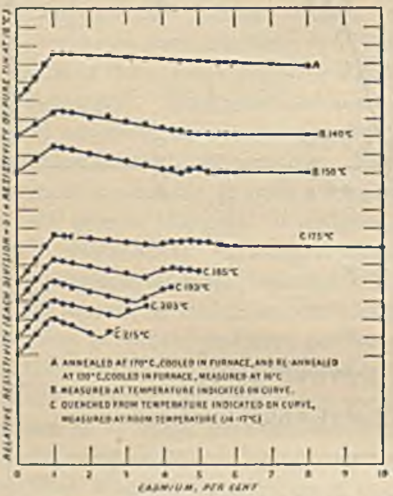


Fig. 21.—Typical Resistivity Curves.

The results were plotted as graphs of the ratio of the resistivity of the alloy to that of the standard, against composition, and some typical curves are shown in Fig. 21.

Discussion of Results of Resistivity Measurements.

In all cases, the addition of cadmium to tin causes a sharp linear increase in the resistivity to a maximum, which corresponds with the limit of the α solid solution. The maximum is sharp and is followed by a linear decrease, so that at each temperature the α phase boundary is determined quite accurately. The inflections of the curve which indicate other phase boundaries are not so definite.

In the case of alloys which are in equilibrium at room temperature, the maximum is at 1·0 per cent. cadmium, and is followed by a gradual linear decrease to 10 per cent. cadmium; the second portion of the curve represents the resistivity of a mixture of the phases α (tin-rich) + γ (cadmium-rich).

The curve for measurements made at 150° C. (Fig. 21) shows a similar increase to a maximum at 1·0 per cent. cadmium, followed by a steep linear decrease to 4·5 per cent. cadmium; from 4·5 to 5·25 per cent. cadmium there is a shallow curve, convex upwards, and a further linear relation from 5·25 to 10 per cent. cadmium. The curved portion, between 4·5 and 5·25 per cent. cadmium indicates a homogeneous phase field, and this is in agreement with the microstructures of these alloys quenched from 150° C., which consists of uniform β. The linear portions on either side of this curve indicate regions of heterogeneous equilibrium and correspond to the (α + β) and (β + γ) phase fields, respectively. The curve for alloys quenched from 150° C. is identical with the former in respect of the positions of the inflections which determine the phase boundaries, but the slope of the (α + β) line is not so steep.

The results for alloys quenched from 160°, 170°, and 175° C. are all similar to the foregoing, but the positions of the inflections change systematically, indicating a widening range of composition of the β field (Fig. 21).

Quenching from 140° C. did not suppress the eutectoid transition, but the results of measurements carried out in an oil-bath at this temperature are shown in Fig. 21. The branches of the curve corresponding to the α, (α + β), and (β + γ) phase fields are quite distinct, but the β field at this temperature is so narrow that it includes only the 5 per cent. cadmium alloy.

The results obtained from specimens quenched from temperatures above 180° C., were more satisfactory, probably owing to the more perfect preservation of the β-phase. These curves are all similar in form, showing (1) a linear increase to a maximum at the limit of the α phase; (2) a fairly steep linear decrease, representing the (α + β) field, and (3) a curved portion representing the β field, which rises from the (α + β)–β boundary to the boundary between the β and (β + liquid) phase fields. Alloys which were annealed in the (β + liquid) field usually broke on quenching due to the presence of a continuous intercrystalline liquid film.

In spite of the somewhat unsatisfactory character of some results of the earlier experiments, the positions of the phase boundaries as determined from the curves of resistivity are in close agreement with the results of microscopical analysis, and are considered to be reliable (Fig. 20).

CONCLUSIONS: CORRELATION OF RESULTS OF THERMAL AND MICROSCOPICAL ANALYSES.

Heating and cooling curves revealed a constant temperature transition at 223° C., indicating a peritectic reaction and the appearance of a new phase. A further invariant transition which occurs at 127° C. on cooling curves of annealed specimens containing more than 1 per cent. cadmium and at 138°–140° C. on heating curves, has been shown previously to be connected with the formation of a eutectoid structure in these alloys.

The present microscopic investigations have confirmed that a secondary phase β is formed at 223° C. by a peritectic reaction between α containing 0·9 per cent. cadmium and liquid containing 3·7 per cent. cadmium. The limits of the α and of the β phase fields have been determined by microscopic examinations and measurements of electrical resistivity, the two methods giving concordant results (Fig. 20). The limits of the α phase change very slightly with temperature, but the β phase which appears at 1·9 per cent. cadmium at 223° C., widens in composition range with decreasing temperature, becoming richer in cadmium and poorer in tin, until 176° C. is reached (eutectic temperature), where the β field extends from 3·9 to 5·7 per cent. cadmium, the latter being the concentration which is present in the $\beta + \gamma$ eutectic. Below 176° C. the solubility of β for both tin and cadmium decreases continuously to 133° C., at which it decomposes to form a eutectoid of α (tin-rich) and γ (cadmium-rich) at 5 per cent. cadmium.

In addition to the eutectoid arrests, certain minor evolutions of heat were noted on the cooling curves of annealed alloys of 1·25–4·5 per cent. cadmium, and these are probably connected with the decreasing solubility of tin in β. The separation of α from β does not take place completely or uniformly at the rate of cooling used, so that at the commencement of the eutectoid transition the β in these alloys is supersaturated with respect to tin. It is probable that the sudden separation of this excess tin as α causes the thermal effects recorded to be greater than the theoretical values (Fig. 3). The microstructures of the cooling curve specimens confirm this explanation, since for the compositions 2–4 per cent. cadmium, there is a greater amount of the fine duplex structure $(\alpha + \gamma)$ than would be present for equilibrium conditions.

During the earlier work of similar nature, a more rapid rate of cooling (2° C. per minute) was used, so that the suppression of the separation of α from β during cooling would occur in greater degree. The authors consider that the minor arrests which were recorded on the curves of alloys containing 2–3·5 per cent. cadmium at 129°–131° C., are caused by a sudden separation of the excess tin from the supersaturated β. The line *ABC* (Fig. 1) joining these arrests therefore represents a metastable position of a portion of the boundary between α + β and β fields (see Fig. 20), but it should not rejoin the transition line at 128° C.

Heating curves of alloys containing 1·25–4·25 per cent. cadmium show additional arrests extending over the range 160°–167° C., but microstructures show no evidence of a transformation in either α or β at these temperatures, and since the compositions concerned come within α + β field at 160° C., the arrests may again be attributed to a hysteresis effect in connection with absorption of α by β during heating.

The positions of the solidus lines as determined microscopically are in close agreement with the results obtained from heating curves except in the case of alloys containing 1·5–3 per cent. cadmium: the solidus arrests of these alloys occur at 1°–3° C. lower than the positions which are determined from the structures of specimens quenched after annealing at the temperatures concerned. The explanation is similar to that advanced for the other anomalies observed, *i.e.* that the rate of heating (1·5°–2° C. per minute) is insufficiently slow for the alloy to remain in equilibrium. Thus, if the β which is formed from α + γ at 140° C. on heating does not absorb α at the rate required for the alloy to remain in equilibrium, then there will be a concentration gradient in the β-phase, some of which will be richer in cadmium than the average composition of the alloy and will commence to melt before the true solidus temperature of the alloy is reached.

The complete revised equilibrium diagram for alloys containing up to 10 per cent. cadmium is given in Fig. 20.

PART II.—CADMIUM-RICH ALLOYS.

In the authors' diagram of the cadmium–tin system,[1] a transition line was shown at 170° C. on the evidence of arrests which occurred at that temperature on cooling curves of alloys containing 40–95 per cent. cadmium. Alloys containing 97–99·5 per cent. cadmium gave only one arrest in the vicinity of 170° C., the temperature decreasing to 164° C. with 99·5 per cent. cadmium. From the apparent absence of the eutectic arrest (176° C.) in these alloys, the authors concluded that the solubility of tin in cadmium was of the order of 3 per cent. at 176° C., but this was not checked microscopically, nor was the solidus of the cadmium-rich phase determined. The microstructures of these alloys contained a precipitate of the tin-rich phase when quenched from between 120° and 170° C., and also when slowly cooled, but the solubility at 170° C. was shown to be less than 0·2 per cent. tin. The sudden change of solubility indicated between 170° and 176° C., was considered to be the cause of the arrests at 170° C., since there was no evidence either of a phase change at that temperature or of a polymorphic transformation in the cadmium-rich solid solution. Similar effects have been observed by Haughton [5] in the copper–tin system, and by Rosenhain and Tucker [6] in the lead–tin system.

During the discussion of the authors' paper, Stockdale [4] proposed a solidus for the cadmium-rich phase as determined by a recent investigation. This indicated a solubility of 0·25 per cent. tin in cadmium at 176° C. He stated that the 95 per cent. cadmium alloy gave only one arrest, at 172° C. on heating, whilst the authors' results from cooling curves showed arrests at 176° C. (eutectic) and at 170° C. (solubility change).

The present investigations, which include a repetition of the authors' previous thermal work on these alloys, with additional heating curves, and a microscopic determination of the solidus, were undertaken to determine the cause of the above-mentioned discrepancies.

EXPERIMENTAL.

Alloys containing 60–99 per cent. cadmium were prepared from Chempur tin and Tadanac cadmium, as described previously.

Cooling curves were taken on 200 grm. samples, under the same experimental conditions as those used for the tin-rich alloys, whilst heating curves were taken for specimens which had been annealed for 1 month at 170° C., cooled in the furnace, and reannealed for 3 days at 120° C.

Microscopic examinations were confined to alloys containing 95–99·9 per cent. cadmium. Specimens were chill-cast, annealed for 1 month at 170° C., and examined after quenching from a series of temperatures at 5° C. intervals from 170° to 265° C., and also after cooling in the furnace. Specimens were prepared by the methods described previously, and were etched in 2 per cent. nitric acid in alcohol. When a specimen had been taken apparently above its solidus temperature, it was sectioned, and re-prepared.

Analyses of alloys used for microstructural investigations are given in Table II.

TABLE II.—*Analysis of Cadmium-Rich Alloys.*

Intended Composition, Tin, Per Cent.	Analysis, Tin, Per Cent.	Intended Composition, Tin, Per Cent.	Analysis, Tin, Per Cent.
0·1	0·099	1·0	0·98
0·2	0·22	2·0	2·03
0·3	0·29	4·0	3·90
0·5	0·51		

DISCUSSION OF RESULTS OF THERMAL ANALYSIS.

The results of the cooling curves are not presented in detail as they agree closely with the authors' previous results.

Alloys containing 60–90 per cent. cadmium show four arrests corresponding to the liquidus, eutectic (176° C.), solubility change (170° C.), and eutectoid transition (128° C.). With 97–99·5 per cent. cadmium, only one arrest occurs between the liquidus and eutectoid arrests, whilst with more than 99·5 per cent. cadmium the liquidus arrest alone is present. In all cases the actual figures agree to within 1° C. with those given in the authors' previous paper.

Heating curves did not give very satisfactory results, owing to the fact that the arrests are not so sharply defined as in cooling. The eutectoid arrest occurs throughout the range of alloys examined at 137°–142° C., but only one arrest was obtained at higher temperatures, commencing at 172°–173° C. and extending over a wide temperature range to 178°–180° C. This appears to confirm the result obtained by Stockdale [4] for the alloy containing 95 per cent. cadmium, and is probably caused by a tendency for the solubility change at 170° C. to take place at a higher temperature on heating, and to occur more slowly than on cooling. This would cause the thermal effect to be prolonged, so that it might not be completed before the eutectic arrest commences at 176° C. A further factor which would have the same effect is the temperature lag between the specimen and its surroundings which is generally greater during heating than during cooling.

RESULTS OF MICROSCOPICAL ANALYSIS.

The structures of specimens which had been annealed for 1 month at 170° C. were very similar to those obtained previously consisting of primary γ (cadmium-rich phase previously called β) [1] with the tin-rich α-phase at the grain junctions and as a precipitate through the γ grains; except in the case of the alloy containing 99·9 per cent. cadmium, which was homogeneous γ.

After annealing for 1 week at 178° C. (2° C. above the eutectic temperature), all alloys containing less than 99·8 per cent. cadmium show the presence of the quenched liquid phase (Fig. 19, Plate XXI). The alloy containing 99·8 per cent. cadmium is homogeneous from 172° to 210° C., when the first traces of liquid appear, while the 99·9 per cent. cadmium alloy is homogeneous when quenched from between 120° and 265° C., indicating no change of structure until melting commences.

The solidus of the cadmium-rich γ phase, as determined from these results, is shown in Fig. 22.

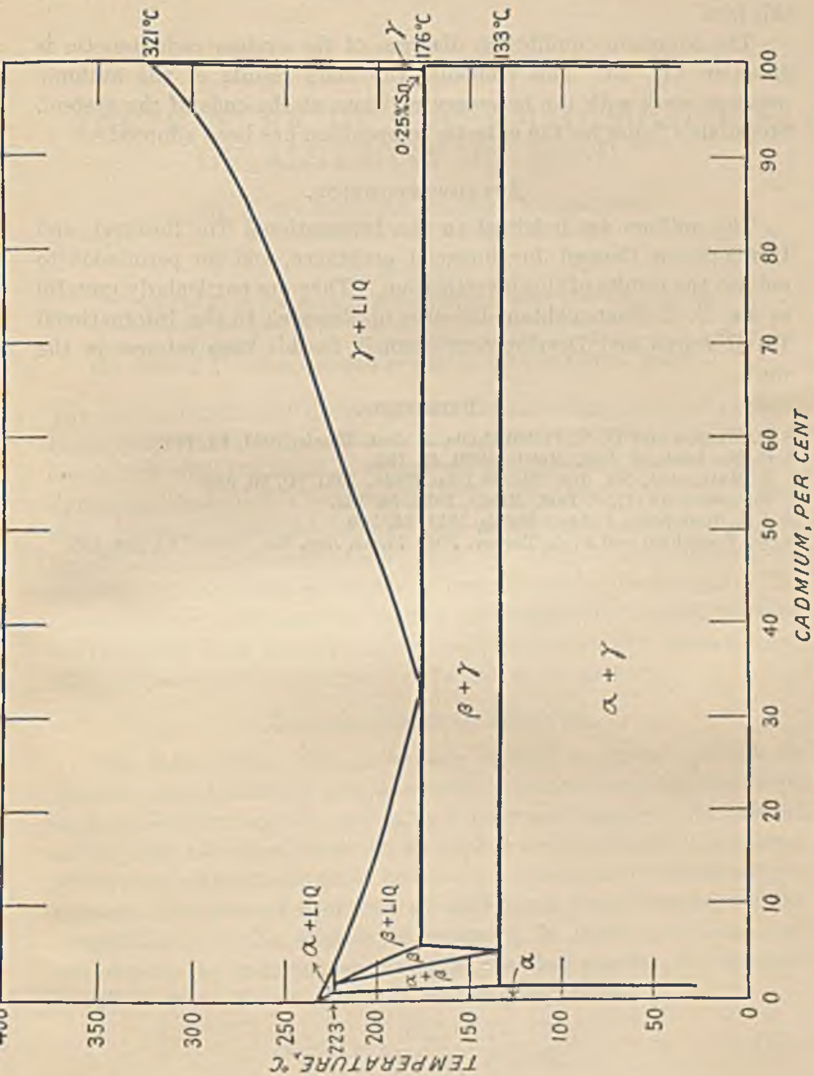


FIG. 23.—Constitutional Diagram of the Cadmium–Tin System.

in the diagram as a fine broken line, since it always occurs on cooling curves, and the authors can think of no more simple way of recording this fact.

The complete equilibrium diagram of the system cadmium–tin is given in Fig. 23. This embodies the main results of the authors' previous work with the necessary revisions at the ends of the system. Stockdale's figure for the eutectic composition has been adopted.

ACKNOWLEDGMENTS.

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REFERENCES.

[1] D. Hanson and W. T. Pell-Walpole, *J. Inst. Metals*, 1935, **56**, 165.
[2] D. Stockdale, *J. Inst. Metals*, 1930, **43**, 193.
[3] Y. Matuyama, *Sci. Rep. Tôhoku Imp. Univ.*, 1931, [i], **20**, 649.
[4] Discussion on (1), *J. Inst. Metals*, 1935, **56**, 184.
[5] J. L. Haughton, *J. Inst. Metals*, 1921, **25**, 309.
[6] W. Rosenhain and P. A. Tucker, *Phil. Trans. Roy. Soc.*, 1908, [A], **209**, 89.

THE NATURE OF THE SOLID SOLUTION OF ANTIMONY IN LEAD.*

748

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SYNOPSIS.

X-ray analysis and density determinations show that the solid solution of antimony in lead is of the simple monatomic type. The thermodynamic analysis is not in contradiction to this conclusion if errors of the order of 2° C. are assumed to exist in the equilibrium diagram.

THE solid solution of antimony in lead has important practical applications, while from the theoretical point of view it is of general interest in connection with the study of the nature of solid solutions. A thermodynamical analysis has been made by Yap Chu-Phay,[1] who concluded that antimony dissolved in solid lead as diatomic molecules and in liquid lead in monatomic form; and by Jeffery [2] who deduced the existence of molecules of Pb_2Sb in both liquid and solid lead. The present paper compares the results obtainable by thermodynamical analysis with those given by X-ray analysis and density measurement, using methods previously described by one of the authors.[3]

THERMODYNAMICAL ANALYSIS.

This method has been previously applied to metal systems by Andrews and Johnston,[4] and since used in various investigations such as that of the iron–carbon system by Körber and Oelsen.[5] The method of the ideal solubility curve can be applied only to the ideal solutions, which form without absorption or evolution of heat, and without volume change. The properties of such a solution are linear functions of the composition. If the solution of antimony in liquid and solid lead conforms to the principal conditions for the ideal solution, it is possible to apply for its examination the following expression:

$$\log \frac{N_s}{N_l} = \frac{H_{Pb}}{2,\ 3\ .\ R} \left(\frac{1}{T} - \frac{1}{T_{Pb}} \right) \quad . \quad . \quad . \quad . \quad (1)$$

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where N_s and N_l represent the atomic per cent. of lead in solid and liquid phases, H_{Pb} is the molal heat of melting, R is the constant of the perfect gas law = 1·986, T_{Pb} is the melting temperature of lead on the absolute scale, and T is the absolute temperature at which the solid and liquid phases of given composition are in equilibrium.

From this equation it is seen that the graph of log $\frac{N_s}{N_l}$ against $\frac{1}{T}$ is a straight line, the slope of which will give the heat of melting of the solvent (lead).

To apply the thermodynamic relation given, it is necessary to have the composition of liquid and solid phases in equilibrium at given temperatures and the heat of melting of lead. The composition of the phases can be taken from the equilibrium diagram of the lead–antimony system.

THE CONSTITUTION DIAGRAM.

Data concerning the liquidus and solidus of the lead–antimony system have been given by Heycock and Neville,[6] Gontermann,[7] Dean,[8] Schumacher and Nix,[10] and by Broniewski and Sliwowski.[11] The limit of solubility at the eutectic temperature (4·1 atoms per cent. antimony) was determined by Dean, Hudson, and Fogler.[9] The change in solid solubility with temperature was studied by the same authors by electrical conductivity measurements, and by Obinata and Schmid [12] by X-ray methods, their results giving a maximum solid solubility of about 4·9 atoms per cent. antimony. The combined results of all these investigators are given in Fig. 1. Consideration of the data, judging from variations in the eutectic temperatures given and quenching intervals used, shows that the accuracy is generally not greater than 2° C., and is in some cases much less.

HEAT OF MELTING OF LEAD.

The heat of melting of lead has been determined by several investigators, the results being given in Table I. The values show a wide

TABLE I.—*Heat of Melting of Lead.*

Cal./grm.	Authors.	References.
5·86	E. Rudberg	*Pogg. Ann.*, 1830, **19**, 133.
5·37	C. C. Person and D. Mazzotto	*Compt. rend.*, 1853, **23**, 162, 336; *Mem. Inst. Lombardo*, 1891, **16**, 1.
5·32	W. Spring	*Bull. Acad. Belg.*, 1886, **11**, (3), 355.
6·45	P. W. Robertson	*J. Chem. Soc.*, 1902, **81**, 1233.
4·78	E. Glaser	*Metallurgie*, 1904, **1**, 121.
5·53	J. Iitaka	*Sci. Rep. Tôhoku Imp. Univ.*, 1919, [i], **8**, 99.
5·5	S. Umino	*Sci. Rep. Tôhoku Imp. Univ.*, 1926, [i], **15**, 597.

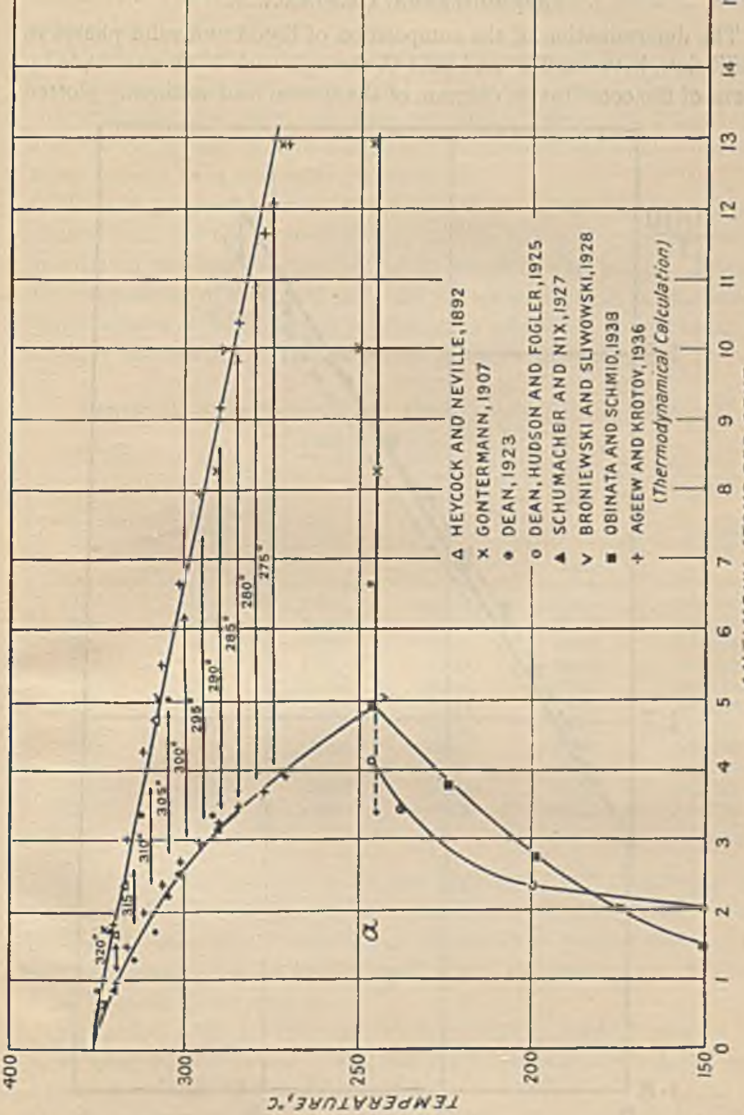

FIG. 1.—Constitutional Diagram of the System Lead–Antimony.

variation, but if the respectively high and low values of Robertson and Glaser are omitted, the mean value from the other observations is 5·51 cal./grm., very near that given by Iitaka and Umino. For the present authors' calculation the value 5·5 cal./grm. was taken.

THERMODYNAMIC CALCULATION.

The determination of the composition of liquid and solid phases in equilibrium between 275° and 320° C. through each 5° C. was made by means of the constitution diagram of the system lead–antimony plotted

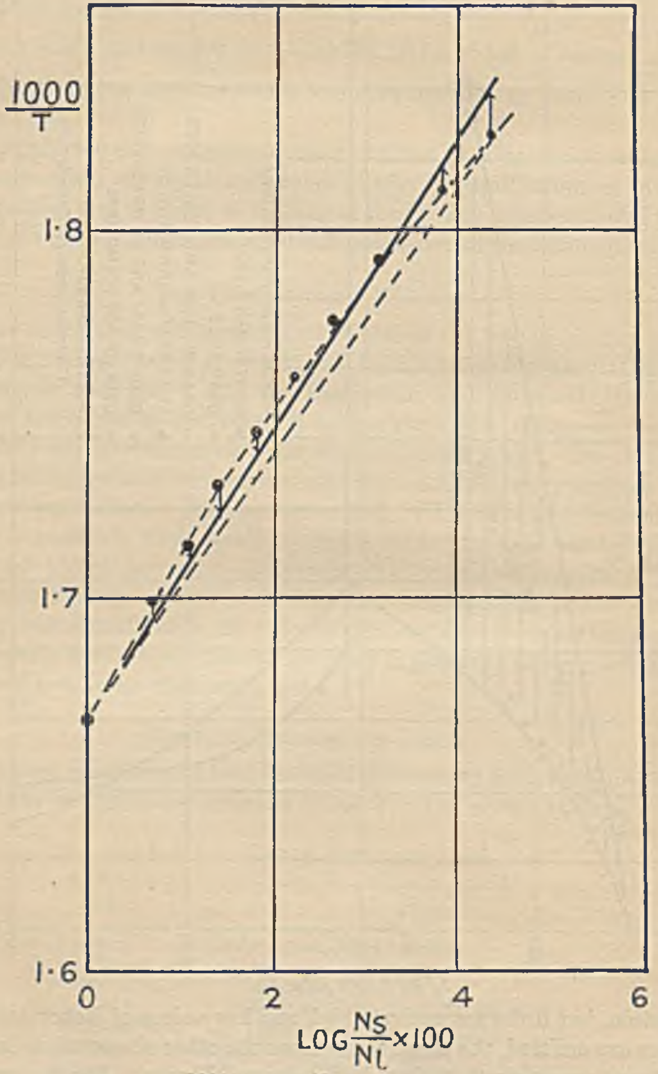

FIG. 2.—Relation of $\frac{1000}{T}$ and log $\frac{N_s}{N_l}$ for Alloys of Lead and Antimony.

in Fig. 1. The results are given in Table II, and the graph of $1000/T$ against log N_s/N_l in Fig. 2.

The points of the diagram cannot be placed exactly on the straight line necessary for the equation (1). This violation of the regularity characteristic for ideal solutions compelled Yap Chu-Phay [1] and Jeffery [2] to explain it by a special constitution of the solution of antimony in lead, *i.e.* a molecular constitution.

It is of particular interest to compare the accuracy of the experimental data and the digression of the points in Fig. 2 from the straight line drawn as closely as possible to the experimental points. Keeping the composition of the liquid and solid phases unchanged, the theoretical temperatures of liquidus and solidus were calculated according to the straight line relation. The values are given in Table III.

TABLE II.—*Temperature and Corresponding Compositions of Liquid and Solid Phases*

Temperature, t° C.	Temperature, Absolute, T.	$\frac{1000}{T}$.	Atoms Per Cent. Lead in Phases.		Log $\frac{N_s}{N_l}$.
			Liquid.	Solid.	
327	600	1·666	100·00	100·00	0·00000
320	593	1·686	98·10	99·12	0·00449
315	588	1·701	97·00	98·55	0·00653
310	583	1·715	95·75	98·04	0·01026
305	578	1·730	94·54	97·68	0·01419
300	573	1·745	93·28	97·35	0·01855
295	568	1·761	92·10	97·05	0·02274
290	563	1·776	90·85	96·80	0·02756
285	558	1·792	89·63	96·55	0·03230
280	553	1·808	88·35	96·32	0·03751
275	548	1·824	87·10	96·12	0·04279

In the last column are given the differences in ° C. between the theoretical and experimentally established temperatures. These differences, only one of which was appreciably greater than 2° C., may be regarded as corrections applicable to the constitution diagram of the lead–antimony system.

From the slope of the straight line relation $1000/T$ against log N_s/N_l (Fig. 2) and Tables II and III can be calculated the molal heat of melting of lead.

$H = \dfrac{0{\cdot}04279 \times 10^3}{0{\cdot}170} \times 2{\cdot}3 \times 1{\cdot}986 = 1150$ cal.; dividing by the atomic weight of lead (= 207·22) we have 5·55 cal./grm., a value in close agreement with the experimental values of Table I.

TABLE III.—*Thermodynamic Calculation of Positions of Liquidus and Solidus Lines of the Lead–Antimony System.*

Experimental.		Theoretical.			Difference $°C_s-°C_t$.
°C.	$1000/T_s$.	$1000/T_t$.	T_t.	°C.	
327	1·666	1·666	600	327	0
320	1·686	1·686	593	320	0
315	1·701	1·696	589·6	316·6	−1·6
310	1·715	1·709	585·1	312·1	−2·1
305	1·730	1·725	579·7	306·7	−1·7
300	1·745	1·741	574·4	301·4	−1·4
295	1·761	1·757	569·1	296·1	−1·1
290	1·776	1·775	563·3	290·3	−0·3
285	1·792	1·792	558·0	285·0	0
280	1·808	1·815	550·9	277·9	+2·1
275	1·824	1·836	544·6	271·6	+3·4

The thermodynamic calculations made by the present authors thus point out the insufficient accuracy of the experimental thermal data, for use in investigating the nature of the solid solutions of antimony in lead. Thus, the conclusion of Yap Chu-Phay [1] and Jeffery [2] may be erroneous. The existing experimental data of thermal analysis and the thermodynamic calculation are not in contradiction to the possibility of the atomic constitution of the solid solution of antimony in lead.

X-RAY ANALYSIS.

General Statement.—By X-ray measurement of the parameters of a solid solution, the density can be calculated in accordance with the supposed constitution, and comparison with the density measured by direct experiment provides in some cases a means of solving the problem of the nature of a solid solution. This method was used in the present investigation in addition to the thermodynamic investigation of the solid solution of antimony in lead.

The alloys were prepared from lead and antimony (Kahlbaum) in a porcelain crucible under paraffin and cast in a steel mould. All samples were annealed at 230° C. for 7 hrs. and quenched in cold alcohol. The samples were forged to close up any porosity and quenched again at 230° C. For X-ray analysis powder from each alloy was prepared and quenched at 230° C. X-ray parameter measurements were made using Preston's type camera [13] and copper radiation with the wavelength $K\alpha_1 = 1{\cdot}53736$ A. and $K\alpha_2 = 1{\cdot}54122$ A. The density was determined by weighing the alloys (samples of about 30 grm.), in water at 20° C.

Experimental Results.

The experimental results are given in Table IV and in Figs. 3 and 4.

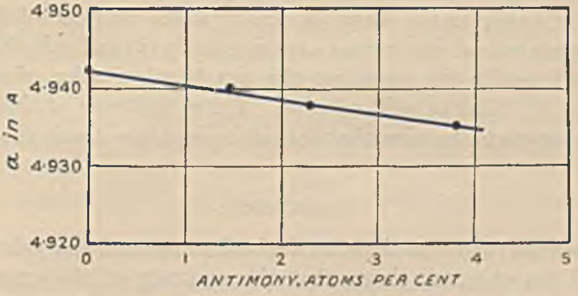

Fig. 3.—Parameters of the Solid Solutions of Antimony in Lead.

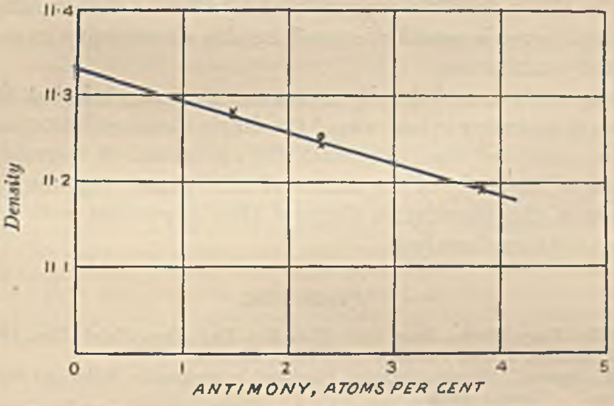

Fig. 4.—Density of the Solid Solutions of Antimony in Lead.

Table IV.—*Parameters and Density of the Alloys of Antimony with Lead.*

Antimony.		a in A.	Density.	
Weight Per Cent.	Atoms Per Cent.		Calculated from Parameter.	Direct Determinations.
0	0	$4·942_1$	$11·33_0$	$11·32_5$
0·85	1·43	$4·940_2$	$11·27_5$	$11·27_7$
1·36	2·29	$4·937_8$	$11·25_4$	$11·24_9$
2·27	3·80	$4·935_3$	$11·19_8$	$11·19_3$

Fig. 3 shows the change of parameter with composition of the solid solution of antimony in lead. It must be pointed out that the parameter values are not in agreement with those of Obinata and Schmid,[12] possibly owing to a difference in the purity of the metals used.

In Fig. 4 is given the change of density in the range of solid solution of antimony in lead determined experimentally (x) and calculated from the X-ray results (o), assuming the simple substitution of atoms of antimony and lead in solid solution. The coincidence of these values strongly supports the view that the lattice is of the atomic substitution type.

CONCLUSION.

A thermodynamic analysis on the basis of thermal analyses made by different investigators shows that the accuracy of the experimental data is not adequate to give a definite indication of the nature of the solid solution of antimony in lead. Accepting a probable error of 2° C., it can be shown that the experimental data were not in contradiction to a simple atomic constitution and involve no necessity to assume a molecular constitution.

X-ray analysis and density measurements indicated that the solid solution of antimony in lead was of the simple atomic substitution type.

It is considered that, in general, the application of thermodynamic analysis to the study of the nature of solid phases requires a greater accuracy in the constitution diagram than is possible with ordinary methods of thermal analysis.

REFERENCES.

[1] Yap Chu-Phay, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, **1931**, 185.
[2] F. H. Jeffery, *Trans. Faraday Soc.*, 1932, **28**, 567.
[3] N. W. Ageew, "Physico-chemical Study of Intermetallic Molecular Solid Solutions." Thesis: **1935.**
[4] D. H. Andrews and J. Johnston, *J. Inst. Metals*, 1924, **32**, 385.
[5] F. Körber and W. Oelsen, *Arch. Eisenhüttenwesen*, 1931, **5**, 569.
[6] C. T. Heycock and F. H. Neville, *J. Chem. Soc.*, 1892, **61**, 888.
[7] W. Gontermann, *Z. anorg. Chem.*, 1907, **55**, 419.
[8] R. S. Dean, *J. Amer. Chem. Soc.*, 1923, **45**, 1683.
[9] R. S. Dean, W. E. Hudson, and M. F. Fogler, *Indust. and Eng. Chem.*, 1925, **17**, 1246.
[10] E. E. Schumacher and F. C. Nix, *Proc. Inst. Metals Div., Amer. Inst. Min. Met. Eng.*, **1927**, 195.
[11] W. Broniewski and L. Sliwowski, *Rev. Mét.*, 1928, **25**, 397.
[12] I. Obinata and E. Schmid, *Metallwirtschaft*, 1933, **12**, 101.
[13] M. L. V. Gayler and G. Preston, *J. Inst. Metals*, 1929, **41**, 191.

CORRESPONDENCE.

Dr. J. H. Watson,* M.C., B.Sc., A.R.S.M. (Member): The authors claim that, although the observations by Yap Chu-Phay and Jeffery do not lie on a straight-line characteristic of an ideal solution, they can be made to do so by assuming an error of ± 2° C. (actually − 2·1° to + 3·4° C.) in the observed temperatures. Although a competent worker might easily make an absolute error of 2° in observing a temperature of 300° C., he would scarcely make a relative one of 5° in comparing temperatures of 275° and 325° C. under similar conditions. It seems *prima facie* improbable, therefore, that the observations of Yap Chu-Pay and Jeffery are really as inaccurate as the authors suggest. It should be noted, moreover, that these observations do, in fact, lie on a tolerably smooth curve, which can be represented by the empirical equation: $\log \frac{N_s}{N_l} = 0{\cdot}4366 \left(\frac{1000}{T}\right)^2 - 1{\cdot}2543 \left(\frac{1000}{T}\right) + 0{\cdot}8776$, and, further, that the curve of $N_l : \frac{1}{T}$ is a straight line: $N_l = 236 - 81{\cdot}6 \left(\frac{1000}{T}\right)$. It is interesting to extrapolate these two equations to the temperature of the lead–antimony eutectic, namely, 246° C. or 519° abs. It will be found that $N_l = 78{\cdot}78$ atomic per cent. lead or 86·34 per cent. by weight, corresponding to 87 per cent. given in Landolt's Tables, and $\log \frac{N_s}{N_l} = 0{\cdot}0818$. Hence, $N_s = 95{\cdot}1$ atomic per cent., or the maximum solubility of antimony in lead is 4·9 atomic per cent., which is the value given by Obinata and Schmid. According to the authors' straight-line relationship for $\frac{1}{T} : \log \frac{N_s}{N_l}$ (and hence curved line for $\frac{1}{T} : N_l$), the corresponding values at the eutectic temperature appear to be approximately: $N_l = 82{\cdot}5$ atomic per cent. lead, $N_s = 96$ atomic per cent. lead, or 4·0 atomic per cent. antimony, which is practically Dean, Hudson, and Fogler's value. In view of the regularity of the temperature observations of Yap Chu-Phay and Jeffery, and their extrapolation (always a searching test) to such close agreement with other observations of the maximum solubility, it would seem on these grounds, at least, doubtful if they are as inaccurate as the authors require, and probable that they do, in fact, contradict the hypothesis of a simple atomic constitution.

The Authors (*in reply*): Dr. Watson's interesting contribution gives us the opportunity of clearing up some points on our work.

Jeffery and Yap Chu-Phay used for their thermodynamical calculations the thermal data of other workers (the references are given in their paper and in ours). Discussion of the accuracy of the observations of the temperature should therefore relate to those data, and not to the papers of Jeffery and Yap Chu-Phay, as do Dr. Watson's remarks. The error which we attribute to those authors is not that of inaccurate observation, but of erroneous interpretation of thermal data, as they do not take into account the accuracy of the data used, which leads to a false conclusion.

We cannot agree with the conclusions which Dr. Watson reaches from our paper. Accuracy of thermal data is not determined by accurate temperature observation alone, but is the sum of a number of factors, such as temperature observation, chemical analysis, undercooling, irregularity in crystallization, &c. Although a competent worker can observe the temperature with great accuracy, the sum total of errors of all the factors required for thermal analysis

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* Royal Mint, London.

may, as can be seen in data published by M. Hansen * on the lead–antimony system, in the aggregate be equivalent to even larger discrepancies in the temperature than those assumed by us. The figure, ± 2° C., given by us is thus not an error of temperature observation, but represents the sum total of a number of experimental errors.

With regard to the extrapolation of the thermodynamic curves for an ideal solution to the composition of the eutectic and the limits of solid solubility, it must be remembered that these thermodynamic relations are applicable only to dilute solutions, and the conclusions suggested by Dr. Watson are merely a matter of coincidence.

We are very interested in the possibilities of thermodynamic analysis for the determination of the nature of metallic phases and the development of the work of Jeffery and Yap Chu-Phay, but we must again emphasize the need for using correct thermal data for the calculations which will otherwise lead to erroneous conclusions.

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* "Der Aufbau der Zweistofflegierungen," Berlin, 1936, p. 985.

THE SOLID SOLUTIONS OF INDIUM AND LEAD.*

By NICHOLAS AGEEW,† M.Eng., Member, and
VERA AGEEWA,† Ch.Eng.

Synopsis.

The constitutional diagram of the alloys of indium and lead has been modified as a result of new data obtained by means of X-ray examination and thermal analysis. The diagram shows that the alloys have limited solid solubility and a peritectic transformation. The physical properties of the alloys are in agreement with this diagram.

Introduction.

The constitutional diagram of the indium–lead alloys has been examined by N. S. Kurnakow and N. A. Puschin,[1] who found by thermal analysis that the metals were soluble in each other in all proportions. Electrical resistivity measurements and extrusion pressure measurements made by N. S. Kurnakow and S. F. Schemtschushny [2] showed that the change of properties with composition was such as would occur in the case of a continuous series of solid solutions.

W. Meissner, H. Franz, and H. Westerhoff [3] investigated the alloys in connection with a systematic study of superconductivity. The temperature of the transition point and the isothermal curves of electrical resistance at 77·7° and 20·4° K. change continually with composition as they must for solid solutions.

C. Benedicks [4] referred to the possibility of coreing in solid solutions of indium and lead, and corrected the transition points of the diagram of W. Meissner, H. Franz, and H. Westerhoff in accordance with this heterogeneity.

The crystal structure analysis made by A. W. Hull and W. P. Davey [5] shows that indium has a face-centred tetragonal lattice with $a = 4{\cdot}58$ A., $c = 4{\cdot}86$ A., and $c/a = 1{\cdot}06$. F. P. J. Dwyer and D. P. Mellor [6] confirmed the tetragonal lattice of indium and gave the lattice constants as $a = 4{\cdot}588$ A., $c = 4{\cdot}946$ A., $c/a = 1{\cdot}078$. Goniometric measurements of a crystal of indium, made by E. Zintl and S. Neumayr,[7] agreed with the results previously obtained and gave $a = 4{\cdot}583$ A., $c = 4{\cdot}936$ A., $c/a = 1{\cdot}077$.

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* Manuscript received February 24, 1936.

† Metallurgical X-Ray Laboratory, Industrial Institute, Leningrad, U.S.S.R.

It is well known that lead has a face-centred cubic lattice [8] with a parameter $a = 4{\cdot}942_1$ A. Measurements made in our laboratory agree with this.[9]

Experimental evidence has shown that a continuous series of solid solutions can only exist when the constituent metals have a similar crystal lattice. From these references it will be observed that while indium and lead have different crystal lattices they form a continuous series of solid solutions. This, if true, is unique, and in order to investigate it the experiments described below were carried out.

X-RAY INVESTIGATION.

For X-ray analysis alloys were prepared by melting together indium and lead (Kahlbaum) in porcelain crucibles under paraffin oil. Specimens 1 mm. in diameter were obtained by sucking liquid alloys into the thin glass tube. After the specimens had been removed from the glass tube, they were rolled between two glass plates and annealed at 25° C. for 10 days. Powder photograms of the alloys were obtained with a Hadding tube using copper radiation ($CuK_\alpha = 1{\cdot}539$ A.; $CuK_\beta = 1{\cdot}389$ A.). The X-ray camera was calibrated against pure lead, the lattice parameter of which was taken as $4{\cdot}942_1$ A.[9] The results obtained are shown in Table I.

TABLE I.—*Structure and Parameters of the Indium–Lead Alloys.*

Lead, Atoms Per Cent.	Lattice.	Parameters.			Parameter.
		a.	*c.*	*c/a.*	*a.*
0	α (tetragonal)	4·635	4·997	1·079	...
5	α	4·622	4·965	1·074	...
10	α	4·567	4·933	1·080	...
20	α + β	4·500	4·824	1·072	4·793
30	α + β	4·500	4·824	1·072	4·775
35	α + β	4·515	4·867	1·077	4·792
40	β	...	...	...	4·792
50	β	...	...	...	4·854
100	β (cubic)	...	...	...	4·942

Fig. 1 (Plate XXII) shows an example of the type of photogram obtained and Fig. 2 shows the change of parameter with composition.

Table I and Fig. 2 indicate that alloys with 5 and 10 per cent. of lead have a lattice similar to that of indium, the parameter and axial ratio changing continuously. Alloys from 40 per cent. of lead to pure lead have a cubic face-centred lattice with varying parameter, while in

PLATE XXII.

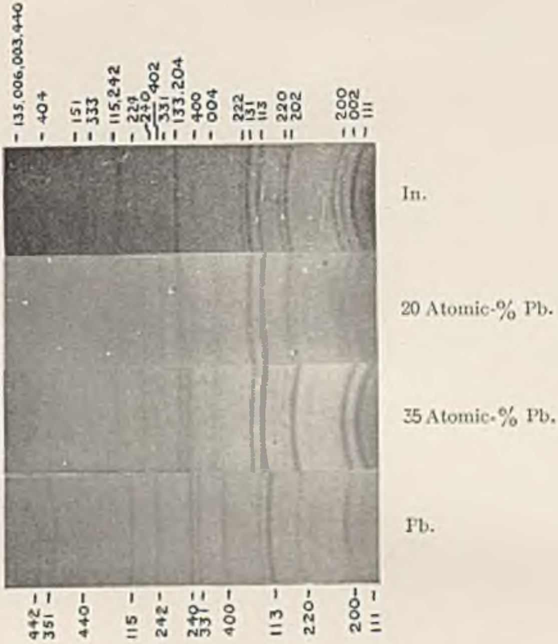


FIG. 1.—Powder Photograms of Indium-Lead Alloys.

the interval from 20 to 35 per cent. of lead the alloys show both lattices with an approximately constant parameter.

It will be seen, therefore, that the investigation shows the presence of a two-phase range between 20 and 40 atomic per cent. of lead. This result differs considerably from the previously published data, and further investigation by thermal analysis was undertaken to check this.

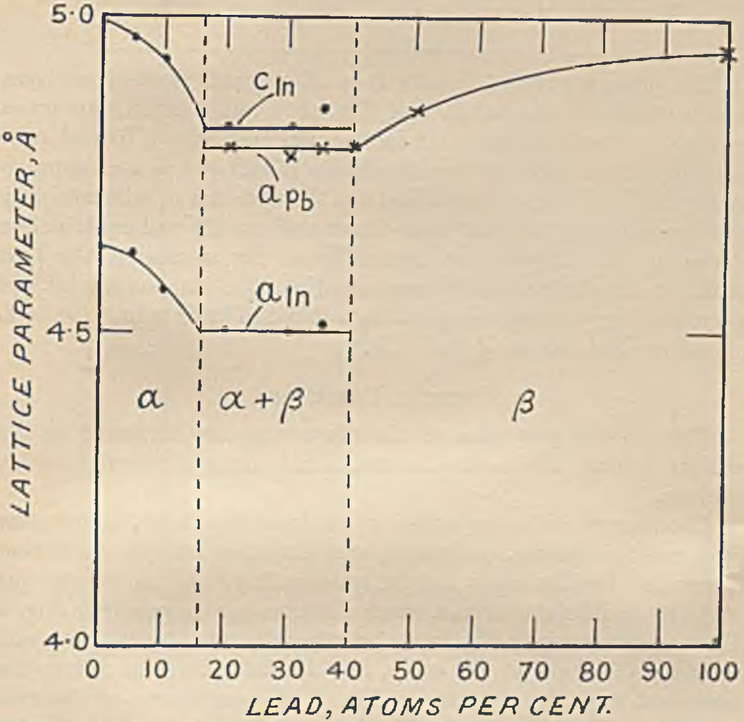


Fig. 2.—Lattice Parameters of the Indium-Lead Alloys.

Thermal Analysis.

The investigation by N. S. Kurnakow and N. A. Puschin [1] was not carried out over the whole range of the alloys. A blank was left at the range of composition from 30 to 60 atomic per cent. of lead, *i.e.* the interval where the X-ray evidence indicates occurrence of duplex structure. To fill up this gap thermal curves were taken of alloys in the range 30–40 atomic per cent. lead. The thermal curves were recorded by means of Kurnakow's self-registering pyrometer.[10] The specimens weighed 4–5 grm. The calibration was made with pure tin

TABLE II.—*Thermal Analysis of Indium–Lead Alloys.*

Lead, Atoms Per Cent.	First Arrest, ° C.	Second Arrest, ° C.	Heat Evolution at Second Arrest.
30	189·3	154	small
32	194·3	154	largest
35	199·0	154·5	large
38	207·1	154	small
40	208·9	...	...

The present authors' results from X-ray and thermal analysis, together with the thermal data of Kurnakow and Puschin,[1] are given in Fig. 3. It will be seen that indium and lead have a limited solid solubility and a peritectic transformation Liquid $+ \beta = \alpha$ at approximately 154° C. Part of the solidus and the variation of solid solubility with temperature have not been determined exactly and are therefore shown on the diagram by dotted lines. By measuring the heat evolution at the peritectic transformation, the composition of the α-phase at the peritectic temperature is found to be 32 atomic per cent. of lead (see last column of Table II).

PHYSICAL PROPERTIES.

The physical properties of the alloys were not measured by the present authors, the results discussed below being obtained by other workers.

The changes with composition of electrical resistivity, temperature coefficient of electrical resistance, and extrusion pressure have been determined by Kurnakow and Schemtschushny,[2] and agree very well with the equilibrium diagram given above, as can be seen from Fig. 4. There are not enough points in the heterogeneity range to determine with certainty the shape of the curve, but the data given are not in disagreement with the diagram in Fig. 3. Measurements of electrical resistance in liquid helium by W. Meissner, H. Franz, and H. Westerhoff [3] also give results in the two-phase range which are not in disagreement with Fig. 3. According to Benedicks,[4] the temperature of a transition point must alter abruptly as it passes through the two-phase range. The values given in the paper by W. Meissner, H. Franz, and H. Westerhoff [3] can be plotted so as to show a change of temperature of the transition point of superconductivity in the α and β range.

CONCLUSIONS.

The equilibrium diagram of indium–lead alloys has been modified as a result of X-ray and thermal analyses. The new diagram differs considerably from the earlier one.

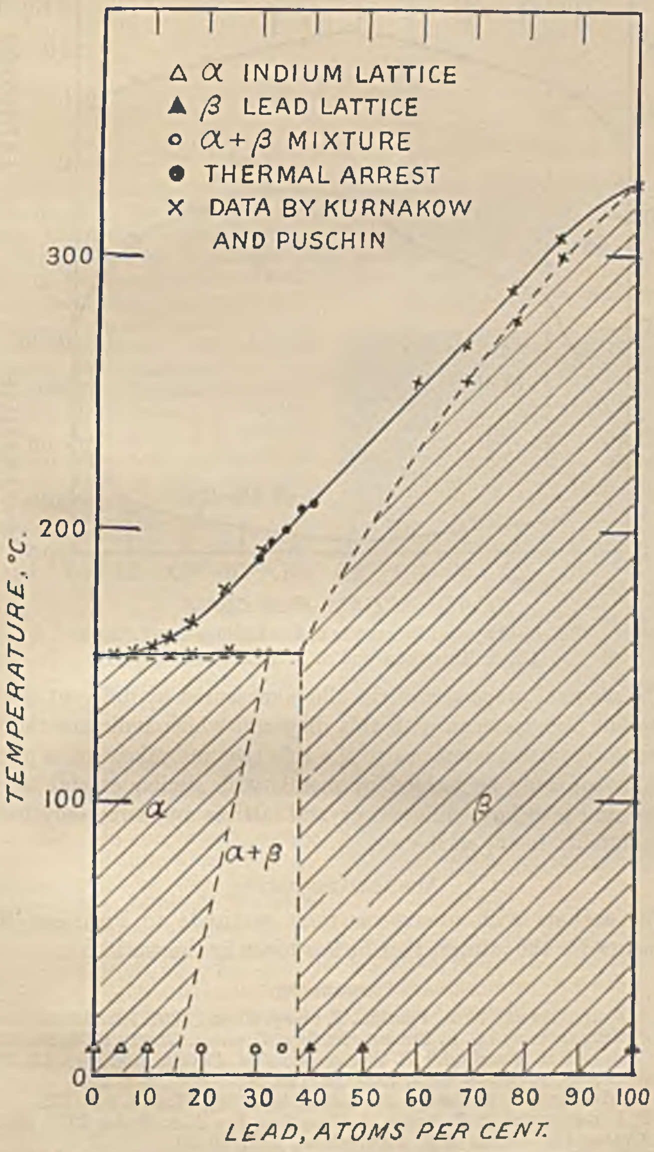


FIG. 3.—Constitutional Diagram of the Indium–Lead Alloys.

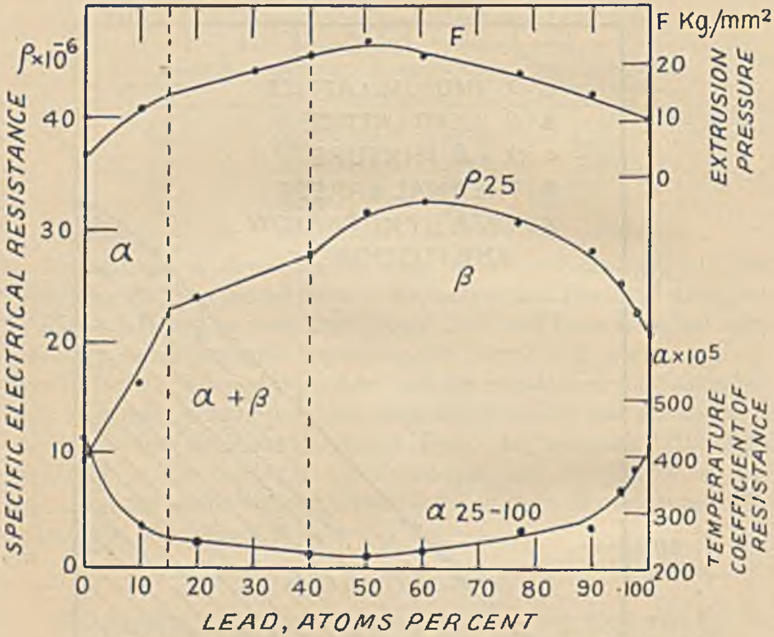


Fig. 4.—Physical Properties of the Indium–Lead Alloys.
(N. S. Kurnakow and S. F. Schemtschushny.)

The physical properties of the alloys measured by different workers are not in disagreement with this diagram, which indicates that the indium–lead system conforms to the rule that unbroken series of solid solutions can only be formed by metals with similar crystal lattices. Indium and lead have different crystal lattices and have only limited solid solubility in the solid state.

Acknowledgments.

The authors wish to express their gratitude to Professor N. S. Kurnakow for the interest that he has taken in the work.

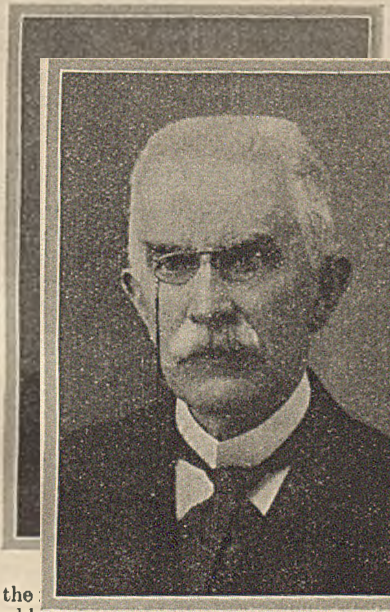
References.

[1] N. S. Kurnakow and N. A. Puschin, *Z. anorg. Chem.*, 1907, **52**, 442.
[2] N. S. Kurnakow and S. F. Schemtschushny, *Z. anorg. Chem.*, 1909, **64**, 149.
[3] W. Meissner, H. Franz, and H. Westerhoff, *Ann. Physik*, 1932, [v], **13**, 507.
[4] C. Benedicks, *Z. Metallkunde*, 1933, **25**, 199.
[5] A. W. Hull and W. P. Davey, *Phys. Rev.*, 1921, [ii], **17**, 266, 549, 571.
[6] F. P. J. Dwyer and D. P. Mellor, *J. Proc. Roy. Soc. N.S. Wales*, 1932, **66**, 234.
[7] E. Zintl and S. Neumayr, *Z. Elektrochem.*, 1933, **39**, 81.
[8] P. P. Ewald and C. Hermann, *Z. Krist.*, "Strukturbericht 1913–1928," 1931, 55.
[9] N. Ageew and I. Krotov, *J. Inst. Metals*, 1936, **59**, 301.
[10] N. S. Kurnakow, *Z. anorg. Chem.*, 1904, **42**, 184.

OBITUARY.

HENRY LE CHATELIER—1850–1936.

French science is in mourning. On September 17, the same day as the tragic death of the celebrated explorer Charcot, the great physical chemist Henry Le Chatelier passed away quietly at Miribel-les-Echelles. Born on October 8, 1850, he was on the point of attaining his eighty-seventh year. Right up to the end, he preserved not only a perfect lucidity of mind, but a power of work less common, and that clear and prompt judgment of men and scientific things which made him the "consulting brain" of physical chemistry and metallurgy.



Entering the École Polytechnique in 1869 and graduating as engineer in the Faculty of Mines he became Professor at the École supérieure des Mines in Paris in 1877, Professor at the Collège de France in 1888, Professor at the Sorbonne in 1907, and finally in 1908 he was called to the Chair of Moissan by the Académie des Sciences.

Henry Le Chatelier leaves an immense amount of scientific work, both on the experimental and on the theoretical and philosophical sides. His work on cements, alloys, refractories, fire-damp and combustible powders, his laws of chemical equilibrium, his theory of teaching applied sciences, and his crusade for the scientific organization of industry have had too important consequences not to be well known to all.

Metallographers owe him the thermocouples which have made possible the thermal analysis of alloys, the physico-thermal methods of analysis, and his classical researches on equilibrium diagrams, on quenching, &c., &c. He has given them that valuable law of displacement of equilibrium which allows predictions to be made of the consequences of a change of temperature, pressure, or magnetic field. His optical pyrometer has rendered more precise the chemistry of very high temperatures, and he has illuminated this by his discovery of the laws of equilibrium. What Professor has not been inspired by the works of the Master who has remodelled the teaching of chemistry? What industrialist, anxious to organize the control of his manufactures, has not meditated on the writings of Henry Le Chatelier or solicited advice always given with inexhaustible kindness?

Grand Officier de la Légion d'Honneur, Honorary Member since 1912 of the Institute of Metals, in addition to being an Honorary Member of numerous

Steel Institute, &c., and Corresponding Member to the Council of the Institute of Metals for many years, Henry Le Chatelier did not refuse the distinctions which were the just recompense of his services, but he had too good a character to seek after them. "I have never," he wrote, "consented to ask either for advancement or for decorations." Accustomed from his youth to live in contact with industry, he devoted his chief activities to the practical applications of science, but he persevered in this path above all because it satisfied his noble ambition to serve. "In my opinion," he wrote, "the rôle of a scientist does not consist in insulating himself in an ivory tower; he should, on the contrary, seek by his work to increase the well-being of his fellows."

By the extent of his science, by the rapidity and rectitude of his judgment, by his integrity and justice, and by his benevolence Le Chatelier was a sure guide and a veritable "fixed point of reference" for numerous disciples, pupils, and friends who had recourse to his advice and who to-day are overcome with emotion. Great scientist, great character, and great heart, Le Chatelier was one of those very rare men "who do honour to man." In the words of his friend Sir Robert Hadfield, "France has indeed lost a great man and that loss is irreplaceable in his own lines of work." P. CHEVENARD.

STANISŁAW M. CHOLEWIŃSKI.

M. Cholewiński, eminent Polish metallurgist and inventor, Director of the "Babbitt" works, Warsaw, died in Warsaw on September 28, 1936. He was born on April 25, 1880. Since 1908, in response to the demand in Poland for anti-friction metals, he had been conducting researches on these alloys and had discovered eight new phosphor bearing metals. In 1910 he established in Warsaw the foundry in which are still produced anti-friction metals of his own invention for the Polish (formerly Russian) State Railway and industrial purposes. Since 1927 M. Cholewiński had carried out much work on the alloys of aluminium and light metal castings for the Polish aeroplane and automobile industries.

M. Cholewiński was known as a man of generous heart; by his death Poland has lost one of her best sons and workers. He was elected a member of the Institute of Metals on October 26, 1933.

FRANCIS GRIMSHAW MARTIN, B.Sc.

By the passing of Mr. Grimshaw Martin, on October 23, 1936, after only a few days' illness, many and varied circles on Merseyside have lost a well-known personality. Mr. Martin was born in 1878 and received his scientific education at Mason's College, University of Birmingham, obtaining the B.Sc. degree of the School of Chemistry in 1907, and also the B.Sc. of London University in the same year. He became an Associate of the Institute of Chemistry in 1910 and a Fellow of the same Institute in 1913.

Mr. Martin's first experiences in Liverpool were in the capacity of Chief Science Master at the Liverpool Collegiate School, which position he left in 1916 to organize and conduct the work of the laboratories of Messrs. Alfred Holt & Company, in connection with the Blue Funnel Line; in this position he became interested in the metallurgical side of chemistry. During recent years he carried on an independent practice as Consulting Chemist and Metallurgist, in which he dealt largely with shipbuilding problems, for which his previous experience eminently fitted him.

Mr. Martin had a great capacity for appreciating and solving difficulties in scientific work and for explaining matters simply and clearly to others less thoroughly trained. He was a well-known member of the Liverpool Engineering Society, and the papers and lectures he gave before its members were typical of the man and enjoyable to his audiences. In these he gave instruction on metallurgical problems of particular interest to engineers, interwoven with wit and humour of a high order, in such a manner that none who heard him could fail to derive benefit and to acquire useful knowledge. His most important scientific work was carried out in connection with the heat-treatment of mild steel for the production of steel plate specially suitable for shipbuilding purposes.

As a member of the Institute of Metals, to which he was elected on March 13, 1918, Mr. Martin took a leading part in the organization of the Annual Autumn Meeting of the Institute held in Liverpool during September, 1928. On this occasion he delivered the Autumn Lecture of the Institute, which was a special feature of the Meeting, on "Non-Ferrous Metals in the Shipping Industry."

C. O. BANNISTER.

GEORGE MURRAY.

Mr. George Murray, Assistant General Superintendent of the Consolidated Mining and Smelting Company of Canada, Ltd., died at Trail, B.C., on November 8, 1936.

Born in Montreal in 1899, Mr. Trail received his technical education at McGill University, of which University he held the degree of M.Sc. On leaving the University he joined the staff of the Consolidated Mining and Smelting Company of Canada, Ltd., working first at the St. Eugene mine at Moyie, then spending a short period at Kimberley. For the past 25 years he had been at Trail, B.C. He worked in nearly all the departments of the Trail plant, and recently had been appointed Assistant General Superintendent.

In 1933 Mr. Murray received the Randolph Bruce Gold Medal of the Canadian Institute of Mining and Metallurgy. His ability was widely recognized. His willingness to assist his fellow metallurgists had made him innumerable friends in all parts of the world.

Mr. Murray was elected a member of the Institute of Metals on March 8, 1926.

ROBERT JOHN WALKER, C.B.E.

Mr. R. J. Walker, Chairman and Managing Director of The Parsons Marine Steam Turbine Company, Ltd., died on October 18, 1936, at the age of 65.

Born in Sunderland in December, 1870, Mr. Walker, at the age of 18, entered the service of the Wear firm of William Doxford and Sons, Ltd., Shipbuilders and Engineers, where he served an apprenticeship in the various branches of shipbuilding. In 1896 he was appointed Lecturer in Naval Architecture at the evening schools in Sunderland, and in the same year was appointed chief of the Designing and Theoretical Department at Doxford's shipbuilding yard.

He joined the Parsons Marine Steam Turbine Company in 1899 as naval architect for the then newly formed Company, and, seven years later, was appointed Joint Managing Director with the late Sir Charles Parsons. In March, 1931, after the death of Sir Charles, he was appointed Vice-Chairman and Managing Director, and in September of the same year, on the death of Mr. Stanley F. Prest, took over the duties of Chairman and Managing Director, a position which he held until his death.

Mr. Walker was associated with the development of the marine steam turbine from its first installation in the steam yacht *Turbinia*, and in his subsequent close collaboration with the late Sir Charles Parsons, both in the practical work of demonstrating the possibilities of the marine turbine and in his lectures and papers given before technical and other societies in this and other countries, he contributed largely to the present-day success of this wonderful propelling agency.

Early in 1920 Mr. Walker was created a Commander of the Order of the British Empire for special services in connection with war work. He was a Past-President of the North-East Coast Institution of Engineers and Shipbuilders, Past-President of the North-East Coast Engineering Employers' Association, for some time Chairman of Turbine Steamers, Ltd., of Glasgow, and was an Assistant on the Court of the Worshipful Company of Shipwrights.

He was elected a member of the Institute of Metals on December 30, 1918.

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