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

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

The INSTITUTE of METALS

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

Founded 1908. *Incorporated* 1910.

To the Secretary,
The Institute of Metals.

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

Name of applicant in full...

Address...

Business or Profession..

Qualification...

Degrees and/or honorific distinctions...

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

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

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

To be filled up by the Council.

....

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

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

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

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

55.

EXTRACTS FROM THE RULES

(MEMORANDUM AND ARTICLES OF ASSOCIATION.)

MEMBERS AND MEMBERSHIP

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

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

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

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

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

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

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

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

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

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

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

SUBSCRIPTIONS

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

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

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

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

DUTIES AND OBLIGATIONS OF MEMBERS

Rule 12.—Every member shall be bound:

(*a*) To further to the best of his ability and judgment the objects, purposes, interests, and influence of the Institute.
(*b*) To observe the provisions of the Memorandum of Association of the Institute, the Articles, and the Bye-laws.
(*c*) To pay at all times, and in the manner prescribed, such entrance fees on election, such fees on transference from one class of membership to another, and such annual subscriptions as shall for the time being be prescribed.
(*d*) To pay and make good to the Institute any loss or damage to the property of the Institute caused by his wilful act or default.

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

No. 2 1934

THE JOURNAL
OF THE
INSTITUTE OF METALS

VOLUME LV

EDITED BY

G. SHAW SCOTT, M.Sc.

SECRETARY

LONDON
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36 VICTORIA STREET, LONDON, S.W.1
1934

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

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1934-1935

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Sir Henry Fowler, K.B.E., LL.D., D.Sc.
Richard Seligman, Ph.nat.D.
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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.

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

December, 1934.

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

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MINUTES OF PROCEEDINGS.

AUTUMN MEETING.

The Twenty-Sixth Autumn Meeting of the Institute of Metals was held in Manchester from September 3–6, 1934.

Monday, September 3.

Autumn Lecture.

The meeting opened in the evening in the Great Hall of the College of Technology, the President of the Institute, Dr. Harold Moore, C.B.E., occupying the Chair, when Dr. J. L. Haughton, Member of Council, delivered the Thirteenth Autumn Lecture on "The Work of Walter Rosenhain," a full report of which is given on pp. 17–32.

On the motion of Dr. Richard Seligman, seconded by the President, a hearty vote of thanks was accorded to Dr. Haughton for his lecture.

Following the lecture, members adjourned to the Midland Hotel for informal conversation.

Tuesday, September 4.

Official Welcome.

At the morning session held in the Reynolds Hall of the College of Technology, Manchester, a civic welcome was accorded to the members by the Rt. Hon. The Lord Mayor of Manchester (Alderman Joseph Binns, M.B.E.), in cordial and well-chosen words. In the course of his speech the Lord Mayor recalled his own early experiences in the application of metals and alloys. He referred to the remarkable developments which have since taken place and to the importance of the industries of Manchester as users of the non-ferrous metals. In concluding, he said: "I am glad to welcome you to this College of Technology, with which I have been associated for over forty years, and to pay my tribute to the progress made in the engineering and metal industries, which to-day stand in the forefront in the efficient use of the materials which Nature provides for the benefit of mankind."

In his reply, the President warmly thanked the Lord Mayor, on behalf of the Institute, and made suitable reference to the Manchester Autumn Meetings of 1909 and 1923 and to the welcome received by the members on the three occasions. Manchester had a peculiar place in their affections as the birthplace of the Institute.

Nomination of Officers for 1935–1936.

The Secretary (Mr. G. Shaw Scott, M.Sc.) read the following list of members nominated by the Council to fill vacancies as officers for the year 1935–1936:

President.

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

Vice-Presidents.

W. R. Barclay, O.B.E.
C. H. Desch, D.Sc., Ph.D., F.R.S.

Members of Council.

Lieutenant-General Sir Ronald Charles, K.C.B., C.M.G., D.S.O.
Engineer Vice-Admiral Sir Robert Dixon, K.C.B., D.Eng.
R. Genders, M.B.E., D.Sc.
A. H. Mundey.
Lieutenant-Colonel the Hon. R. M. Preston, D.S.O.
H. B. Weeks.

The President: I have to remind members that this list is that submitted by the Council. In accordance with the rules, any ten members may at this present meeting nominate a candidate other than one of those nominated by the Council.

ELECTION OF MEMBERS AND STUDENT MEMBERS.

The Secretary announced that the following members and student members had been elected on July 12 and August 30, 1934:

MEMBERS ELECTED ON JULY 12, 1934.

Bosqui, Francis Lawrence	Nkana, Northern Rhodesia.
Butterfield, Leslie John, B.Sc.	London.
Coles, Carl Featherstone, B.Sc.	Ewell.
Cosbie, Arthur James Curtin	London.
Dörge, Friedrich, Dr.-Ing.	Düren (Rhld.), Germany.
Gordon-Luhrs, Lieut.-Colonel Henry, C.M.G., T.D.	London.
MacDonald, George, B.Sc.	Edinburgh.
Milbourn, Maurice, B.Sc., A.R.C.S., D.I.C.	Birmingham.

MEMBERS ELECTED ON AUGUST 30, 1934.

Bastien, Paul Gaston, Dr. es Sci.	Paris, France.
Bell, Donald Helliar, B.Met.Eng.	Port Kembla, Australia.
Bentham, Cecil	Stockport.
Brucklacher, Hermann	Hettstedt/Südharz, Germany.
Carder, Charles Henry	Birmingham.
Charles, Lieut.-General Sir James Ronald Edmondston, K.C.B., C.M.G., D.S.O.	London.
Chatwin, Sidney Shilvock	Birmingham.
Clements, Waldo John	Prescot.
Dechaume, Henri	St. Nazaire (Loire Inf.), France.
del Fresno, Professor Carlos, D.Sc.	Oviedo, Spain.
Harris, Edward Percival, B.Sc., A.R.S.M.	London.
Headlam-Morley, Kenneth, B.A.	London.
Hoare, William Edward, B.Sc.	London.
Kusaka, Kazuji	Dairen, South Manchuria.
Poulton, Winifred E.	Ilford.
Raub, Ernst, Dr.-phil.	Schwab, Gmünd, Germany.
Read, Henry Colin Seabrook, B.Sc., A.R.S.M.	London.
Reuter, Hans, Dipl.-Ing.	Duisburg, Germany.
Roche, John Fenwick Adair, B.A.	Bristol.
Scheller, Ernest, B.S.	Louisville, Ky., U.S.A.
Sohon, Julian A., B.Chem.	Bridgeport, Conn., U.S.A.
Warren, Althea	Los Angeles, Cal., U.S.A.
Williams, Charles Garrett, M.Sc.	London.

STUDENT MEMBERS ELECTED ON AUGUST 30, 1934.

Foden, Robert Frederick	Birmingham.
Proctor, William Leonard	Fence, nr. Burnley.
Rawlins, Kenneth Sidney	Banbury.

COMMUNICATIONS.

Communications by the following authors were then presented and discussed: D. J. Macnaughtan; A. S. Kenneford, M.Sc., and H. O'Neill, D.Sc., M.Met.; R. Arrowsmith, B.Met., M.Sc.; H. Greenwood, M.Sc.; Professor D. Hanson, D.Sc., E. J. Sandford, B.Sc., and H. Stevens, M.Sc. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

The proceedings adjourned at 12.30 p.m. until 10 a.m. on the following day, Wednesday, September 5.

Afternoon.

Members and their ladies were the guests at luncheon, at the Midland Hotel, of the Local Reception Committee, Dr. A. G. C. Gwyer occupying the Chair.

In the afternoon members visited, by invitation, the British Cotton Industry Research Laboratory and the works of the following firms: The Broughton Copper Company, Ltd.; W. T. Glover and Company, Ltd.; Mather and Platt, Ltd., and Metropolitan-Vickers Electrical Company, Ltd.

Wednesday, September 5.

Communications by: H. Sutton, M.Sc., and W. J. Taylor; H. Quinney, M.A.; W. E. Alkins, M.Sc., and W. Cartwright, O.B.E., M.Sc.; Professor E. A. Owen, M.A., D.Sc., and L. Pickup, M.Sc., Ph.D.; and M. Cook, M.Sc., Ph.D., and E. C. Larke were presented and discussed. Papers by the following were taken as read and not discussed: T. P. Hoar, M.A., Ph.D.; L. Kenworthy, M.Sc., A.R.C.S., and J. M. Waldram, B.Sc., A.C.G.I.; C. H. Samans, Ch.E., M.S., Ph.D; M. Milbourn, B.Sc.; D. M. Smith, B.Sc., A.R.C.S.; and S. G. Willimott, B.Sc., Ph.D. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

CONCLUDING BUSINESS.

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

(1) The Rt. Hon. the Lord Mayor of Manchester (Alderman Joseph Binns, M.B.E.) for his welcome to the city.

(2) The Chancellor, Council, and Senate of the University, for their hospitality.

(3) The Principal of the College of Technology, the Registrar and his staff for their kindness in providing facilities for these meetings to take place in the College.

(4) The local members and business houses, for their hospitality.

(5) The Manchester and Salford Corporations, for their courtesy in providing transport facilities.

(6) The firms in the Manchester district who have granted permission to members to visit their works, and for their hospitality.

(7) Those who have provided entertainment for the ladies.

(8) The Chairman (Dr. A. G. C. Gwyer), the Hon. Secretary (Mr. J. A. Todd), and members of the Local Reception Committee for their very valuable work.

To all of whom the Institute is indebted for the careful planning and most successful arrangements made for the visit to Manchester.

The resolution was seconded by Dr. H. W. BROWNSDON and carried by acclamation. The business meeting then terminated.

Afternoon.

In the afternoon members visited, by invitation, the works of the following firms: The British Copper Refiners, Ltd.; British Insulated Cables, Ltd.; Callender's Cable and Construction Company, Ltd.; and Chloride Electrical Storage Company, Ltd.; while ladies visited the works of Courtaulds, Ltd., or Richard Haworth.

In the evening members and their ladies were the guests of the Chancellor, Council, and Senate at a reception held in the University.

Thursday, September 6.

Members and their ladies took part in a whole-day motor-coach excursion to the works of Messrs. Thomas Bolton and Sons, Oakamoor, Staffordshire, returning to Manchester in the evening, when the meeting terminated.

AUTUMN LECTURE, 1934

THE WORK OF WALTER ROSENHAIN.

THIRTEENTH AUTUMN LECTURE TO THE INSTITUTE OF METALS, DELIVERED SEPTEMBER 3, 1934.

By J. L. HAUGHTON,* D.Sc., Member of Council.

Walter Rosenhain was born in Victoria, Australia, in 1875, and graduated as a civil engineer in Melbourne University in 1897. After spending three years at Cambridge as 1851 exhibitioner, he worked for some time at the optical glass works of Messrs. Chance Brothers, and in 1906 became Head of the Metallurgy Department of the National Physical Laboratory. These three subjects—engineering, optical glass, and metallurgy—were always his chief interests in life, but the greatest of these was metallurgy. He wrote a text-book on glass manufacture, whilst his "Introduction to Physical Metallurgy" has a much greater bias towards engineering than any other book on metallography. He was at various times President of the Optical Society, the Institute of Metals, and the International Association for Testing Materials. The first paper which he published (in 1897) dealt with a method of determining the specific heat of a liquid, whilst the last one was read last year before this Institute and discussed "Some Steps in Metallurgical Progress."

In a lecture to this Institute, important though it was, Rosenhain's work on optical glass may be dismissed briefly. His first contact with the subject on a large scale appears to have been when he was appointed as optical adviser to Messrs. Chance Brothers of Birmingham, and, doubtless partly as a result of his experience there, he wrote, in 1908, a book on "Glass Manufacture." Two years previous to this he had read a paper to the Optical Convention on "Possible Directions of Progress in Optical Glass." After the outbreak of the War, when the supply of optical glass from Germany was cut off, the National Physical Laboratory was asked to undertake research on its production in this country, and this was directed by Dr. Rosenhain, who erected an experimental plant for making glass in the foundry of the Metallurgy Department and—what connects this very closely with metallurgical work—for the study and production of refractory materials. Whilst

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

the research on optical glass ceased in 1926, the work on refractory products has been continued, and has proved of great value to the more purely metallurgical studies carried out in the Laboratory, especially those dealing with materials of high purity which melt at high temperatures. The contamination of such materials, either by the crucibles in which they are melted or by the atmosphere with which they are surrounded, constituted one of the great difficulties in the study of the equilibrium diagrams of iron alloys, and Rosenhain always insisted that, in the carrying out of such work, not only must the metals used be as pure as possible, but that every precaution must be taken to maintain the purity throughout all the subsequent processes to which the alloy was subjected. It was largely to assist in this direction that the work on refractories of high purity was carried on.

I will now turn to that part of Rosenhain's work which is of more direct interest to members of this Institute. Most of the metallurgical research which he carried out may be considered under four headings, which must not be taken too rigidly. They may be stated broadly to deal with :

(*a*) The production of new alloys and improvements in existing ones;
(*b*) The study of the structure and constitution of metals and alloys;
(*c*) Investigations of the effect of strain on metals and alloys;
(*d*) Design of apparatus and methods.

Of a total of about 100 papers * which he published, the numbers in the above classes are approximately 15, 25, 20, and 14, respectively, the remainder being concerned with optical glass or miscellaneous other subjects.

Dealing first with the production of new alloys and improvements in existing ones, Rosenhain's name is inseparably connected with "Y" alloy, but this was by no means his first contribution to the development of stronger and better non-ferrous metals. In the Ninth Report to the Alloys Research Committee of the Institution of Mechanical Engineers he described the properties of some ternary copper–aluminium–manganese alloys. The work, which was carried out in conjunction with Lantsberry, dealt chiefly with the copper-rich alloys, and showed that under certain conditions remarkably high tensile strength and elongation could be obtained from some of these materials. In addition to ordinary tensile tests on the alloys, alternating stress and impact

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* The bibliography at the end of this lecture lists some 150 papers and articles; some of these are reviews or semi-popular articles and are not included in the 100 original papers mentioned.

tests were carried out, and, what was much more unusual at that time, tests at high temperatures. This was a continuation of the work on the strength of aluminium–copper alloys at high temperatures to which Rosenhain referred in the discussion on the Eighth Report to the same committee. Abrasion tests, and hardness tests by means of the scleroscope, which was then a very new machine, were also undertaken, the results obtained with the scleroscope being correlated with the values given by the normal Brinell machine.

Whilst the greater part of the report dealt with copper-rich material, that section which was concerned with the alloys of the series high in aluminium is perhaps of greater interest in view of later developments. The alloy which was found to be the best of those examined contained 3 per cent. of copper and 1 per cent. of manganese, and Rosenhain pointed out in later years that Duralumin, which contains 3·5–5 per cent. of copper and 0·5–1 per cent. of manganese, together with a certain amount of magnesium, was the logical development of this alloy, and that had the results published in the Ninth Report been utilized, this country might have had the credit for the discovery of what is still one of the most successful of the light alloys in use to-day.

The Ninth Report has been referred to here somewhat fully, as it was the precursor of a number of similar papers dealing with the mechanical properties of alloys. The next in importance was published, in collaboration with Archbutt, as the Tenth Report of the Alloys Research Committee, and dealt with the alloys of aluminium and zinc. Whilst none of the alloys mentioned in this report has proved of great value in practice, it has been invaluable as the starting point for other investigations which led to the development of some of the best-known alloys, such as "A," "E," and "L5." The report is also of interest as introducing for the first time the extremely valuable property, known under the somewhat unfortunate name of "specific tenacity," which is obtained by dividing the ultimate stress of a metal in tons per sq. in. by the weight of a cubic inch of the material.

After the publication of the Tenth Report, work was carried out on the ternary alloys of aluminium, copper, and zinc and had reached an advanced stage when the War broke out. Rosenhain was abroad at the time, attending the British Association Meeting in Australia, and two out of the four remaining members of the scientific staff of the Metallurgy Department were called to the colours. On his return Rosenhain threw all his energy into the service of the country. The study of the aluminium–copper–zinc alloys was energetically advanced, and the scope of the research was extended to include many other alloys of aluminium. This work, and indeed much more of the same kind which was carried out at the National Physical Laboratory, was greatly facilitated by the fact that just prior to the outbreak of the War a rolling mill had been installed in the Department. This installation was characteristic of Rosenhain's foresight and of his determination that the equipment of his department should be second to none.

It was naturally not possible to publish, until after peace was signed, any of the work carried out during the War on the production of new alloys, so that a long interlude of eight years occurs between the dates of publication of the Tenth and Eleventh Reports to the Alloys Research Committee; it was not until 1921 that the latter appeared under the names of Rosenhain, Archbutt, and Hanson. It is stated in the introduction that " any attempt to give an account of the work in the fully detailed manner adopted in earlier Reports would have been impossible, owing to the prohibitive bulk of such a paper." As it is, the Report is an impressive volume of more than 250 pages, and it contains details of the development of " Y "-alloy, of 3/20, and of many others the names of which are everyday words with aircraft and internal combustion engine constructors. A further interesting feature of the Report is that in it is put forward the hypothesis that the age-hardening which occurs in Duralumin and similar alloys is due to the precipitation, from solid solution, on a sub-microscopic scale, of the compound Mg_2Si.

About the same time Rosenhain and his colleagues published papers on special copper alloys, on bearing metals, on zinc–copper–aluminum alloys, and on many other practical subjects connected with new alloys or the improvement of existing ones, whilst later he published work dealing with gas removal in aluminium castings and with alloys (mainly ferrous) for use at high temperatures.

The origin of the work on zinc–copper–aluminium alloys is of some interest. At one stage of the War it was feared that a scarcity of copper might arise and the laboratory was asked to undertake work in order to find a substitute for brass for making shell fuses. Rosenhain suggested that some alloy of zinc might be suitable, and work was immediately started on the effect of the addition of other elements to zinc. It was found that copper and aluminium together, in comparatively small quantities, gave rise to alloys which appeared to possess the requisite properties, and a thorough investigation was undertaken into the properties of alloys of zinc containing not more than 10 per cent. of copper or 15 per cent. of aluminium. The mechanical properties of the alloys in the cast, rolled, and pressed states, together with their rolling and ageing properties, were investigated, and an alloy containing 4 per cent. of copper and 7 per cent. of aluminium was finally selected as the most suitable material. There is reason to believe that for a short time about 200,000 fuses of this material were produced weekly.

We must now leave this part of our subject, and pass to the consideration of Rosenhain's work in connection with the study of the structure and constitution of metals and alloys.

Rosenhain's earliest constitutional work was done at a time when Heycock and Neville had finished most of their work on alloy systems, and when their magnificent research on the copper–tin system had set a standard far above that of all other similar investigations. A steady stream of papers on constitutional work was proceeding from the laboratory of our distinguished Honorary Member, Professor Tammann. This work was definitely undertaken with the object of establishing, approximately, the shape of the liquidus curves in as many alloy systems as possible, and as such it was excellent. Unfortunately, many people regarded the results obtained as completely accurately determined equilibrium diagrams. Such they never were, nor was this ever claimed for them, but when other investigators published as equilibrium diagrams, results obtained by the same methods, the whole subject was in danger of falling—indeed, had fallen very far—from the high plane on which Heycock and Neville had set it. Rosenhain's first paper to this Institute, "Metallographic Investigation of Alloys," was a fighting criticism of this attitude and a plea for a much higher standard both in the purity of the metals used, in the methods of thermal analysis, and in preparation of specimens for microscopic examination. To the end of his life he insisted on a high standard in constitutional investigations and it is probably true to say that the great improvement in the work on equilibrium diagrams, which has been so noticeable in the last fifteen years or so, is at any rate in some measure due to his influence.

Rosenhain's first paper on the constitution of alloys, dealing with the lead–tin system, was read before the Royal Society. The Ninth Report to the Alloys Research Committee of the Institution of Mechanical Engineers, to which reference has been made above, contains work on the constitution of the copper–aluminium–manganese alloys. All his other papers on the subject of metallic equilibria were read before the Institute of Metals. Reference must, however, be made to a group of papers, read before the Iron and Steel Institute, of which five deal with the constitution of iron alloy systems. Although Rosenhain's name does not appear as author of any of these papers, the work was carried out under his direction, and he wrote the introduction to them.

Some of the constitutional work was of special interest. Reference may be made, for example, to that carried out with S. L. Archbutt on the constitution of the aluminium–zinc alloys. An equilibrium diagram for the system had been put forward by Shepherd, and Rosenhain and Archbutt had at first accepted it as the basis for the work they had commenced on the mechanical properties of these alloys—work which was afterwards published as the Tenth Report to the Alloys Research Committee. A few cooling curves, however, which were taken to confirm Shepherd's results, showed that the constitution must be much more complex than had been supposed by him. They therefore reinvestigated the system, and obtained a diagram which remained unchallenged for eleven years, when Hanson and Gayler, using apparatus and methods which had been developed since the original work, modified Rosenhain and Archbutt's diagram in certain respects, and completed that part of it which was admittedly incomplete.

The representation of the constitution of a binary system of alloys presents no difficulties, but in a ternary system a solid model is required. In the Ninth Report to the Alloys Research Committee, Rosenhain and Lantsberry used a model made of plaster-of-Paris to represent the liquidus surface of a part of the system. Such a method is satisfactory where the representation of one surface is all that is necessary, but if much more than this is required, it may become necessary to build a very complicated model in which the different phase volumes fit into each other. Rosenhain first tried to overcome the difficulty by building a wire framework and stretching threads across it to represent the various surfaces, in the same way that crystallographers build up models of their crystals. Owing, however, to the fact that many of these surfaces are not planes, but are curved, he soon abandoned the threads, and replaced them by wires, thinner than the framework. These wires he coloured to represent the various phases separating on the different surfaces, and in this way obtained models which showed very clearly the constitution of the alloys.

Referring now to the third heading, investigations into the effect of strain on metals and alloys, this was a subject very near to Rosenhain's heart, and, paradoxically, it appears at present as if it were the one in which his work will have the least permanent result, although his early research, with Ewing, on slip bands will doubtless ever remain a classic. This was the subject of the Bakerian Lecture to the Royal Society in 1899, a lecture delivered by Ewing and Rosenhain, no small honour for a young man of twenty-four! This work proved conclusively that deformation in metals under stress takes place by slip along the cleavage planes of the crystals, a conclusion which, so far as I am aware, has never been challenged. When, some years later, Beilby showed that during the polishing of a metal the surface temporarily behaved like a viscous liquid, Rosenhain seized on the idea and carried it much further. He used Beilby's suggestion that the same liquid, vitreous, or amorphous phase was formed at the slip surfaces when a crystal was deformed, to explain a large number of the phenomena which occur when a metal is subjected to stress; further, he suggested that the phenomena occurring at the crystal boundaries of a metal could be explained by assuming the existence of an amorphous film round each crystal. He used the theory to predict other phenomena, and then showed that these phenomena did, in fact, occur. At the present time the amorphous theory is regarded by the majority of metallurgists as not proven but, even if in the end it may be necessary to relegate it to the fate which has befallen innumerable unproved hypotheses, it can always be said that as advanced by Rosenhain it not only gave a wonderfully clear explanation of many phenomena that otherwise appeared mysterious, but also was the cause of the initiation of a vast amount of work—some of it of the highest order and of outstanding value—not only on the part of Rosenhain and his collaborators in defence of the theory, but also on the part of his opponents. Up to the end Rosenhain believed in the theory—slightly modified in detail naturally, but substantially as originally advanced—and on the last occasion on which I saw him, only two or three weeks before his death, he said that he believed the evidence in favour of the amorphous theory was at that time stronger than ever it had been.

Rosenhain also published a considerable amount of theoretical work in connection with the lattice distortion of metals, and showed how in many cases the same results were produced whether the distortion was due to strain or to alloying; for example, both the hardness and the electrical resistivity are increased when a pure metal is strained, but the same result can also be produced by the addition of some other metal which will dissolve in it. Reference should also be made to the work which he carried out on the effect of the rate of deformation on the production of Neumann lines, the rate being varied from a deformation of 10 per cent. in 20 minutes, carried out in an ordinary tensile testing machine, to that obtained by firing a detonator mounted on the specimen. Intermediate rates were obtained by more rapid loading in the testing machine and by dropping weights on to the specimen from varying heights.

Finally, we come to Rosenhain's work in connection with the design of methods and apparatus in connection with metallurgical research. Opinions will naturally differ in assessing the relative importance of the various parts of a man's work, but my belief is that, next perhaps to his insistence on a high standard, the assistance he rendered to metallurgical workers by providing them with apparatus and methods was Rosenhain's greatest accomplishment. With reference to methods, mention has already been made to his advocacy of the use of wire models for representing ternary equilibria. Whilst he did not introduce the inverse rate way of plotting cooling curves, and indeed at first opposed it in favour of the much more sensitive difference method, yet he soon realized that for the vast majority of work the simplicity of the inverse rate curve more than outweighed its relative lack of sensitivity, and ever afterwards he was an enthusiastic supporter of this way of recording the observations.

Another method introduced by Rosenhain concerns the polishing of specimens for microscopic examination. In his early work on slip, he wanted, in order to show that the slip bands were actual steps on the metal surface, to cut a section at right angles to the polished face, and to polish and re-examine this. He soon found that the unsupported edge of the specimen was destroyed during cutting and polishing to such an extent that even relatively coarse features were obliterated. He therefore electrodeposited a thick layer of copper on to the face, and then cut a section through the specimen and the copper. On polishing this, the copper supported the edge of the specimen and enabled it to be seen under the microscope. He also applied this method to the examination of sections through fractures and it is to-day the standard technique in work of this kind.

It is sometimes a little difficult to differentiate between methods and apparatus. Rosenhain laid great stress, in his early work on the constitution of iron–carbon alloys, on the method of examining the microstructure of samples of the metal which had been annealed *in vacuo* and then quenched very rapidly, and in order to render this possible he designed his quenching apparatus, wherein he made use of the then comparatively new fused silica tube to enable him to wash the specimen out of the hot furnace with a stream of cold water.

In somewhat the same category is the work carried out by Rosenhain and Murphy on the microstructure of solid mercury and of amalgams which are liquid at ordinary temperatures. It was necessary to freeze these so as to obtain a "polished" surface, etch them while solid, and examine the etched surface, still keeping it solid, under the microscope. To do this successfully, as they did, meant devising a new technique and modifying existing apparatus in order to carry it out.

Having quenched and polished a metallic specimen, it is generally necessary to etch it before examining it under the microscope, and Rosenhain introduced several reagents for this purpose. Perhaps I may be permitted to recount here the story of the discovery of the so-called N.P.L. reagent for mild steel. Shortly after my arrival at the Laboratory, I wanted to etch a piece of bronze to which a piece of mild steel was soldered. I used the standard ferric chloride reagent, but accidentally immersed the whole specimen in the liquid, and while the copper alloy was, naturally, not attacked, I observed with surprise that the steel was etched in marked bands or layers. I had no idea what this meant, and took the specimen to Rosenhain, who immediately deduced that the banding was due to uneven distribution of phosphorus in the metal, and apparently without any need for thought, sketched out a programme for investigating the matter. I mention this in detail because it was the first of very many occasions when Rosenhain's extreme rapidity of thought impressed me tremendously.

Rosenhain's design of apparatus was mainly concerned with microscopic work and thermal analysis. The quenching apparatus just mentioned comes, of course, under the first heading, as does the microscope which Messrs. Beck made to his specification. When he started his metallurgical work there was no microscope specially made for metallographic use, and he soon realized the shortcomings of the ordinary instrument for this special work, and had one built "on engineering lines" as he expressed it. He also designed two devices for levelling the specimen before transferring it to the microscope stage. The second of these, which works on an optical principle, has very great advantages over all the usual ones, although it is naturally much more costly.

Rosenhain's two great contributions to apparatus for thermal analysis are the gradient furnace and the plotting chronograph. The first arose out of the realization that on an inverse rate thermal curve it is much easier to see the result of small heat evolutions or absorptions when the curve is nearly vertical than when it is at a large angle to the vertical; and as in any ordinary furnace it requires complicated apparatus to ensure that the rate of change of temperature is uniform over the whole curve, and therefore that the curve is approximately vertical, Rosenhain designed the gradient furnace to give this uniformity. As is now well known, the furnace consists of a lagged tube which is heated at one end, and cooled at the other, and the specimen is moved at a constant velocity through the furnace. If the latter has a uniform gradient along it, and the specimen moves steadily and slowly through this gradient, the transfer of heat will be uniform providing there is no anomalous evolution or absorption of heat by the specimen. In the first furnace made the tube was wound over its whole length, the turns being much closer together at one end than at the other, but it was found that the difference in temperature between the ends was much too small, and that quite a satisfactory gradient could be obtained by winding 12–15 cm. of one end and water-cooling the other. The winding was first put on the bottom of the furnace, but it was found that serious irregularities in the curve were produced by the convection currents set up in the air inside the tube, whilst no such trouble was experienced if the winding was placed at the top. Of recent years modifications have been introduced into the apparatus, the specimen being fixed and the furnace moved passed it, instead of using a fixed furnace and moving specimen, as was originally done, but the principle remains the same.

A word as to the limitation of the gradient furnace may not be out of place here. Where a thermal curve of a metal is to be taken over a short range of temperature—150°–200° C.—this type of furnace offers little or no advantage over an ordinary one, and, further, for temperatures above about 1000° C. it has not so far been found possible to design a furnace which gives a reasonably straight line gradient owing, presumably, to the greater influence of heat radiated from the hot part of the furnace. In all other cases, however, the use of a gradient furnace is to be recommended, and where it is required to obtain a smooth curve reaching both above and below room temperature, its use is probably essential.

The merits of the plotting chronograph are somewhat different from those of the gradient furnace. It may perhaps be described as a luxury instrument. It is very expensive, and it is possible to get just as good results without its use, but only with a much greater expenditure of time and labour, and where a very large number of thermal curves are taken yearly, as is the case in the National Physical Laboratory and similar institutions, it does not take very long before the plotting chronograph repays its first cost.

The instrument is too well known to metallographists to require any detailed description here; suffice it to say that it plots the points on an inverse rate curve, the observer having merely to tap a key as the galvanometer spot passes the lines on the scale.

This concludes the discussion on Dr. Rosenhain's purely scientific work. There are, however, at least three other fields of his activity to which reference must be made. The first is his work in connection with international co-operation in science. His high linguistic capacity helped, of course, greatly in this, and those who saw him in the chair at section A of the International Association for Testing Materials will realize what the Association as a whole will have lost in losing him as President for the 1935 meeting. In addition, however, to the more obvious and public work of this kind, he was continually in correspondence with foreign metallurgists, acting as the apostle of British metallurgy abroad, and at the same time advocating the claims of continental work in this country.

Secondly, Dr. Rosenhain's non-scientific work at the National Physical Laboratory was remarkable. He came to the Laboratory when the Metallurgy Department was housed in the kitchen of Bushy House and had a total scientific staff of four : he left it with a staff of about seventy housed in a large three-storey building and several subsidiary ones, and this increase was in large measure due to Rosenhain's energy and enthusiasm and his capacity for communicating this enthusiasm to his staff. It must also be remembered that the building up of this great department was carried out while the builder was also hard at work in other directions—serving on innumerable committees, carrying out the work on international co-operation referred to above, working for the good of this our Institute, and many other such things.

This brings me to the third field of Rosenhain's activity—his work in connection with the Institute of Metals. He read a paper, which aroused considerable controversy, at the first meeting, and three years later was elected to the Council. For the next twenty-one years, that is until a few months before his death, his guiding influence was always felt, and he was in no small way responsible for the high position the Institute occupies in the metallurgical world. He was, as most of you know, President during the years 1928–1930, and was, over very long periods, chairman of various committees of its Council. During his Presidentship the Institute held an autumn meeting in Düsseldorf. It was largely due to his energy and skill that this was one of the most successful meetings that the Institute has held, and one which is remembered with pleasure by all who took part in it. In this, as in all other matters, Rosenhain was always ready to work for the good of the Institute, and was continually being called on by his colleagues on the Council to undertake difficult or critical correspondence for the Institute—more especially, though by no means exclusively, in connection with foreign matters.

A lecture dealing with the work of a man is no place for referring in detail to his personal characteristics, but I feel compelled to mention one thing—his approachableness by members of his staff, which was a very marked and greatly appreciated trait of his. In discussions at meetings he may sometimes have appeared very formidable, perhaps even unduly fierce, but there was no ill feeling behind the fierceness—only a keen desire that nothing which he did not regard as first class should pass unchallenged. This combination of approachableness and keenness helped him greatly in communicating the inspiration which others derived from him—an inspiration which was, I believe, by no means confined to his staff at the National Physical Laboratory.

In this brief lecture I have attempted the impossible—to do justice to the memory of a great man. Those who knew him well will probably realize more than the others how far I have failed. But while the man has gone his work remains *monumentum aere perennius.*

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THE IMPROVEMENT OF WHITE BEARING METALS FOR SEVERE SERVICE: SOME GENERAL CONSIDERATIONS.* 673

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SYNOPSIS.

Development in the internal combustion engine is imposing increasingly severe conditions on the bearings. Consideration is given to the theoretical functions of an ideal white metal, and the manner in which the stresses produced in service tend to cause failure by cracking. Since the normal action of the stresses are compressive, special attention is given to the tension stresses which are shown to lower the fatigue range of the metal and to open up incipient cracks. Based on this analysis the mechanism of crack formation is discussed.

The following directions in which improvement in service behaviour may be secured are considered: (1) diminishing the intensity of the stresses in the metal by modifications in (*a*) certain features of design; (*b*) the material used for the liner: (2) increasing the fatigue-resisting properties of the white bearing metal in respect to which results obtained in preliminary investigations of the fatigue properties of high tin–antimony–copper alloys with and without addition of a further element are given.

INTRODUCTION.

It is nearly a century since Isaac Babbitt introduced a bearing comprising two essential parts: a liner of relatively strong and rigid material coated with a thin layer of white metal. The advantages of this combination have proved of great importance in engineering practice but have not even yet revealed themselves clearly in terms of fundamental scientific principles. More attention has been directed to the metallurgy of the white metal coating than to the mechanics of the combination.

The alloy used by Babbitt consisted largely of tin, with small additions of copper and antimony; and in subsequent developments, the additions of copper and antimony in this ternary alloy have been varied within limits to suit different applications. Lead-base alloys with antimony and tin and frequently also with copper, have also

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found extensive use; and more recently, copper-base alloys have been employed in special cases although they possess only certain of the qualities that hitherto have been regarded as essential in bearing metals.

Investigation has proceeded in two distinct directions. On the one hand, engineers have compared different available alloys with special regard to technical and economic considerations under varied conditions of service and manufacture; and on the other hand, metallurgists have studied the structures and properties of the several groups of alloys with special attention to certain physical properties. In recent years, efforts have been made to ascertain what particular physical properties do indeed contribute to the success of bearing metals, and, although progress in this essential direction is difficult, valuable light has been thrown on the problem, and it appears reasonable to expect that material advances will be made as a result. It is natural that efforts in this direction should have been stimulated by difficulties experienced by engineers.

Recent development in the internal combustion engine in particular has produced a combination of three difficult conditions: high bearing pressures, high temperatures, and rapid change of loading. The connecting rod and main crank-shaft bearings in such engines have to face conditions more severe than in any other important class of engine or machine. In view of their superior merits, particularly at elevated temperature, tin-base alloys have been used in preference to lead-base alloys, and have undoubtedly given excellent service under severe conditions. The conditions of service, however, are increasingly advancing to a stage that calls for further improvement in tin-base alloys, or, alternatively, for the substitution of some other type of alloy.

The need for higher bearing pressures arises from two distinct causes: (1) higher maximum gas pressures, required to give higher mean effective pressures, as, for example, when superchargers are used in petrol engines, or to give the conditions required for effective combustion and high economy in the compression-ignition engines now increasingly used in transport; and (2) higher piston speeds. It is an important matter for consideration that whereas the power of an engine increases approximately in proportion to the piston speed, the inertia forces imposed on the bearings and other parts increase with the square of the piston speed. It follows that the efforts that engineers have made to gain more power by increasing the speed of the piston have reacted severely in many directions as well as on the bearings.

The higher temperatures involved arise also chiefly from the higher speeds, although bearings are in some degree heated from the combustion chambers and valve casings. The chief source of heat in the bearing is friction, and the conditions are eased appreciably when the oil is circulated enough to carry away heat that otherwise would have to be conducted through the white metal and adjacent parts of the engine.

The need for high revolutions and rapidly fluctuating loads on the bearings arises directly from the increasing use of relatively small, high-revolution engines giving high power per unit of weight. Rapid advance in this direction has tended to make fatigue-cracking more important than in former times and has tended to redirect inquiry to ascertain the true theoretical functions of an ideal white metal and the physical properties that it ought to possess.

GENERAL CONSIDERATIONS.

Fig. 1, which illustrates a longitudinal section of a bearing, gives an impression of the stresses induced in a white metal coating supported by an ideally rigid liner. The radial pressure p tends to spread the white metal laterally—and also circumferentially—and this spreading tendency is resisted by lateral pressure p', the action of which, since it reduces the shear stress in the white metal, enables it to withstand a greater pressure p than it can resist in a simple compression test carried out on a sample surrounded by air at atmospheric pressure. A graph plotted below the section indicates how the pressures p and p' decrease towards the ends of the bearing where the pressure of the oil is less. The pressure p' is ordinarily less than p, and the difference may be roughly constant when the metal is loaded so severely that it yields in a plastic manner. The gradient in the lateral pressure p', tending to push the white metal out at the ends of the bearing, is resisted by shear stresses acting along the surface between the white metal and the rigid liner. The success of a bearing metal in practice depends largely on its being able to accommodate itself to changes in load, and in accommodating themselves to such changes white metals possess important advantages over other materials. If the changes demanded are unduly severe, however, it appears that white metals as well as other alloys are liable to suffer from fatigue-cracking.

One of the first requirements in a bearing metal is a certain degree of strength, sufficient to carry severe pressure p without undue lateral pressure p' and sufficient to resist the shear stress q without undue displacement from the ends of the bearing. The strength, however, should not be excessive, because it is the very weakness of the metal that enables it to yield plastically and to flow away from places where the pressure may increase locally. If the bearing metal is not soft enough to flow, or if it does not retain some measure of its original softness in continued service, lubrication may fail locally and the bearing will then seize-up and fail.

It is believed that a capacity for retaining softness after long continued service is intimately related to low melting point, and low melting point possesses also another great advantage since, in the event of undue increase in temperature, melting out occurs without the bearing alloying itself to the shaft, thereby avoiding complete seizure and irreparable injury to the shaft. When an alloy hardens unduly under cold-work, it tends to score the shaft even when seizure may not immediately result. The merits of the tin-base alloys in these respects are well known. The advantage of melting out when there is a considerable increase in bearing temperature applies also to certain cadmium alloys which have been proposed, but at the present time their general merits as bearing materials have not been evaluated and they certainly present much greater difficulties in casting on steel or bronze liners than in the case of the tin-base alloys.

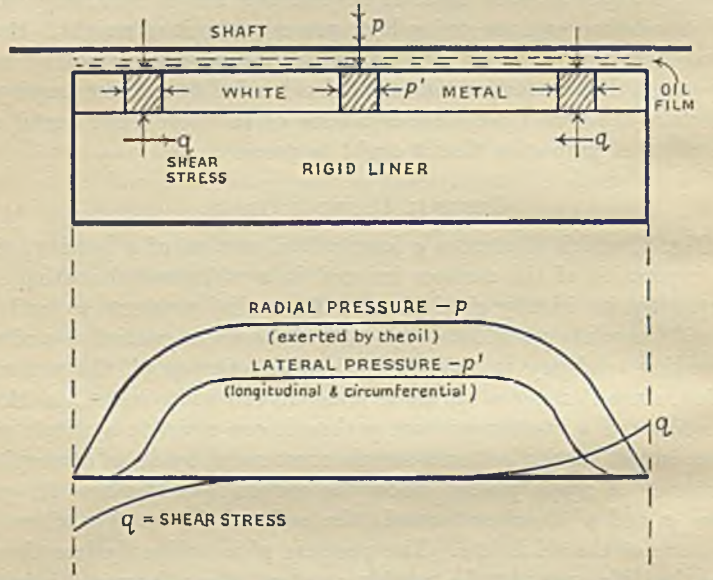

Fig. 1.—Ideal Representation of Radial and Circumferential Pressures and Shear Stresses in a White Metal Coating.

In addition to the limited degree of strength required to withstand the normal working stresses already described, some degree of temporary resistance to "cold-working" is desirable to assist the white metal to stand severe pounding caused by excessive vibration or irregular loading, but it is important to distinguish between temporary and permanent hardening by cold-work. Although temporary resistance may be desirable to resist rough treatment, permanent hardening is undesirable and is one of the greater faults to be avoided. A bearing metal that tends to harden permanently may run well enough for a time but will be likely eventually to lose its essential character and then to score the shaft or break in a brittle manner. It is believed that a capacity for self-annealing is one of the more valuable characteristics of a successful bearing metal, and that low melting point tends to afford the quality in question.

It is desirable that a limited degree of hardness, sufficient to withstand normal stresses, should be retained up to the temperatures that the lubricant can withstand without rapid deterioration. Temperatures of 120° to 140° C. have, in the past, been regarded as sufficient, but improved lubricants now permit of higher temperatures up to a possible limit approaching 200° C.

FATIGUE-CRACKING.

Although failure by pounding is occasionally important, the outstanding difficulty experienced in current severe conditions, particularly in internal combustion engines, is a peculiar form of fatigue-cracking. After a period of service under pulsating stress and high temperature, numbers of fine cracks appear on the surface of the bearing and spread in all directions to form a network similar in appearance to a tesselated pavement. For some considerable time the bearing continues to run in this condition without overheating or other difficulty, but eventually the cracks spread laterally below the surface of the metal, and when one or more pieces become detached the bearing fails by increase of friction and overheating produced as a consequence of the destruction of the surface and faulty flow of oil in the irregular film. The bearing melts out. To cope with this trouble, it is important to ascertain the cause of the initial cracking and the reason why the cracks spread laterally in such a manner that pieces become detached.

In 1930, Sir Thomas Stanton [1] published the results of certain tests in which thin rings of steel with coatings of white metal on their inner surfaces were subjected to repeated bending. The rings were caused to revolve between three rollers that applied forces to the outer surface of the steel, and the white metal was subjected to stresses that acted alternately as tension and compression in the circumferential direction only. Fatigue produced cracks in the white metal in a pattern corresponding to that observed in practice although the character of the stresses in the test was indeed very different from that of the complex combination of radial and lateral pressures in the bearing. The range of stress used in this investigation is quoted as 20·7 tons/in.^{2} for the steel, but no corresponding figure is given for the range of stress in the white metal. Assuming that the values of the elastic modulus E are taken as a direct measure of the stress without detailed calculations, and that the values for white metal and steel are approximately 8·5 and 26 million lb./in.^{2}, the range of stress in the white metal would be in the order of 6 tons/in.^{2}, which value is greatly in excess of any determined in fatigue tests carried out by other more familiar methods. (Compare results of endurance tests for similar alloys given below.)

When the conditions of loading in a bearing are contrasted with those produced in this or any other ordinary fatigue test, a difficulty in making comparison is immediately evident. Whereas in ordinary fatigue tests the metal is subjected to tensile stresses that tend to open any cracks that may be formed, the normal action of the stresses in white metal in bearings is compressive in all directions. It is difficult to see how fatigue, even if it occurs, can tend to open cracks in the manner that is actually observed. This difficulty might lead to the conclusion that the cracking is really due to bending, as in Sir Thomas Stanton's tests.

Against this view, however, examples have been cited by Ricardo [2] in describing the distribution of cracking in white-metal bearings of connecting-rod big-ends in compression-ignition engines, in which cracking is most evident immediately below the shank of the connecting rod, where the radial pressure is greatest and the more rigid support tends to reduce flexure to a minimum. It appears necessary, in view of much similar evidence, to consider whether the cracking may not be produced by stresses acting in a different manner from that illustrated in Fig. 1, and particularly whether tension stresses are present in the circumferential and longitudinal directions in the white metal. The stresses to produce fatigue, of course, must vary in magnitude and possibly in direction during each cycle.

The importance of tension in provoking accelerated fatigue in white metal is illustrated in Fig. 2, which is drawn from results of tests carried out by Haigh. The range of stress required to cause failure in direct stress is plotted on a base representing the mean stress applied during the cycle. It is clear that tension reduces the range of stress required, and that compression increases the range in a corresponding degree.

As the action of tension seems necessary before cracks can open, or even before fatigue can be caused by variations of pressure of reasonable magnitude, it is proposed to consider different causes which, in different cases, may tend to produce tension in the white metal. Five possible causes can be recognized. Of these the following are obvious: (1) In some instances, doubtless, tension may be produced by flexure of the liner, *e.g.* in engines with overhanging bearings or big-ends of extremely light construction; (2) Tension may be produced by flexure of the white metal even in cases in which no flexure of the liner occurs. This may arise when the adhesion of the white metal coating is imperfect and may account for failures under conditions in which the white metal normally is found to function satisfactorily. Less obvious causes of tension are as follows: (3) Although only pressure is initially produced in the lateral directions by applied radial pressure it would appear that as a result of the local spread of the metal around the area subjected to maximum pressure, tensions may be produced circumferentially and longitudinally as indicated in Fig. 3. These tensions would diminish to zero on removal of radial pressure which had not exceeded the elastic limit, while residual tensions would remain if the elastic limit had been exceeded. It is to be noted, however, that these tensions are produced around and outside the actual zone of maximum pressure in which there is the greatest tendency for cracking to occur; (4) The friction of the oil upon the surface of the white metal, although chiefly transmitted by shear-stress in the white metal may perhaps in some cases produce circumferential tension. The magnitude of such forces, however, cannot be large. Assuming a nominal pressure of 1000 lb./in.², giving a peak pressure perhaps as

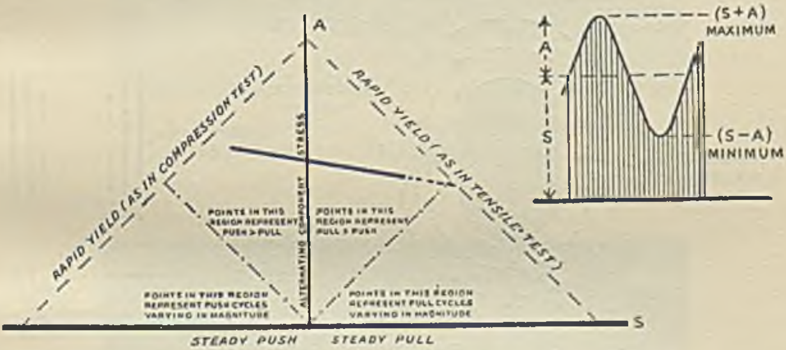

Fig. 2.—The Effect of Altering the Compression/Tension Ratio on the Range of Stress Required to Cause Fatigue in White Metal (Haigh Fatigue Test).

great as 6000 lb./in.^{2} and a coefficient of friction 0·015 (a high value) the tangential drag on the surface of the white metal is only of the order of 90 lb./in.^{2}; (5) Tension is set up when the white metal cools after solidification or subsequently, and the stress that may be produced in this manner is considerable. Assuming that the white metal and liner cool simultaneously, and that both are free from stress at a temperature $T1$, then the strain that has to be produced by tension after cooling to $T2$ to neutralize the contraction due to cooling is given by f in the equation that follows :—

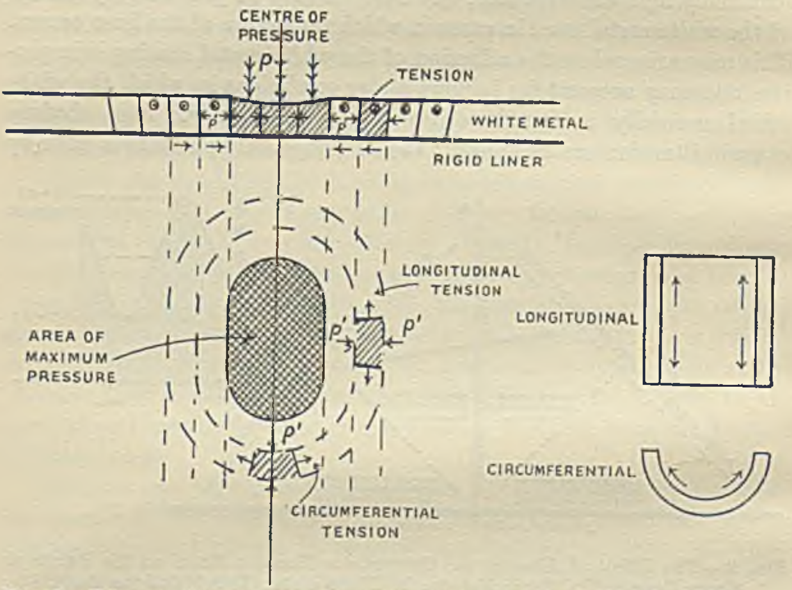

Fig. 3.—Diagram Showing how Circumferential and Longitudinal Tensions may be Produced during Application of Radial Pressure p.

$$\frac{f}{E}(1 - \sigma) = (\alpha_{wm} - \alpha_s)(T_1 - T_2)$$

where E denotes Young's modulus and σ Poisson's ratio for the white metal, and α_{wm} and α_s are the coefficients of thermal expansion for the white metal and steel, respectively. In this simple form, the equation neglects the effects of the stress in the steel—which is assumed to be practically rigid. The equation indicates that a difference in temperature of 100° C. would produce approximately 6·8 tons/in.^{2} in the white metal, in circumferential and longitudinal tension if the metal remained elastic. In reality, however, a range of temperature only a

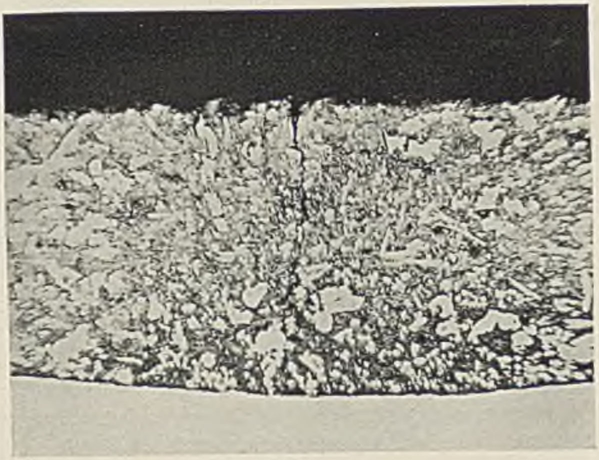

FIG. 5.—Cross-Section of a Cracked White Metal Coating, Showing a Typical Radial Crack. × 50.

FIG. 6.—Cross-Section of a Fatigued White Metal Coating, Showing Separation during Service of a Cracked Section. × 50.

little greater than 50° C. produces tensile stresses reaching the yield-point of any ordinary white metal. The importance of thermal contraction in relation to fatigue is therefore obvious.

The manner in which cracks form in a network on the surface of the white metal appears to be entirely consistent with the idea that tension acts both longitudinally and circumferentially in the manner indicated under headings (2) and (4) above. No evidence has appeared, so far, that the location of the cracks is related to macrostructural features, and the pitch of the network seems to be governed by mechanical considerations. When any one crack forms and opens, the tension is relieved in the immediate vicinity, being absorbed by shear stress between the white metal and liner as indicated in Fig. 4.

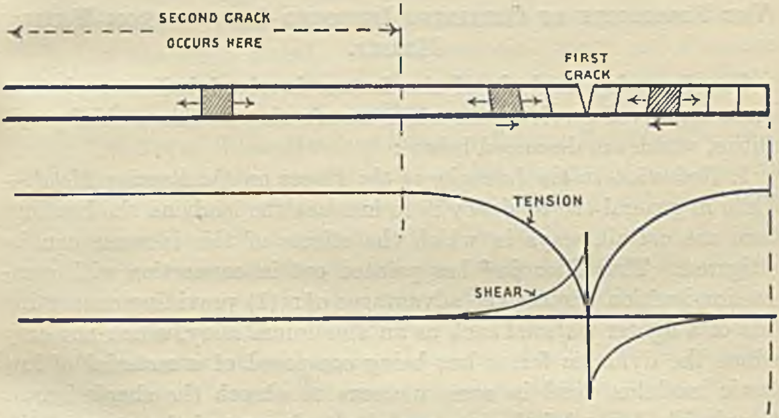

Fig. 4.—Diagrammatic Representation of Possible Mechanism that Determines the Spacing of the Cracks in a Fatigued White Metal Coating.

As a consequence of this relaxation, the next crack forms at a distance such that tension is present in sufficient degree to affect the fatigue limit adversely.

The sequence of events in the formation of a crack is important because it may indicate the measures required to cope with the trouble. If, as Murphy [3] has implied, the crack originates at the junction between the white metal and liner, and works up to the surface, the solution of the problem may lie in improved adhesion to the liner.

Micro-examination of a number of cracked bearings indicates that the cracks start at the surface and work downwards; an example is shown in Fig. 5 (Plate I). Moreover, as shown in Fig. 6 (Plate I), the circumferential cracks do not necessarily follow the bond between the white metal and liner, but may keep definitely clear of the bond. In the figure reproduced, details of the microstructure of the alloy are clearly discernable between the crack and junction. More detailed examination of the cracks and structure does not suggest any close relation between the two.

The evidence appears to support the view that the cracks originate at or very near to the surface, and that they are caused by fatigue under the action of wide variation of normal pressure coupled with circumferential and longitudinal tension.

The observed tendency of the radial cracks, after penetrating a certain proportion of the depth of the white metal, to turn laterally is possibly due to the action of pulsating shear stresses acting laterally around the margins of the "tesselations."

THE POSSIBILITY OF OBTAINING IMPROVED SERVICE FROM WHITE METALS.

The foregoing analysis of the factors involved indicates that to secure improved service from white metals there are two chief possibilities, which are discussed below:

I. *Reduction in the Intensity of the Forces on the Bearing Metal.*—While in general the tendency is to increase the loads on the bearings there are certain ways in which the effects of this increase can be mitigated. Thus Ricardo [2] has pointed out in connection with compression-ignition engines the advantages of: (1) providing connecting rods of a lighter material such as an aluminium alloy, which not only reduce the dynamic forces but being composed of a material of low elastic modulus, tend in some measure to absorb the shock forces; (2) suitable design of the manner of attachment of the stem of the connecting rod to the big-end, whereby distribution of the explosion pressure over a wider area of the white metal can be secured; (3) the employment of floating bushes, whereby the shock loading is not always maintained on the same area on the white metal.

It would further appear that a diminution in the intensity of forces on the white metal would be secured if the coating were cushioned with a material of lower elastic modulus than the steel normally used for the liner. In this respect bronze is superior in that it has a considerably lower elastic modulus than steel.

The above are matters of design. The most promising metallurgical contribution appears to be in the direction of reducing the tensile forces that lower the fatigue range of the material. Here the chief possibility would be to secure the minimum stresses in the white metal which result from its contraction during cooling. This involves consideration of: (1) the casting conditions as regards temperature of metal and liner, to determine the conditions for minimum stress compatible with satisfactory adhesion: in this connection the experimental methods of Müller[4] are of interest; (2) the thermal changes that occur during conditions of service. The ideal type of liner would be one having the same coefficient of expansion and contraction as white metal. The adoption of steel instead of bronze liners has been disadvantageous in this respect, since the coefficient of expansion of the low or medium carbon steel used is of the order of 0·000012, that of bronze 0·000017–0·000018, and that of the white metal 0·000024. Since bronze has been displaced on grounds of lack of strength it is possible that the use of a heat-treated bronze, for example of the type recently described by Wise and Eash,[5] which has greater strength than ordinary bronze, might produce a liner having the requisite physical properties and a coefficient of expansion more closely approximating to that of the white metal. Certain austenitic steels and aluminium alloys which have a coefficient of expansion very similar to that of white metal may also merit consideration.

II. *The Use of White Metals of Superior Fatigue-Resisting Properties.*—The tin-base alloys in general broadly form two groups, one consisting of alloys in which the antimony is below the limit of solubility in tin and in which the hard constituent is supplied by the presence of needles of the copper–tin compound, and the other consisting of alloys in which the antimony exceeds the limit of solubility, so that antimony–tin cubes are also present.

A considerable amount of data has been obtained concerning these two groups with respect to wear resistance, friction under test conditions in bearings, and such physical properties as are revealed by determinations of Brinell hardness, proportional limit in compression, &c. There is, however, almost an entire absence of information concerning fatigue properties. To determine the respective proportions of antimony and copper to give the maximum fatigue properties would require an extensive series of lengthy endurance tests. Short-cut methods, such as the use of ultimate tensile strength/fatigue ratio or a Brinell hardness number/fatigue ratio as are successfully employed for wrought steel, would, therefore, be of great service.

In some preliminary work the effect of increasing the antimony content in a series of alloys in which the copper content was kept constant has been investigated. Fatigue tests were carried out by the rotating cantilever method at the Engineering Department of the National Physical Laboratory and by the Haigh test by Professor B. P. Haigh. The results are shown plotted in Fig. 7. It appears that there is an increase in the fatigue-resisting properties as the antimony content is raised to about 8 per cent., above which the rate of increase tends markedly to fall off. It would thus appear that the chief governing factor is the amount of antimony in solid solution.

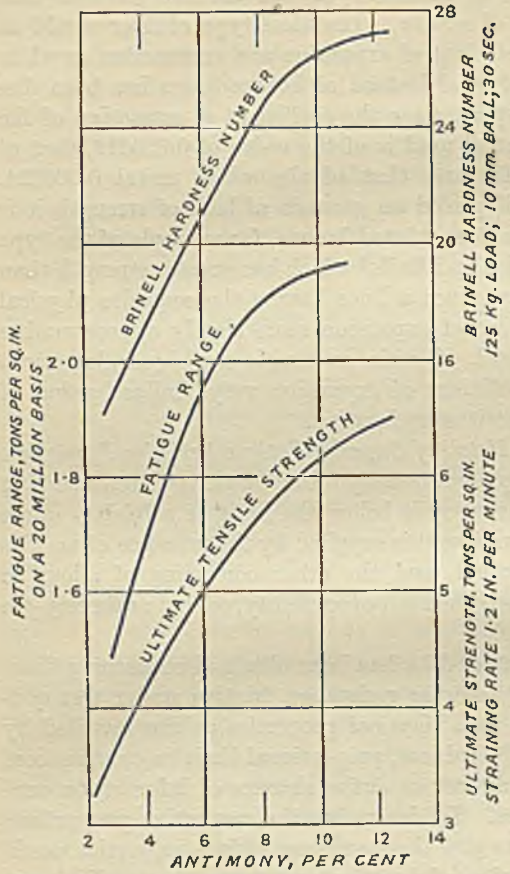

FIG. 7.—The Effect of Increasing Antimony Content in a Series of Copper–Antimony–Tin Alloys of Constant Copper Content (approx. 3·5%) on the Fatigue Range, Brinell Hardness, and Ultimate Tensile Strength. Other Elements Present in Alloys 0·25% Lead, 0·03% Arsenic, Iron trace. Casting Temperature 350° C., Mould Temperature 150° C.

The results of determinations of the Brinell hardness at a constant time of indentation and of the ultimate tensile strength at a standard rate of loading are also shown in Fig. 7. The general similarity in the slopes of the curves gives promise that for exploratory purposes the Brinell hardness and tensile tests are a useful guide to the fatigue-resisting properties.

In view of the statement by Boegehold and Johnson,[6] and Smart,[7] that in alloys of the type under consideration it is disadvantageous to increase the copper content much above 3·5 to 4 per cent. since in service this makes the alloy less resistant to shock at elevated temperatures, an investigation on the effect of copper was postponed and chief consideration has been given to the determination of the effect of the addition of other elements to alloys containing various amounts of antimony but with a constant copper content of about 3·5 per cent. The effect of an addition of 1 per cent. of cadmium[8] in increasing the Brinell hardness number and ultimate tensile strength is shown in Fig. 8. Consistent with its effect on the tensile properties and the hardness, from actual determination of the fatigue limit of the alloy containing 3·5 per cent. copper and 7 per cent. antimony, made by Professor B. P. Haigh, it appears that the addition of 1 per cent. cadmium increases the fatigue limit from 2·07 tons to 2·47 tons on a 20 million cycle basis. This improvement in the fatigue properties indicates the desirability for further investigations on the effect not only of cadmium but of other elements on the tin–copper–antimony alloys.

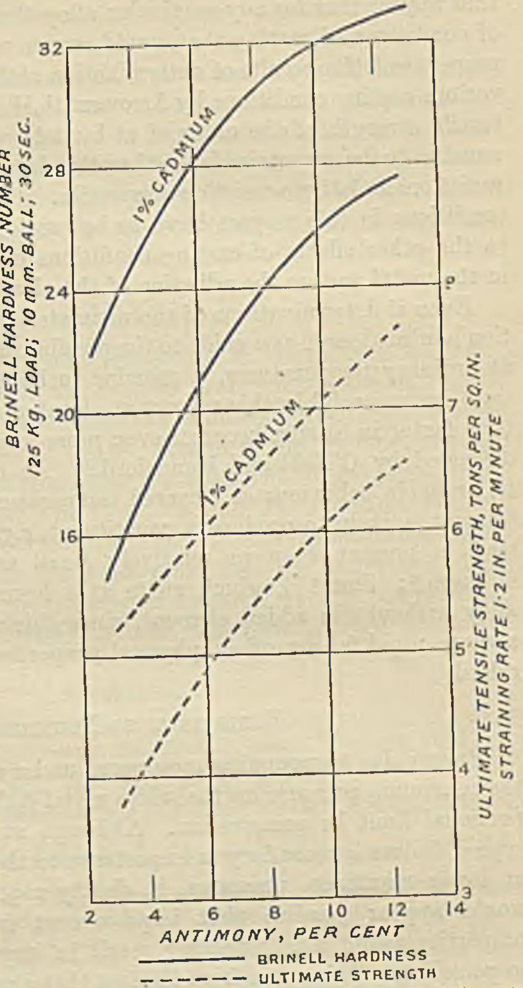

Fig. 8.—Effect of the Addition of 1% Cadmium to Copper–Antimony–Tin Alloys with a Constant Copper Content (approx. 3·5%). Cd Present: Casting Temperature 360° C., Mould Temperature 150° C. Cd Absent: Casting Temperature 350° C., Mould Temperature 150° C. Other Elements Present in Alloys: Lead, 0·04%; Iron and Arsenic, Traces only.

That marked differences in structure and physical properties of white metals can be obtained by varying the casting temperature and the temperature of the mould has been shown by various investigators, *e.g.* Hudson and Darley,[9] Rolfe,[10] and others. Thus, in the above tests, these conditions were kept constant except that in the case of the addition of cadmium it was found necessary to raise the temperature somewhat to ensure sound castings. It would thus appear that for any particular alloy there is likely to be a range of conditions of casting that would ensure maximum fatigue-resisting properties. The results of determination of the tensile properties under various casting conditions by Arrowsmith,[11] indicate that variations of tensile strength of the order of at least 10 per cent. are possible. It remains to be ascertained whether this is an index of corresponding variation in fatigue-resisting properties. In any case, the optimum conditions in this respect have to be carefully considered in relation to the other effects of casting conditions on the contraction stresses in the metal and on the adhesion of the alloy to the liner.

Even if determinations of the ultimate tensile strength or indentation hardness serve as a guide to the possible fatigue-resistant properties at ordinary temperatures, it remains to be ascertained whether such tests are as useful in this respect at elevated temperatures. Here the time factor in testing becomes even more important, a matter that is discussed by O'Neill and Kenneford.[12] An obvious consideration as to probable behaviour at elevated temperatures is whether an added element is likely to produce a constituent, *e.g.* the lead–tin eutectic if lead is present even in relatively small amounts (Boegehold and Johnson [6]; Smart [7]), which melts at a lower temperature than the alloy without the added element, since this would tend to result in a more rapid falling off in physical properties as the temperature is raised.

RESISTANCE TO POUNDING.

Failure due to pounding may occur under service conditions when the maximum pressure on the white metal definitely exceeds the proportional limit in compression. Although at the present time this type of failure is secondary in importance to the cracking which occurs at lower maximum pressures, it clearly requires consideration. It would appear possible that improvement in the fatigue-resisting properties would simultaneously result in improvement in resistance to pounding. This arises from the fact that a white metal of enhanced fatigue properties is likely to have a higher proportional limit not only in tension but in compression. On the other hand, such material is likely to have lower ductility. This raises the question whether the higher strength required to ensure a higher fatigue-resistance may not lead to another kind of cracking, namely, that which would result when the material is deformed beyond the limits of its ductility. To determine whether this may occur, pounding tests are required in addition to endurance tests.

The results of pounding tests on similar alloys to those considered above are described by Greenwood,[13] and they provide evidence that while a marked decrease in ductility does result in cracking in the material extruded from the bearing it does not cause cracking in the metal remaining in the bearing. At the temperatures at which deformation under pounding becomes severe, such work-hardening as occurs and which tends to lower the ductility of the alloy and therefore encourage cracking under deformation in the case of an alloy of low order of ductility, is counter-balanced by the softening by annealing which takes place at the temperature involved.

ACKNOWLEDGMENTS.

The author desires to thank Professor B. P. Haigh, M.B.E., D.Sc., for invaluable discussions on the matters dealt with in the paper, and also for his kind permission to include the results of fatigue tests obtained by him. Thanks are also due to the Director of the National Physical Laboratory for permission to publish the results of fatigue tests carried out for the International Tin Research and Development Council, which results are incorporated in Fig. 7. The experimental work referred to, and in which the author has had the assistance of his colleagues, is part of a programme of research by the International Tin Research and Development Council, who have granted permission to publish this paper.

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[13] H. Greenwood, *ibid.*, Part III.

THE BEHAVIOUR OF WHITE BEARING METALS WHEN SUBJECTED TO VARIOUS DEFORMATION TESTS.

Part I.—INDENTATION TESTS. By A. S. Kenneford, M.Sc., Student Member, and Hugh O'Neill, D.Sc., M.Met., Member. With an Appendix on AN X-RAY EXAMINATION OF BABBITT METAL AND OF THE AGE-HARDENING OF CAST LEAD–ALKALI ALLOY.* By G. S. Farnham, B.A., M.Sc., Ph.D., Member. **674**

Part II.—TENSILE TESTS.† By R. Arrowsmith, B.Met., M.Sc. **675**

Part III.—POUNDING TESTS.† By H. Greenwood, M.Sc., Student Member. **676**

Investigations carried out by members of the Metallurgical Department of the Victoria University of Manchester.

Introduction.

The following work was undertaken in the first place with a view to obtaining data for assessing the relative merits of different white bearing metals according to various laboratory tests. The need for such information is becoming more urgent owing to the developments taking place in engineering practice which are making more exacting demands on bearing alloys. In the second place it was hoped that the information gained in this way might act as a guide to the production of improved materials.

The tests reported in the present paper might be considered inadequate in themselves since they exclude many of the factors operating under running conditions. Elsewhere, however, studies under such conditions have been made and published. Jakeman and Barr,‡ for instance, examined in an actual bearing at various loads, speeds, temperatures, and conditions of lubrication, a series of alloys of the tin-

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† Manuscript received March 24, 1934.
Presented at the Annual Autumn Meeting, Manchester, September 4, 1934.

‡ *Brit. Non-Ferrous Metals Research Assoc.*, Research No. 43, 1931; *Engineering*, 1932, 133, 200–202.

base, lead-base, and lead-alkali types. Measurements were made of wear, frictional losses, and behaviour with different oils. To provide complementary information, therefore, the present work was carried out on alloys similar to those investigated by Jakeman and Barr, and in Table I such materials are marked with an asterisk.

TABLE I.—*Composition of Alloys.*

Ref. No.	Tin.	Antimony.	Lead.	Copper.	Iron.	Arsenic.	Description.
*I	92·3	3·78	0·30	3·55	0·04	0·03	High tin
*IB	92·8	3·50	0·47	3·21	0·03	trace	
INC	88·8	7·14	0·25	3·74	trace	0·03	
ICd	No. I plus 1% Cadmium.						
II	85·5	9·88	0·33	4·21	0·05	0·03	
IIA	85·0	10·75	0·30	3·90	0·04	trace	
IIMg	No. II plus 0·79% Magnesium						
IICd	No. II plus 1% Cadmium						
IINi	No. II plus 1·96% Nickel						
*IIPb	No. II plus 4% Lead						
	81·7	10·1	4·1	3·99	0·07	0·06	
*IV	39·8	10·5	48·6	1·03	0·04	0·06	Medium tin
*V	5·05	14·9	79·9	0·09	trace	0·06	High lead
*VA	5·40	14·6	79·1	0·04	trace	0·06	
*LA	" Bahnmetall " Pb 98·65 (sodium 0·6, calcium 0·7, lithium 0·04)						Alkali-hardened lead
Tin	" Chempur " brand 99·99%						
Lead	" Tadanac A " brand 99·99%						

Of those which are not marked in this way, attention may be drawn to Nos. ICd and IICd. Additions of cadmium have recently been recommended as enhancing the physical properties of tin-base bearing metals at ordinary and elevated temperatures.

The experimental work may be divided into three groups, and has been reported in sections as follows :

Part I.—Indentation Tests.
II.—Tensile Tests.
III.—Pounding Tests.

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The International Tin Research and Development Council provided financial assistance for these investigations, and gave permission for the results to be published. The authors are indebted to Mr. D. J. Macnaughtan, Director of Research to the Council, for very useful discussions and information. The work was carried out with facilities kindly placed at the authors' disposal by Professor F. C. Thompson, D.Met., and with his constant advice and encouragement.

PART I.—INDENTATION TESTS.

By A. S. KENNEFORD,* M.Sc., STUDENT MEMBER, and
HUGH O'NEILL,† D.Sc., M.Met., MEMBER.

With an Appendix on AN X-RAY EXAMINATION OF BABBITT METAL AND OF THE AGE-HARDENING OF CAST LEAD-ALKALI ALLOY.

By G. S. FARNHAM,‡ B.A., M.Sc., Ph.D., MEMBER.

SYNOPSIS.

The effect of viscous flow, ageing, and prolonged heating on the resistance to indentation of tin- and lead-base bearing metals has been investigated. Flow tests with a 120° steel cone at 19° and 96° C. show that Babbitt metal containing 1 per cent. cadmium or 2 per cent. nickel, or a lead-alkali bearing metal, give better indentation results than a plain Babbitt alloy.

The hardness of the different metallographic constituents of bearing metals and their softening on heating to 100° C. have been measured by scratch and micro-indentation tests. The matrices lose 40–45 per cent., and the cuboids 20 per cent. of their hardness, but the cuboids in a Babbitt remain somewhat harder than those in a lead-base alloy.

Two new simple tests are suggested. In the first a lubricated 60° conical casting of the alloy is flattened under 100 kg. load for 30 seconds, and the Mallock hardness number determined. By increasing the duration of loading a flow index may be measured on lines similar to "Hargreaves' analysis." Then, by compressing until cracks appear on the extruded edge, the ductility of the specimen and its cracking stress may be measured. At room temperatures the lead-base alloys show relatively low ductility, and this agrees with their low work-hardening capacity as determined by specially conducted ball tests and repeated impact tests with the scleroscope.

The second method employs an instrument similar to the Herbert pendulum, and measures the damping effect. It may not only be used to give rapid indications of hardness at different temperatures, but is also sensitive to the effect of different lubricants.

INTRODUCTION.

THE resistance to indentation of soft alloys having lead or tin as their basis, must be considered with reference to the duration of the indenting load. The lead–tin eutectic, for instance, "creeps" continuously under a tensile stress [1] of 0·14 kg./mm.^{2}, whilst the compressive proof stress (0·0005 in.) of Babbitt metal [2] is only 1·3 kg./mm.^{2}. Properties such as these have affected the ball hardness tests of the two cold-rolled pewters represented in Fig. 1. Using a load maintenance of 30 seconds or more, alloy A appears harder than alloy B; whereas at very low times of

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loading the order of hardness is reversed. In this present case it is obvious that the Brinell value for a standard fixed time of loading is arbitrary, and may be misleading; consequently, unless such graphs as those in Fig. 1 run parallel to each other, it is not justifiable to use the standard Brinell number for making hardness comparisons of soft metals. The present difficulty is due to the different inclination of the two alloy curves, and the work of Hargreaves [3] shows that these slopes depend on the viscous properties of the specimens. Numerically, the inclination is given by the value S in the empirical expression $d = ct^S$, and it appears that *the higher its* S *value, the more a metal is liable to deform by creep.*

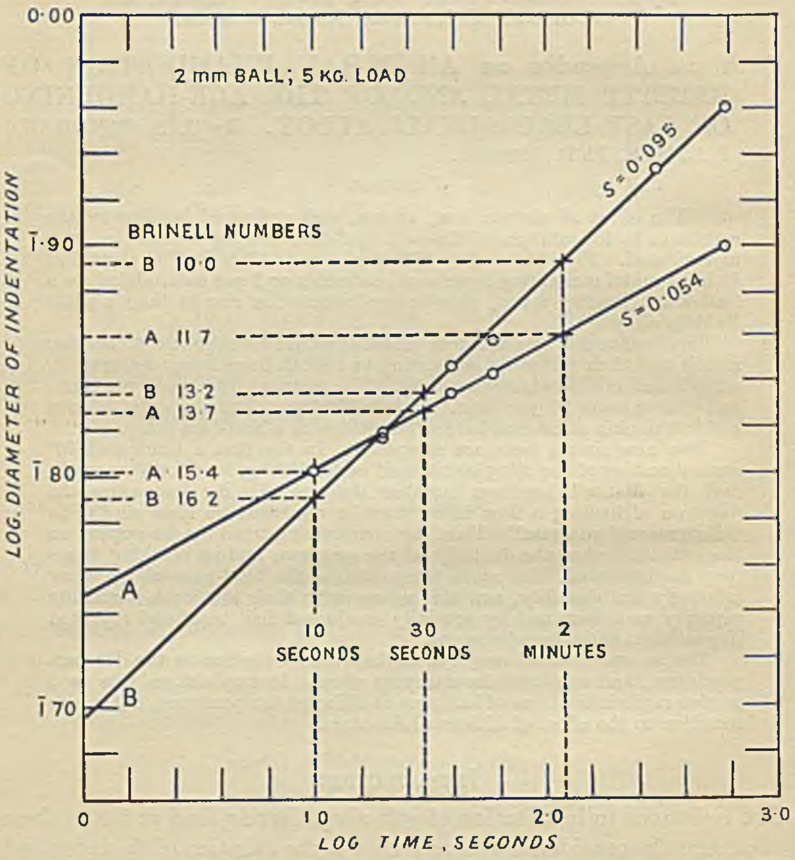

Fig. 1.—Effect of Duration of Load on Two Alloys Having Different S Values.

The temperature of bearings increases when in use, and their failure is therefore more likely to depend on properties at elevated than at room temperatures. Whilst the S values of different bearing metals at various temperatures might therefore be of some interest, consideration must first be given to a point concerning their determination by means of ball tests. Just as the Brinell number varies with the test loading ratio (*i.e.* L/D^2, where D = ball diameter), so the S value may depend on this same quantity. The authors have therefore investigated the point, with the results shown in Fig. 2. It is evident that

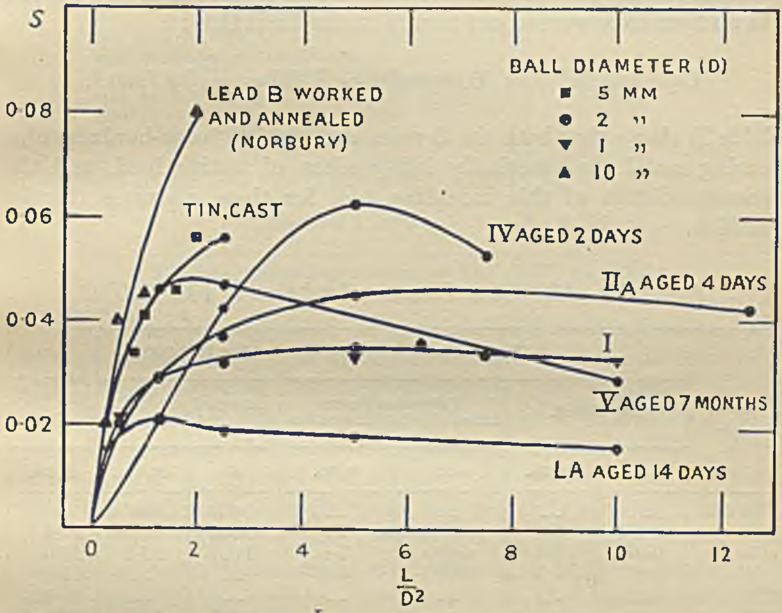

Fig. 2.—Variation of S with $\frac{L}{D^2}$. (See Table I for Compositions of Alloys.)

S is not independent of L/D^2, but passes through a maximum as the loading ratio is increased.

The Use of a Cone for Hargreaves' Analysis.

In many respects cone or pyramid indenters have advantages over the ball, since their angle of indentation is independent of the size of the impression. A given cone or pyramid, therefore, yields hardness values which are truly comparable—though creep effects will still be involved. If the cone obeys Hargreaves' law it ought to be of more general application for this work than the ball indenter. A polished 120° cone of hardened high-speed steel was therefore fitted to the Alfred

Herbert dead-loading machine, and was always lubricated with pure paraffin during tests. A contacting device and lamp were also added to the machine to indicate when the load had been fully applied. The results of many experiments have proved that, in general, Hargreaves' law holds for this cone from 10 up to 600 seconds loading; and in many cases over a very much longer period. Whilst keeping Fig. 1 in mind, hardness comparisons of a sort may conveniently be made on an arbitrary time basis. Lieber[4] recommends not less than 3 minutes loading, but the British Standards Institution's period is 30 seconds, so the authors have worked out results on the basis that :

$$\text{Cone number } (t = 30 \text{ seconds}) = P_c/30 = \frac{4L}{\pi d^2} \text{ kg./mm.}^2.$$

Table II shows that both the S value and the 120° cone-hardness of a bearing metal are practically independent of testing load, and the recommendation of this indenting tool for these alloys is thereby justified.

TABLE II.—120° *Cone Tests on Metal Cast at* 400°–200° *C.*

Load, Kg.	Tin (19° C.).				Alloy IB * (19° C.).		Alloy I * (19° C.).
	Unpolished.		Polished on Papers Annealed at 100° C. for 4 Hrs.		Annealed at 100° C. for 5 Days.		
	S.	$P_c/30$.	S.	$P_c/30$.	S.	$P_c/30$.	$P_c/30$.
1·065	...	...	...	...	0·030	18·6	...
5	0·071	6·1	0·054	7·2	0·030	21·5	22·4
10	0·072	5·8	0·060	7·1	0·031	22·3	22·6
15	0·075	4·5	0·063	6·9	...	...	21·9
20	...	...	...	...	...	...	21·9
30	...	...	...	...	0·029	22·2	24·8 (?)

* See Table I.

HARGREAVES' ANALYSIS OF TYPICAL BEARING METALS.

A selection of typical white bearing metals, together with some experimental alloys, have been examined for hardness and flow properties by the 120° cone test. The compositions of the alloys are given in Table I.

Casting conditions are known to play a part in determining the mechanical properties of these alloys. A few tests on one of them in which the mould conditions were varied, are reported in Table III. The cone numbers were calculated for $L = 10$ kg. in all cases.

TABLE III.—*Effect of Casting Conditions on Alloy II.**

Conditions.	120° Cone Values.	
	S.	$P_c/30$ (kg./mm.²).
(*a*) Alloy held at 284° C. for 10 minutes in a graphite mould; cooled in air.		
Aged for 3 days	0·041	27·0
,, 11 ,,	0·041	27·8
(*b*) Cooled slowly from 500° C. in the furnace in a clay crucible.		
Aged for 2 days	...	28·2
(*c*) Alloy held at 284° C. for 30 minutes in a fire-clay crucible; cooled in air.		
Aged for 10 days	0·038	29·0
(*d*) Metal at 400° C. cast into a chill mould at 200° C.		
Aged for 1 day	0·037	27·1
,, 2 days	0·036	26·9
(*e*) Metal re-cast from 400° C. into a chill mould at 100° C.		
Aged for 2 days	0·031	34·2

* Thermal arrests on cooling at 310°, 252°, and 234° C.

Conditions (*e*) (400°–100° C.) gave the best results from the point of view of hardness, but to avoid any zoning effects due to the chill,[5] a mould temperature of 200° C. (400°–200° C.) was eventually decided on. Subsequent ingots were cast in rectangular form and 0·5 in. thick, from an electrically-heated bottom-pouring graphite crucible. Within a few hrs. of casting the test surface was prepared on emery papers from 0 to 000 grade, and the metal was generally allowed to age for a day or more. Ageing effects have always to be considered with these alloys, for room temperature is relatively so near to their melting points as to constitute an annealing temperature on the absolute scale. Examples of various changes are given in Table IV.

The ageing process in cast lead–alkali bearing metal is found to be somewhat irregular.

The specimens prepared as described were tested in an oil-bath at room temperature, and also at an increased temperature. For the latter purpose, the platform of the indenting machine was fitted with a steam-bath, and the specimen remained in paraffin within this bath at 95°–96° C. Results which are considered to be representative are given in Table V.

The effect of the increased temperature on the properties of the alloys may be observed from Fig. 3, and the good qualities of No. IICd are noteworthy. Alloy II retains its hardness better than any of the others, but it appears to be liable to viscous flow (high *S* value) at the

TABLE IV.—*Ageing Effects in Soft Metals.*

Reference No.	Treatment.	120° Cone Tests.	
		S.	P_c/30 (kg./mm.^{2}).
Sn	Cast at 400°–200° C. Unpolished	0·072	5·75
	,, 350°–50° C. Cold-rolled and water-quenched from 200° C.		
	Aged for 1 hr.	0·070	6·25
	,, 10 days	0·070	6·25
I	Cast at 400°–200° C.		
	Aged for 1 month	0·039	20·2
	Cold-rolled 50% R.T.		
	Aged for ½ hr.	0·175±	23·5±
	,, 24 hrs.	0·093	18·1
	,, 48 ,,	0·082	16·7
	,, 11 days	0·062	16·3
	,, 22 ,,	0·058	16·4
IINi	Cast at 500°–200° C.	0·056	29·8
	Quenched from 200° C. At once	0·060	31·8
	Aged for 1 day	0·045	30·3
	,, 7 days	0·050	31·8
	,, 14 ,,	...	34·2
	,, 2 months	...	34·2
LA	Cast at 500°–200° C.		
	Aged for 3 minutes	...	23·6
	,, 30 ,,	...	24·4
	,, 50 ,,	...	23·6
	,, 1 hr.	...	24·7
	,, 3 hrs.	...	27·5
	,, 21 ,,	...	29·9
	,, 3 days	...	33·1
	,, 13 ,,	...	34·2

higher temperature. Incidentally, the change of *cS* values has been plotted as well as that of the *S* values, since Fell [6] considers the former to be more representative of the viscosity effect. No great difference between the two is to be observed in Fig. 3. The lead–alkali bearing metal—like IICd—remains quite hard at 96° C., but then shows a greater percentage increase of creep value than either Alloy IICd or Alloy V. The addition of 4 per cent. lead to the Babbitt metal raises P_c/30 at room temperatures, but this advantage has been lost at 96° C.

The contribution made by the various micro-constituents to the changes in properties reported in Table V was next investigated.

SCRATCH AND FLOW TESTS ON THE DIFFERENT CONSTITUENTS OF BEARING METALS.

By using the ball sclerometer equipment,[7] it has been possible to obtain indentation data for the different phases at different temperatures

TABLE V.—120° *Cone Tests.* (*Most Alloys Cast at* 400°–200° *C.*)

Alloy.	19° C.			96° C.		
	$P_c/30$.	*S*.	*cS*.	$P_c/30$.	*S*.	*cS*.
Tin (*a*)	5·8	0·072	0·083	...	...	...
(*b*)	5·5	0·038	0·051	3·0	0·077	0·121
I	22·6	0·039	0·029	11·0	0·074	0·063
IB	20·0	0·033	0·023	11·8	0·075	0·061
IB (*c*)	22·3	0·031	0·021	10·9	0·072	0·061
INC	29·2	0·045	0·026	13·0	0·078	0·059
ICd	30·4	0·039	0·023	17·6	0·108	0·063
II	26·9	0·036	0·022	16·9	0·105	0·066
IIA	30·8	0·027	0·016	...	...	...
IICd	41·4	0·054	0·024	18·5	0·074	0·047
IINi (*d*)	31·1	0·034	0·019	15·1	0·077	0·054
	29·8	0·056	0·031	14·7	0·086	0·059
IIMg	32·5	0·046	0·025	15·2	0·078	0·055
IIPb	34·6	0·050	0·025	12·8	0·080	0·061
IV	23·1	0·067	0·040	9·5	0·142	0·102
V (*e*)	25·7	0·047	0·028	11·7	0·076	0·061
LA (*f*)	38·0	0·028	0·015	17·4	0·071	0·048
Lead (*g*)	5·2	0·059	0·076	2·7	0·064	0·111

(*a*) Unpolished; (*b*) cast at 350°–50° C., polished; (*c*) annealed at 100° C. for 5 days, tested at 96° C. without cooling; (*d*) cast at 500°–200° C.; (*e*) cast at 425°–150° C.; (*f*) as received; (*g*) cast, polished, annealed at 100° C. for 4 hrs., aged for 14 days.

of some of the bearing metals. Two types of test have been employed: (*a*) scratch tests with the 0·5 mm. hemispherical diamond * under a load of 0·090 kg., and (*b*) micro-indentations using a sharp 120° diamond cone under a static load of 1·065 kg. Cone flow tests were made under the latter conditions; whilst the resistance to scratching ($P_s = 8L/\pi w^2$) was measured in the former. The appearance of sclerometer scratches may be seen in Fig. 4 (Plate II).

Satisfactory results were difficult to obtain on the fine copper–tin needle constituent of alloy II. Scratch tests have been made on impure liquated needle constituent kindly secured for the authors by Mr. F. Moreland, of Messrs. Fry's Metal Foundries, Ltd., from a somewhat similar alloy (2 per cent. copper). They support the view that the copper–tin constituent is harder than the tin–antimony cuboids. With low copper contents the needles will consist of the CuSn phase (see Appendix), but by increasing the amount of copper, Cu_3Sn first separates during freezing and should change to CuSn by a peritectic reaction.

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* This diamond was kindly prepared and presented by Mr. P. Whitaker.

Needles in Babbitt alloys are therefore sometimes observed to have a central core differing from the outer coating. In the present work only homogeneous needles were to be seen.

Synthetic SnSb (50 atomic per cent. tin) has also been prepared, which after annealing at 300° C. for 1 week became free from cores and consisted of a single phase. The test result for this alloy is included with the values for polished and etched bearing metals given in Tables VI and VII.

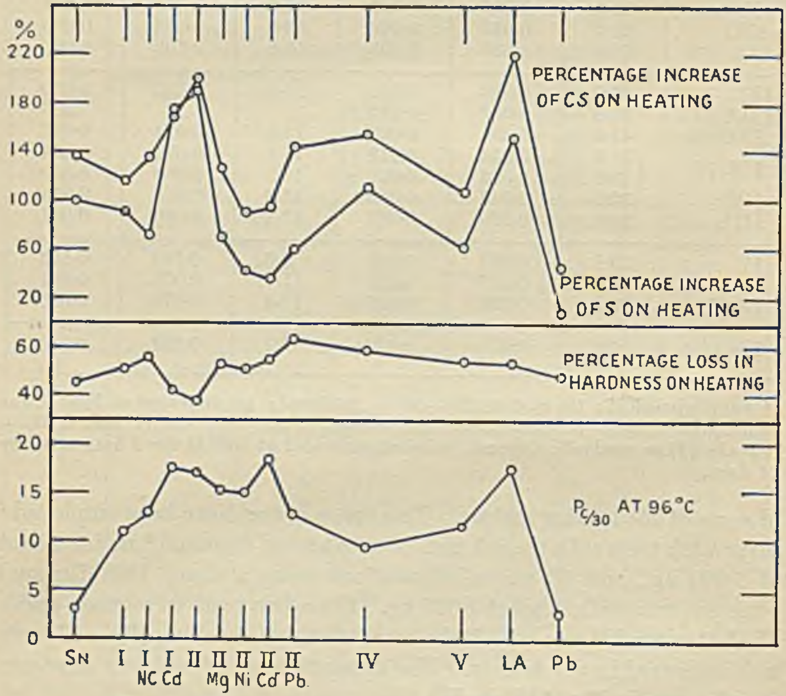

FIG. 3.—Effect on Steel Cone Values of Heating to 96° C.

It will be observed that the softening of the alloys is chiefly due to loss of hardness of the matrix, whilst the cuboids of No. II remain somewhat harder than those of the lead-base alloy No. V. The test on cast antimony indicates that the cuboids in No. V do not consist of this metal alone, but probably of an antimony–tin alloy. The hard constituent of LA metal was too fine to give satisfactory results. Cone flow tests in Table VII indicate that the matrix of No. II is more liable to viscous flow than that of No. V, and this must be responsible for the high *S* value of alloy II (Table V) when heated.

TABLE VI.—*Resistance to Scratching of the Micro-Constituents.*

Alloy.	Constituent.	At 19° C. kg./mm.^{2}.	At 100° C. kg./mm.^{2}.	Decrease on Heating. Per Cent.
I.—Cast at 400°–200° C.	matrix	32	...	...
II.—Cast at 400°–300° C.	matrix	34	...	...
	cuboids *	127	...	...
Slowly cooled from 500° C.	matrix	33	20	39
	cuboids *	117	92	21
Babbitt alloy (83% tin, 9% antimony, 2% copper). Test on solid separated at 230° C., polished and etched.	needles	260 †	...	...
	cuboids	97–103 †	...	...
SnSb phase.—Cast at 450°–200° C.; annealed at 300° C. for 7 days.	...	104	82	21
	...	109 †	...	...
IV.—Cast at 400°–200° C.	matrix	20	...	...
	cuboids	101	...	...
V.—Cast at 425°–150° C. Slowly cooled from 500° C.	matrix	36	20	44
	cuboids	101	82±	19
LA.—As received.	matrix	57	32	44
Antimony.—As Cast.	...	58	...	...

* Scratch parallel to cube edge. Different orientations gave hardness values ranging from 91 to 127 kg./mm.^{2}.

† 0·165 kg. load.

TABLE VII.—120° *Cone Flow Tests on the Micro-Constituents.*

Alloy	Constituent.	*S.*			$P_c/30$. Kg./mm.^{2}.		
		At 19° C.	At 100° C.	Increase, Per Cent.	At 19° C.	At 100° C.	Decrease on Heating, Per Cent.
II.—Slowly cooled from 500° C.	matrix	0·036	0·134	270	27	17	37
	cuboids	...	...	...	77	42	45
SnSb phase.—Cast 450° – 200° C. Annealed at 300° C. for 7 days.	...	0	0	0	72	46	36
IV.—Cast 400°–200° C.	matrix	...	...	...	11	...	...
	cuboids	...	...	...	77	...	...
V.—Slowly cooled from 500° C.	matrix	0·040	0·078	95	23	13	43

Effect of Prolonged Heating at 100° *C.*—With long periods of running at temperatures in the region of 100° C., white-metal bearings may undergo the equivalent of annealing treatments. Chilling or coring effects remaining from casting may thus be removed, and the eutectics will tend to coarsen. The authors have investigated the effects of this possible softening influence, certain alloys being tested with the cone, heated in paraffin for 14 days at 100° C., air-cooled in the oil, and then re-tested. The two tin-base alloys, II and IICd, showed no pronounced change, but the lead-rich alloys had softened as shown in Table VIII.

TABLE VIII.

Alloy.	Before Heating.		1 Day after Annealing.		Aged after Annealing.	
	S.	$P_c/30$.	*S.*	$P_c/30$.	*S.*	$P_c/30$.
IV	0·067	23·1	0·038	22·6	...	...
V	0·047	25·7	0·040	18·6	...	...
LA	0·029	36·8	0·021	15·2	0·020	22·6

Freeman and Woodward [8] have reported a similar lowering of compressive proof stress in lead-base alloys.

BALL TESTS AT DIFFERENT LOADS.

The ball test has normally one advantage over the cone in that Meyer analysis may be carried out to determine the work-hardening capacity (n value) of a metal. A knowledge of this property might be of interest as an indication of general ductility, and possibly of resistance to cracking by fatigue. In the present case, the time factor again creates a difficulty, as may be seen from the following experiments.

Certain specimens were indented for four periods of loading (*e.g.* 30, 100, 300, and 600 seconds duration) under weights such as 5, 10, 20, and 50 kg. The results for each period of loading when plotted logarithmically gave the straight lines of the Meyer equation, $L = ad^n$, though the 50 kg. load generally gave unduly high values of diameter. Fig. 5 shows the figures obtained for alloy IIA. The soft metals which have been examined in this way fall into two categories: those having an n value (inclination of the Meyer graphs) practically independent of load-duration (t), and those giving a decrease of n with increase of t. The latter group tend to show an "intersection effect" *on extrapolation*, *i.e.* the Meyer graphs for various times of loading tend to meet in a point which theoretically would represent a value of load and diameter where time has no effect. The mean stress at such a point should be a limiting creep stress, if any such property exists in a metal. The authors are not inclined to believe that it does, and have actually found slight creep effects in tin when indented at its observed stress of intersection. Nevertheless, if "intersection" occurs at a relatively high stress value it might indicate a relatively high resistance to creep. For this purpose, such results as have been obtained are included in Table IX.

Norbury [9] has already noticed what the authors have called the "intersection effect" in lead, and his figures have been used for lead B in calculating the values given in Table IX. Incidentally, the authors find that Norbury's results for lead A do not obey Hargreaves' law.

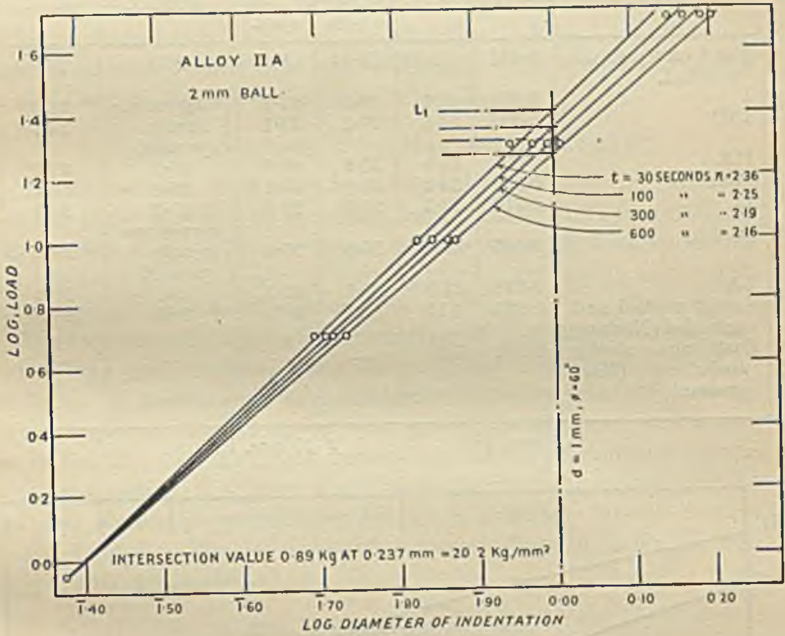

Fig. 5.—Meyer Graphs.

To make strict comparisons of ball hardness equal angles of indentation ϕ must be chosen. Introducing the time factor, the authors have therefore measured *the resistance to indentation* (*mean pressure* P_m) *for* $\phi = 60°$ *and unit time of load maintenance* ($t = 1$ *second*). The method used is to interpolate from the Meyer graphs (such as Fig. 5) the values of load (L_1) to give an indentation such that $d/D = \sin \frac{60°}{2} = \frac{1}{2}$. For the authors' 2 mm. ball, this is in fact the load (a) to give $d = 1$. Plotting L_1 against t it is found that the following empirical relation holds quite well: $L_1 = mt^k$, from which m can be obtained by extrapolation. This value m is the load theoretically to give a standard impression ($\phi = 60°$) in 1 second, and on multiplying it by $4/\pi d^2$ the corresponding mean stress, P_m, is obtained. Whether the

Table IX.—*Ball Tests.* (2 *mm. Ball.*)

Alloy.	S ($L/D^2 = 1$).	Brinell No. ($L/D^2 = 1$).	Ball Number.		Mean Stress at "Intersection Point," kg./mm.².	Meyer n Value for $t = 1$ second.
			P_m for $\phi = 60°$. $t = 30$.	P_m for $\phi = 60°$. $t = 1$.		
Tin,* cast and unpolished.	0·041	5·30	5·94	8·80	2·78	2·70
I	0·028	18·6	20·8	27·2	curves are nearly parallel	2·22
INC	0·032	23·8	27·2	37·1		2·37
IIA	0·025	25·0	33·8	49·5	20·2	2·60
IINi	0·030	28·2	40·2	62·4	25·4	2·48
IV	0·017	22·3	26·0	29·6	17·3	2·29
V	0·045	26·5	26·5	36·4	curves are nearly parallel	2·00
LA	0·020	33·0	37·1	43·5	do.	2·12
Lead,† worked and annealed (Norbury)	0·055	4·12	4·48	5·70	2·92	2·35
Cast and slowly cooled (Hargreaves)	0·054	3·25	...	...	...	...

* 5 mm. ball. † 10 mm. ball.

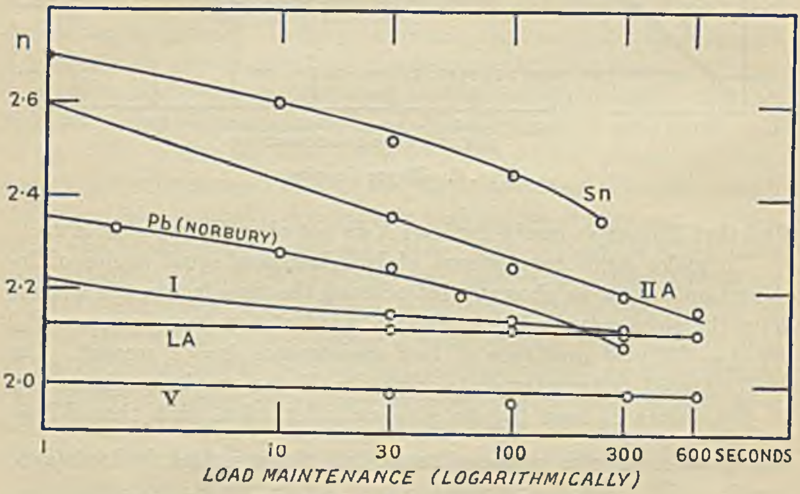

Fig. 6.—Variation of n with t.

hardness value for this short period of time—representing as it does, conditions approaching those of a slow dynamic test—is more useful than that computed after considerable flow of the specimen, it is difficult to say. The values obtained are given in Table IX, and for comparison purposes those corresponding to $t = 30$ seconds have also been calculated. The latter may be compared with the $P_c/30$ values recorded in Table VI, since a 120° cone should give an angle of indentation of (180°–120°) = 60°. The agreement may be considered satisfactory in most cases.

The Meyer n value, which in harder metals than these is a measure of work-hardening capacity, has also to be considered on a time basis. In Fig. 6 there has been plotted the variation of n with t, and an extrapolation back to unit time has been made. The n values for $t = 1$ obtained in this way are included in Table IX.

DYNAMIC TESTS AND WORK-HARDENING CAPACITY.

The time-factor effect may be mitigated by substituting dynamic tests for those in which an indenting load is maintained for relatively long periods of time; furthermore, measurements of work-hardening capacity may then be made by varying the impact energy of the test, and substituting in the expression $E = a \,.\, d^{n1}$.

The authors could only avail themselves of a scleroscope tester, but results with this machine, using the magnifier hammer, are given in Table X. A measure of work-hardening capacity was obtained by making repeated impacts on the same spot of the specimen, and noting the initial and the maximum rebound numbers. According to this method of testing, it appears that the work-hardening capacity of the lead-base materials—particularly No. V—is definitely inferior to that of the tin-base. The extrapolated n values given in Table IX also support this conclusion.

TABLE X.—*Scleroscope Tests.*

Alloy.	Initial No.	Maximum Induced No.	Increase by Impacting, Per Cent.
Tin.—Cast at 400°–200° C., polished.	4·5	10·5	133
I.—Remelted at 400°–200° C.	14	26	86
IB.—Cast at 400°–200° C.	11	25	127
INC " "	13·5	27	100
IIA " "	22·5	41	82
IV.—Cast at 400°–200° C.	15·5	26·5	71
V.—Cast at 425°–150° C.	21	31	48
LA. As received.	29·5	48	63
Pb. Cast at 400°–200° C.	3	4·5	50

The initial scleroscope numbers put the alloys of Table X in the same hardness series or sequence as that given by the $P_c/30$ values (Table V) and the P_m values for $\phi = 60°$ and $t = 30$ (Table IX).

Application of Mallock's Test to Bearing Metals.

Mallock's hardness test [10] consists of loading a conical piece of the metal to be examined against a smooth hard plate, and measuring the diameter d of the flat produced on the point of the cone. Mallock found for steels that $L \propto d^2$, and so the hardness values given by:

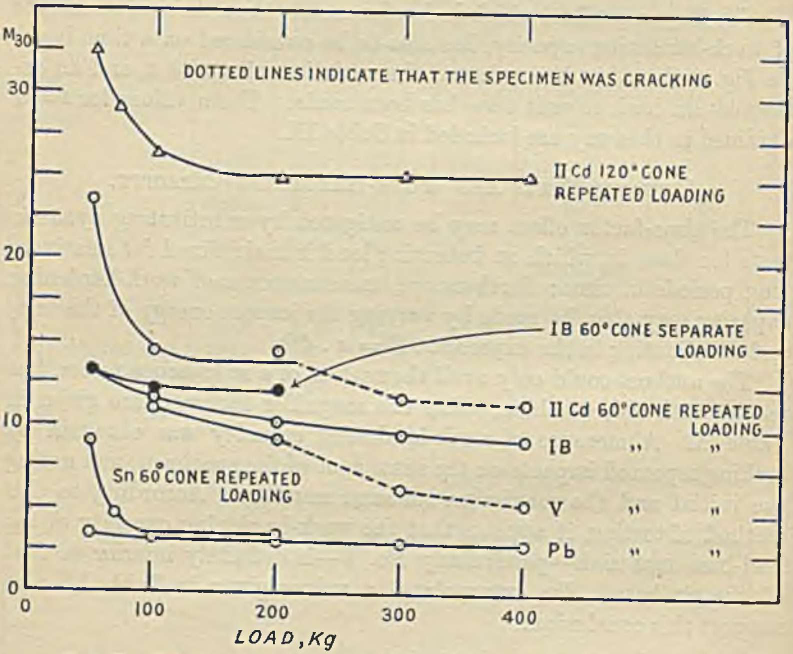

Fig. 7.—Effect of Load on Mallock Number (30 Seconds Loading).

$$\text{Mallock number} = M = \frac{4L}{\pi d^2}$$

should be independent of testing load and truly comparable. Owing to "work-softening" and recrystallization effects, white metals may not behave in quite the same way as ferrous alloys. Two cast-iron moulds were therefore prepared for the casting of 60° and 120° conical test-pieces, and the latter were lubricated with paraffin and flattened against a hard steel plate in a lever machine. Preliminary experiments were undertaken to investigate the effect of (*a*) cone angle; (*b*) repeated loading with increasing loads on the same specimen, as compared with the separate loading of new cones with the various individual loads; and (*c*) the effect of time of load-maintenance with repeated loading but a constant load.

The results are represented in Figs. 7 and 8. As was expected, the larger cone angle gave higher Mallock numbers. Furthermore, the Mallock number with repeated loading decreased as the load increased from 50 kg., but beyond 200 kg. the decline was not great. For alloys IB at least, separate loading on 60° cones resulted in more constant hardness values than did repeated loading (Fig. 7). Some of the 60° specimens gave an extruded edge to the flat, and with repeated loading at 200 kg. and increasing times this commenced to crack when the deformation became severe. It may be inferred from Fig. 8 that for repeated loading of 100 kg. there is a logarithmic relation between *d* and *t*. To be strictly comparable with Hargreaves' experiments and our own work with the 120° steel cone, separate loading should have been used in the time tests. It is possible, however, that repeated loading of a Mallock cone will yield a flow value, S_M, equal in interest to the *S* values previously discussed. In this way the use of several conical specimens would be avoided.

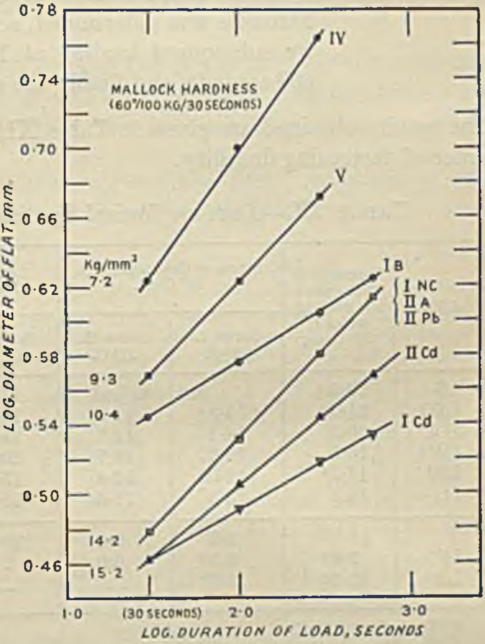

Fig. 8.—Effect of Time of Load-Maintenance with Repeated Loading on 60° Mallock Cones and 100 kg. Load.

The cracking of the edge of the 60° cones seemed to be a useful and simple method of measuring the ductility of the alloys, and the authors have determined the stress, M_c, at which it just became visible during compression on a motor-driven machine. This incipient cracking was quite easy to observe at a constant straining speed of 0·008 cm./second and Fig. 9 (Plate II) is a photograph of a series of alloys after test. Two experimental methods were tried as follows:

Series I.—Specimens as cast were compressed directly to the cracking point and M_c determined. The Mallock hardness and flow properties had to be measured on a separate set of specimens.

Series II.—A single set of specimens was used, and firstly the Mallock hardness was determined, secondly the flow value S_M by subsequent loading at 100 kg. for periods up to 600 seconds, and finally the cracking values.

The results obtained are given in Table XI, the alloys being listed in order of decreasing ductility.

Table XI.—*Tests on Conical Specimens, Cast as Before.*

Alloy.	Diameter of Flat (mm.) at Cracking. Series I, 60° Cone.	Stress at Cracking (M_c). 60° Cone.		Mallock Hardness, 100 kg./30 seconds.		S_M Series II. 21° C.
		Series I. 14° C.	Series II. 21° C.	Series I. 14° C.	120° Cone. 14° C.	
IB	25·5+	not	cracked	13·3	19·2	0·060
INC	21·5*	13·8*	13·8	14·2*	20·4	0·104
IIA	20·2	14·1	12·2	14·7	26·9	0·104
IICd	16·3	16·9	16·7	20·4	32·9	0·080
ICd	14·3*	12·0*	12·8	15·2*	22·1	0·054
IIPb	14·1	13·3	11·6	15·7	29·8	0·104
V	11·1	9·7	8·8	10·4	17·5	0·106
IV	9·6*	6·5*	6·9	7·2*	12·4	0·140
LA	9·2†	12·2†	...	...	24·1‡	...

* Tested at 21° C.

† Specimen had previously been subjected to 200 kg. for more than 600 seconds and then aged 25 days before this cracking test.

‡ Aged 7 days after casting and perhaps not fully hardened.

It is believed that this modified Mallock test deserves consideration since (*a*) indentation with a steel ball or cone does not indicate the cracking limit of these alloys, and (*b*), compression tests with cylindrical specimens lack the geometrical conditions of similarity which hold for the Mallock cone.

THE EFFECT OF LUBRICANTS.

Tests of bearing metals which ignore the effect of lubricants have only a limited value. So far in the present work, pure paraffin has been used throughout. The Mallock cone test, however, would almost certainly be sensitive to the application of different lubricants, just as the work of Hankins,[11] and particularly of Kuntze and Sachs,[12] shows how friction effects may be introduced quantitatively into the 120° steel-cone test. The authors have made no experiments along these lines but have investigated a method used by Rehbinder [13] for studying the effect of liquids on the surface energy of mineral crystals. Rehbinder employed a modified Kuznetzov pendulum,[14] and after various experiments the authors have adopted a simple tester very similar to the Herbert pendulum. The latter in fact could almost certainly be used for work of this kind.

The instrument weighs 5 kg. and consists of a rigid 9-in. cross-bar carrying cylindrical weights at each end. A 5 mm. steel ball and holder is fixed rigidly at the middle of the cross-bar, and supports the pendulum on the specimen. A pointer, collinear with the ball-holder but on the upper side of the cross-bar, enables the swinging of the pendulum to be read against an adjustable scale. The dimensions of the tester were such that if set to swing on a horizontal glass plate, the time for 10 oscillations was 23 seconds. When the different bearing metals were substituted for the glass plate, this time was practically the same for each specimen, ranging from 22·2 to 22·7 seconds. Observations of the amplitude at the end of each swing for a total of 10 swings were therefore made, and these are the results plotted in Fig. 10. They not only show the different behaviours of the alloys, but also variations due to the type of lubricant applied to the test surface.

TABLE XII.—*Effect of Lubricant on Pendulum Test. Amplitude of* 10*th Swing from an Initial Amplitude of* 20°.

Alloy.	" Wiped Dry."		Oil 1.		Oil 3.	Oil 7.	
	21° C.	90° C.	21° C.	90° C.	21° C.	21° C.	90° C.
I (Remelted) .	3·35	...	3·5	...	...	3·2	...
INC . . .	3·35	0	4·25	...	...	3·5	1·2
IIA . . .	5·8	3·1	5·15	2·1	6·1	5·9	3·0
IICd . . .	8·9	...	8·8	...	...	9·1	...
IV . . .	4·5	2·0	3·9	1·0	...	5·0	1·0
V . . .	5·8	2·5	6·2	2·15	...	6·3	2·9
Glass . . .	19·5	...	...	...	19·35	19·45	...

Three different oils were chosen: *No.* 1, a light mineral oil of the paraffin-lamp type; *No.* 3, a fairly thick mineral oil, and *No.* 7, the same as No. 3 plus 0·5 per cent. oleic acid. Tests were also made with no applied lubricant but after wiping the specimen and indenter with benzine. This "wiped" condition does not of course represent a chemically clean surface. Values of amplitude of the 10th swing are given in Table XII. The material which shows least damping is likely to be the best bearing metal from the present point of view. The lead-base alloy No. V is somewhat superior to the ordinary Babbitt at room temperature, but at 90° C., however, the test indicates that No. IIA is slightly better than No. V. The addition of cadmium improves

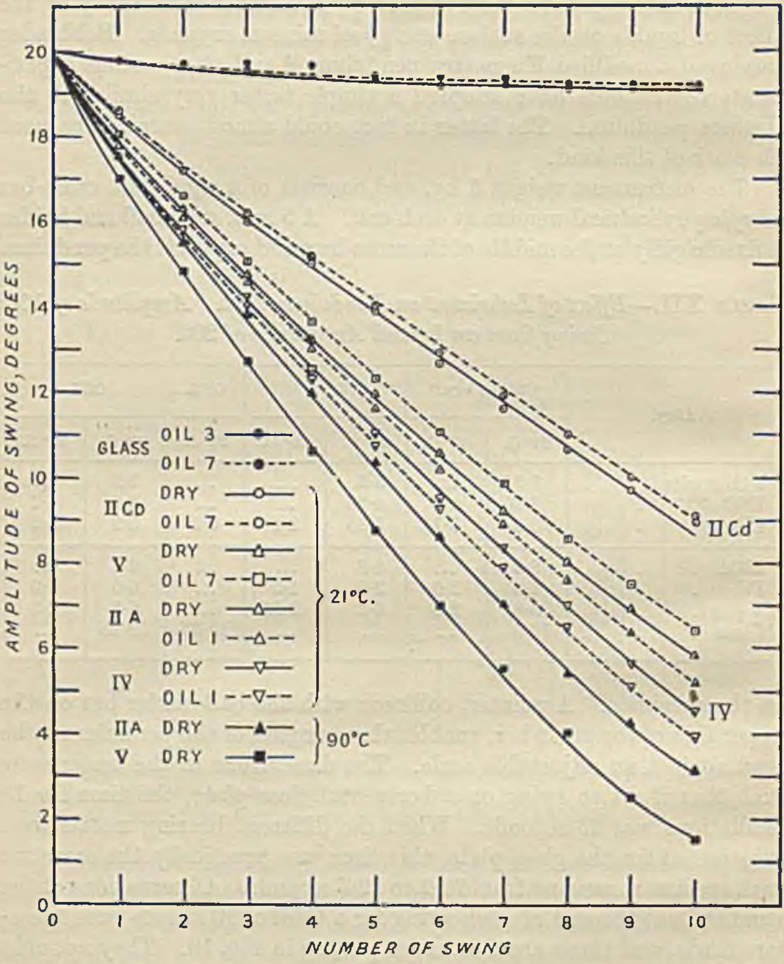

Fig. 10.—Pendulum Tests.

No. IIA, apart from the loss of ductility which has been shown in other tests.

These experiments with a pendulum are submitted for consideration because of their simplicity, and because of the way in which they indicate that oils 3 and 7 are superior to oil 1.

APPENDIX.

AN X-RAY EXAMINATION OF THE PHASES IN BABBITT METAL, AND OF THE AGE-HARDENING OF CAST LEAD–ALKALI ALLOY.

By G. S. FARNHAM, B.A., M.Sc., MEMBER.

(1) *SnSb Phase.*—A synthetic alloy of this composition was examined after annealing for 1 week until free from coring. A spectrogram from an etched plate specimen was obtained by reflection of Cu X-radiation from the surface, as in the Bragg method. The structure proved to be of the NaCl type. By taking a "back-reflection" spectrogram from the same specimen the length of the cube edge was found to be 4·099 A.

This result confirms the work of Morris-Jones and Bowen,[15] who found an NaCl structure with $a = 4{\cdot}092$.

A fine-grained plate specimen of alloy No. II was also photographed by the Bragg type of arrangement. In the complex spectrum obtained the lines corresponding to SnSb ($a = 4{\cdot}099$) were clearly identified. The other lines are reflections from the matrix, a constituent with the spacing of nearly pure tin being identified. This must be the "tin" component of the eutectic.

(2) *Cu–Sn Phase.*—A mass of "needle constituent" was obtained by liquation from a Babbitt alloy. Some brittle needles were carefully broken off, ground in a mortar, and sieved. Portions of ductile alloy remained on the sieve but the fine brittle material passed through. This was packed into a Lindemann glass tube and a Debye–Scherrer spectrogram obtained. The position of spectral lines corresponding to the phase "CuSn" (63 per cent. tin) was calculated from formulæ given by Westgren and Phragmén,[16] and compared with the lines of the spectrogram. The latter were consistent with the assumption that the powder was CuSn, or what Westgren calls the η phase. A few extra lines present seemed to correspond with SbSn, some of which had probably adhered to the needles during liquation.

(3) *The Age-Hardening of Lead–Alkali Alloy.*—A plate specimen of lead–alkali alloy was examined by the "back-reflection" method, both in the newly-cast condition and then after ageing at room temperature for several days. The X-ray spectrum consisted of the lines of

two phases, one of which changed with ageing whilst the other did not. The latter was of the face-centred cubic type with $a = 4{\cdot}889$ A.

Measurements for the former were :—

Phase I.—Newly-cast	F.C.C.	4·930 A.
Aged	,,	4·937 ,,
N.B. Lead	,,	4·94 ,,
Sodium	,,	4·24 ,,

The facts could be accounted for as follows: About 0·8 per cent. of sodium can dissolve in lead at 300° C.,[17] but the equilibrium solubility is small at room temperatures. The newly-cast alloy appears to contain supersaturated lead which precipitates a sodium constituent (?Na_2Pb_5) during ageing, and brings about age-hardening. The other phase may be $CaPb_3$,[18] since the solid solubility of calcium in lead is said to be very low.[19]

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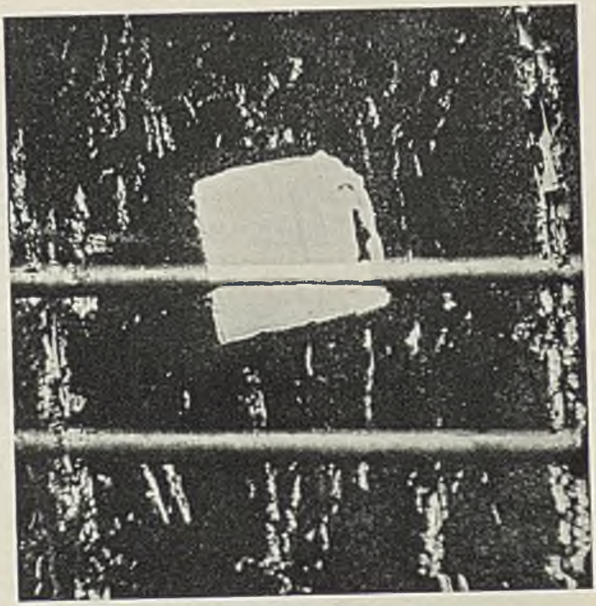

FIG. 4.—Scratch Tests on Babbitt No. II. × 75.

1B. IIA. IICd. IIPb. VA. LA.

FIG. 9.—Cracking Tests.

Plate III.

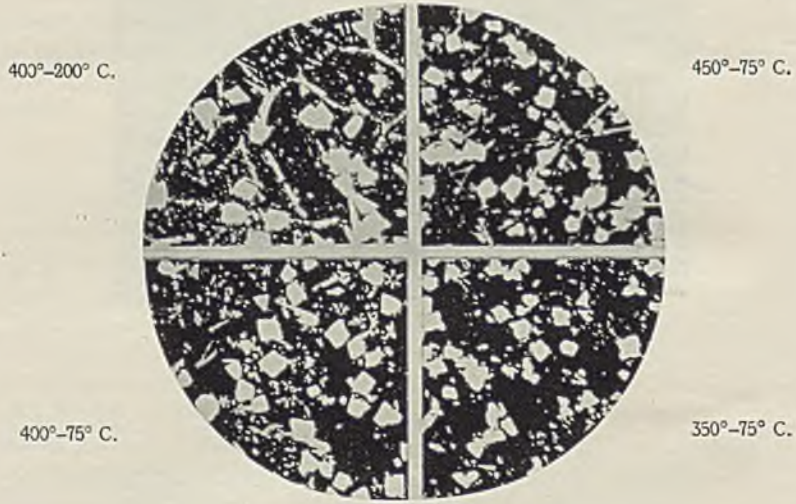

Fig. 14.—Alloy IIA Cast Under Various Conditions.
× 100.

PART II.—TENSILE TESTS.

By R. ARROWSMITH,* B.Met., M.Sc.

SYNOPSIS.

The tensile properties of white metal specimens, prepared by gravity die-casting and without any machining, have been determined at room temperature on a Hounsfield "Tensometer." Various casting conditions were examined for each alloy. Babbitt metal with additions of cadmium gave the highest values of limit of proportionality and ultimate stress. The greatest ductility was obtained from an alloy No. INC containing 89 per cent. of tin.

TENSILE tests are not usually carried out on white metal bearings. Although the ultimate strength may be of little obvious importance as a measure of the value of a bearing alloy, yet there is the possibility that it will serve as an indication of the metal's resistance to fatigue.[1] Furthermore, the tensile test provides information as to yield-point and ductility which may throw some light on service failures.

Many bearing troubles are probably due to improper casting conditions. According to Corse,[2] white metals having a coarse-grained structure due to being cast from too high a temperature and then slowly cooled, are unsuitable for bearings. On the other hand, too rapid chilling with resulting fine-grain is equally undesirable. In view of this, the effect of casting conditions on tensile values has been taken into consideration.

Measurements of the tensile properties of *machined* test-pieces of certain white metals have been made by a number of workers, including Smith and Humphries,[3] Mundey, Bissett, and Cartland,[4] and Rolfe.[5] Mundey, Bissett, and Cartland used test-pieces 0·564 in. in diameter and 2 in. long, machined from metal poured into a cast-iron stick mould, which was heated to 100° C., the metal being poured at 350° C. Rolfe included in his work the effect of varied casting conditions on the properties of a typical 85 per cent. tin alloy. He showed that, generally speaking, the tensile strength increases with rise of casting temperature, and decreases as the mould temperature is increased.

EXPERIMENTAL WORK.

The chemical composition of the alloys which have been investigated is given in Table I.

The thickness of the white-metal lining of a bearing will not generally exceed 0·25 in. To reproduce as nearly as possible the conditions of the

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* Department of Metallurgy, The University, Manchester.

metal in the bearing the diameter of the test-piece should therefore not exceed this figure, whilst in addition it should be cast, rather than machined from a larger ingot. The tests recorded here were made with a Hounsfield " Tensometer " using specimens 0·226 in. diameter and a gauge-length of 0·884 in. These were gravity die-cast in a relatively heavy iron mould preheated to the desired temperature, and were not machined. In order to minimize any possible loss due to oxidation, the alloys were melted rapidly under a cover of carbon, great care being taken to avoid overheating. That very little change occurs in the physical properties of an alloy on such careful remelting, is well illustrated by the following preliminary tests on alloy No. IIA.

TABLE XIII.—*Effect of Remelting Alloy No. IIA.*

Material.	Yield-Point, Tons/in.^{2}.	Maximum Stress, Tons/in.^{2}.	Elongation, Per Cent.	Reduction of Area, Per Cent.
Received . .	3·70	5·76	11·7	16·0
First remelt . .	3·65	5·86	10·7	13·4
Second remelt . .	3·65	5·88	11·6	14·5
Slow, oxidizing melt	3·70	5·78	10·6	14·5

With the Tensometer, the load is applied to the specimen through a screw-and-lever mechanism, operated by turning a handle. In carrying out a test, the handle was turned either through a complete, or a definite part of a revolution during a given time, and the scale reading of the mercury gauge noted. This method was found to be more accurate than using the autographic system which is fitted to the machine.

As it is now clearly recognized that in the tensile test the time factor may have a profound bearing on the strength of the material, some tests were made on No. IIA alloy, in which the rate of straining was varied.

TABLE XIV.—*Effect of Rate of Straining.*

Time for Complete Revolution of Handle, Seconds.	Yield-Point, Tons/in.^{2}.	Maximum Stress, Tons/in.^{2}.	Elongation, Per Cent.	Reduction of Area, Per Cent.
60	3·41	5·58	11·3	16·0
30 (= 0·017 in. per minute)	3·70	5·76	11·7	16·0
15	3·90	5·94	13·1	16·5

In the present work, the 30 seconds rate—equivalent to 0·017 in. per minute—was used in all tests, a stress reading being taken every quarter of a complete revolution of the handle. Some typical stress–strain curves so obtained are shown in Fig. 11. Hooke's law is approximately obeyed, and for present purposes the apparent limit of proportionality has been termed the "yield-point."

With the exception of the lead–alkali alloy LA, no appreciable ageing effect was observed with the alloys investigated, and the test-pieces were broken approximately 1 hr. after being cast. The tensile strength and ductility of the lead–alkali specimens which were allowed to age for varying times are given in Table XV.

The accuracy of these results is in some doubt, however, as in every case fracture occurred in the shoulder of the specimen. This is believed to be due to cracks existing in the castings, possibly caused by the shape of the specimens.

The results obtained on alloys I–VA, all of which are the mean values of two or more concordant tests, are given in Figs. 12 and 13. Fig. 14 (Plate III) shows the structures resulting from variation in mould and casting temperatures of the best all-round alloy No. IIA.

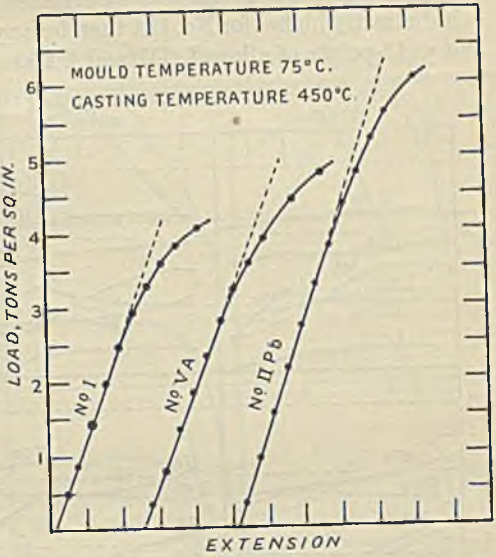

FIG. 11.—Stress–Strain Curves from Tensometer.

TABLE XV.—*Alloy LA. Cast at* 500° *C., Mould Temperature* 200° *C.*

Ageing Time, Hrs.	Yield-point, Tons/in.^{2}.	Maximum Stress, Tons/in.^{2}.	Elongation, Per Cent.
1	3·12	4·93	7·5
48	3·31	6·07	8·5
144	4·25	6·02	4·8

DISCUSSION OF THE RESULTS.

It will be seen from Fig. 12 that at room temperature, of all the alloys examined, No. IICd is the strongest. Alloy No. IIPb comes next, whilst No. IIA is but little inferior. With the lower mould temperatures, alloys IIA and IIPb are reversed so far as the yield-point is concerned, that of IIA and IICd being the highest of the series.

As is shown in Table XVI, the hardening effect of 1 per cent. of cadmium on alloys I and IIA is very marked, especially in the case of the former. The improvement, however, is only obtained at the expense of a large amount of ductility. The same may be said for the addition of 4 per cent. of lead to alloy IIA.

The yield ratio—within limits a criterion of the quality of a material—is distinctly higher for No. IIA than for any other alloy. The strength and yield-points of alloys I, IV, and VA are definitely inferior.

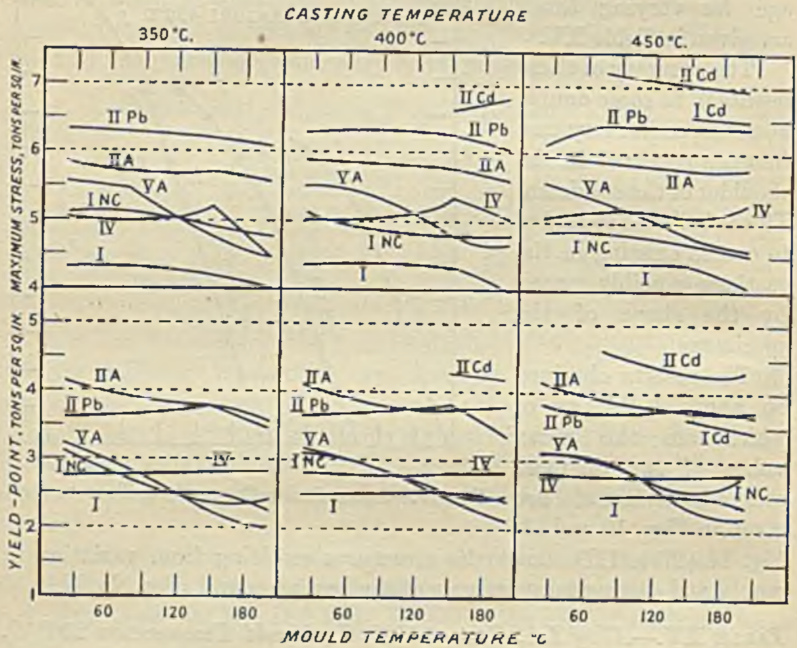

Fig. 12.

Table XVI.—*Effect of* 1 *Per Cent. of Cadmium.*

Alloy.	Mould Temperature, ° C.	Casting Temperature, ° C.	Yield-Point, Tons/in.².	Maximum Stress, Tons/in.².	Elongation, Per Cent.	Reduction of Area, Per Cent.
I	150	450	2·52	4·32	19·0	31·5
ICd	,,	,,	3·65	6·54	6·6	7·5
IIA	,,	,,	3·70	5·74	9·2	15·5
IICd	,,	,,	4·45	7·00	3·2	5·0

Passing to a consideration of the ductility, the high values of the elongation and reduction of area of alloys I and INC are especially remarkable. The highest elongation figure recorded was for alloy INC cast at 350°–150° C. The elongations of IIA and IV for the colder moulds are much the same, whilst from this aspect No. IIPb and especially VA are much less satisfactory.

The very few tests carried out on the lead-alkali alloy do not justify any dogmatic generalization. From Table XV, however, it appears that its yield-point is similar to that of No. IIA (see Fig. 12), whilst the elongation is only about one-third that of this alloy.

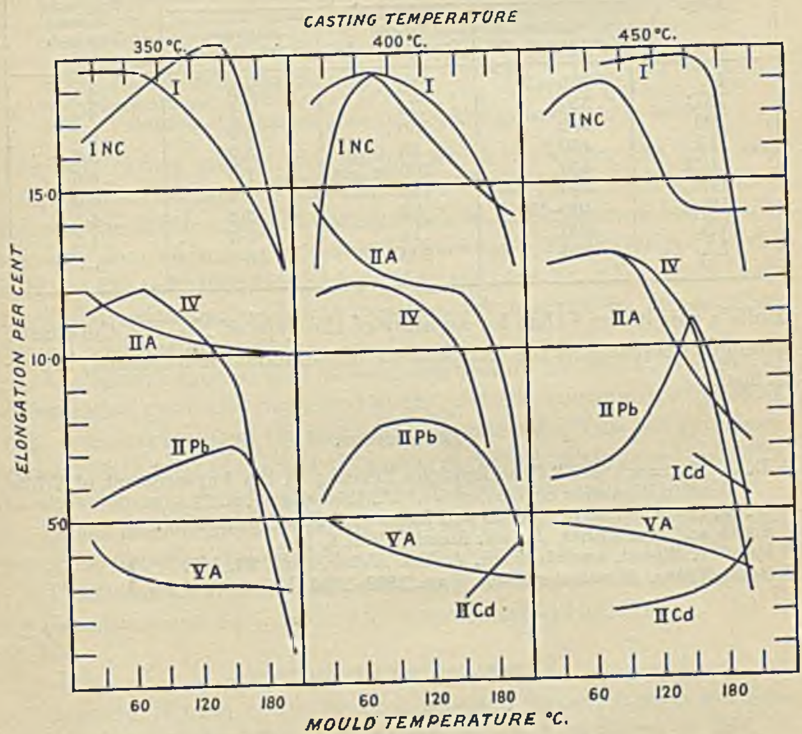

Fig. 13.

The best casting conditions simply to give maximum tenacity for bearing metal just under 0·25 in. thick are given in Table XVII, together with minimum values for comparison. It is to be noted that these conditions will not necessarily give optimum all-round results in service; *e.g.* a cold mould will certainly result in poor adhesion between lining and shell.

The chief difference between the values obtained by the author and those of Mundey, Bissett, and Cartland[4] is in connection with the elongation. The latter reported no elongation on alloys similar to IIPb and IV; a fact for which it is difficult to provide an explanation.

TABLE XVII.

Alloy.	Optimum Conditions.			Lowest Maximum Stress, Tons/in.^{2}.
	Casting Temperature, ° C.	Mould Temperature, ° C.	Maximum Stress, Tons/in.^{2}.	
I	350–450	75	4·3	4·0
INC	350	75	5·1	4·5
ICd	450	150	6·6	6·5
IIA	450	18	5·9	5·6
IICd	450	200 or less	7·0	6·6
IIPb	450	150	6·4	6·0
IV	400–450	75	5·2	4·5
VA	400	18	5·5	4·5
LA	500	200	6·0	...

Rolfe's conclusion[5] that for an alloy of the type of No. IIA the tensile strength decreases as the temperature of the mould is increased, is confirmed.

REFERENCES.

[1] D. J. Macnaughtan, "Considerations Relating to the Improvement of White Bearing Metals for Severe Service," *J.*, this volume, p. 33.
[2] W. M. Corse, "Bearing Metals and Bearings," New York: 1930.
[3] Smith and Humphries, *J. Inst. Metals*, 1911, 5, 194.
[4] Mundey, Bissett, and Cartland, *J. Inst. Metals*, 1922, 28, 141.
[5] Rolfe, *Trans. Manchester Assoc. Eng.*, 1929–1930, 13.

PART III.—POUNDING TESTS.

By H. GREENWOOD,* M.Sc., STUDENT MEMBER.

SYNOPSIS.

A modified form of the Stanton impact tester suitable for the testing of white metals by pounding at different temperatures is described. Results on cylindrical specimens are given, and the unsuitability of this type of test-piece is shown. The use of bearing-shaped specimens with a cylindrical indenter is described. Results are recorded for eight different white-metal bearing alloys and a lead–alkali alloy, cast under various conditions, and tested at 18°, 100°, and 150° C. A Babbitt metal with an addition of cadmium gave the greatest resistance to pounding.

THE only earlier work on this subject which the author has been able to trace was that done by Herschman and Basil † who used a modified form of the Stanton impact testing machine, the specimens being chill-cast cylinders 0·8 in. long by 0·4 in. in diameter. These test-pieces were subjected to only 1000 blows, the energy per blow being 0·33 ft.-lb., and the deformation produced was measured at intervals by means of an optical micrometer.

The results showed that at temperatures up to 100° C. the rate of deformation gradually decreased as the test was continued, suggesting that work-hardening of the material had occurred. This is a surprising conclusion in view of the fact that some of the materials used are known to anneal spontaneously after cold-work, even at room temperatures.

In the present investigation it was felt that more useful information would be obtained if the specimen was subjected to 100,000 blows.

The materials investigated were similar in composition to those used by Herschman and Basil, and their compositions will be found in Table I, p. 50.

DESCRIPTION OF APPARATUS.

A modified form of the Stanton repeated impact testing machine was used for this work, a photograph of which is shown in Fig. 15 (Plate IV). The apparatus for holding the normal Stanton specimen was removed from the anvil, the steel weight on the hammer was replaced by lighter lead ones, and by altering the gearing on the machine the frequency of the blows was increased (except in the preliminary tests) to 250 per minute. In order to accommodate a small furnace on the anvil, the lifting mechanism was removed and placed at a point 2 in. along the hammer shaft, a new lifting arm being made 2 in. shorter than that of the standard model, so that when working it did not come in contact with the furnace.

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* Metallurgical Department, The University, Manchester.

† *Proc. Amer. Soc. Test. Mat.*, 1932, 32, (II), 536–555.

The first tests, for comparison with Herschman and Basil's results, were carried out on chill-cast lead cylinders 1 in. high by 1 in. in diameter, and on chill-cast white-metal specimens of the same height and 0·8 in. in diameter. Both metals were poured at 300° C. By means of a short brass bolt the specimens were securely fastened to a plate of hard asbestos, which was bolted on to the anvil. The asbestos was intended to serve as a heat insulator. A loosely fitting steel cap was placed on the top face of the specimen so that the energy of the hammer might be the more evenly distributed.

The deformation of the specimen was measured by means of the apparatus visible on the right of Fig. 15 (Plate IV).

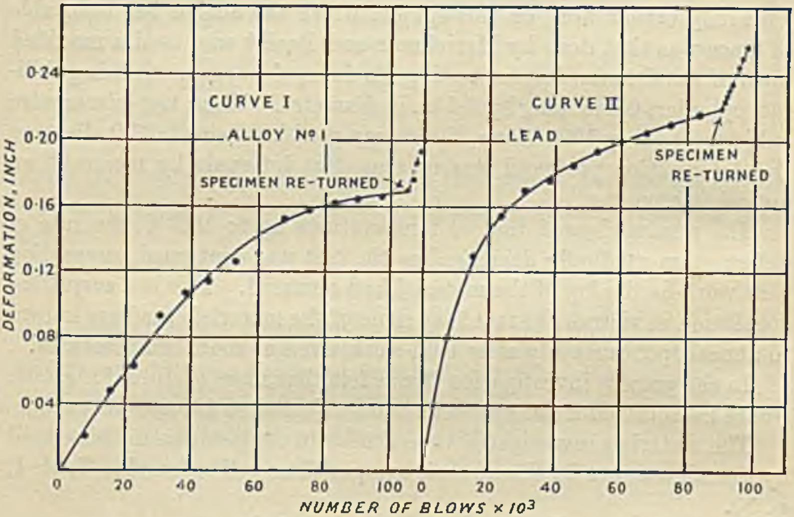


Fig. 16.—Tests at 200° C. on Cylindrical Specimens Cast at 300° C.

Through a hole near the top of the hammer-head a short steel rod ¼ in. in diameter was fastened, the end of which came in contact with the short arm of a system of levers, *A*, *B*, and *C*, giving a magnification of 100. At the end of the final lever arm of the system, a barograph pen recorded the movement in a vertical plane on a revolving drum, *D*, driven through reduction gearing by a synchronous-speed gramophone motor. As the specimen decreased in height, therefore, the first lever was progressively depressed and the pen raised 100 times this distance. The drum was rotated once in each hr., one revolution of the drum corresponding to 15,000 blows on the specimen. The curve thus drawn shows, therefore, decreases in height against the number of blows. The weights of the lever arms were so arranged that there was no tendency for the first lever to spring back after it had been struck by the rod on the hammer, nor for the pen to creep up the paper due to the vibration induced.

The test-piece was mounted on the anvil as described above, its top face covered with a layer of stiff grease to correct the tendency of the cap to bounce off the specimen, and the steel cap placed in position. For tests at elevated temperatures the specimen was surrounded by a small electric furnace and was in contact with a copper–Constantan thermocouple for temperature measurement. The hammering commenced when the test-piece had been at the desired temperature for 30 minutes. An automatic switch was incorporated so that the whole apparatus was shut down after 100,000 blows had been delivered.

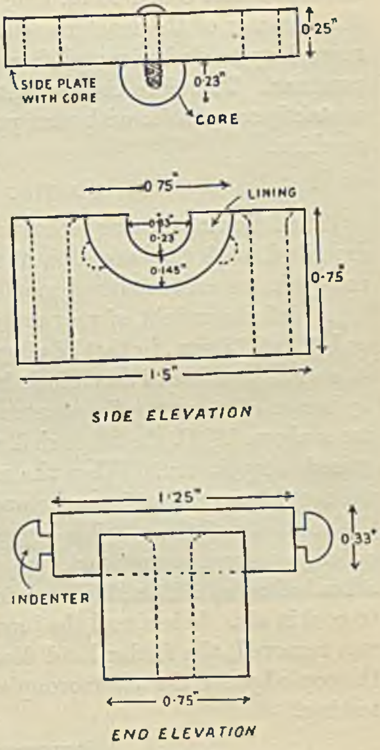


Fig. 17.

The results obtained from these specimens of alloy No. 1 and lead, both tested at 200° C., are given in Fig. 16. For alloy No. 1, the energy of the hammer was 0·42 ft.-lb. per blow, the deformation after 100,000 blows being 17 per cent., whilst for lead the energy per blow was 0·0625 ft.-lb., and the deformation after 90,000 blows, 22 per cent. The deformed specimens spread considerably at the ends, and it is reasonable to suppose that this spreading is the cause of the decreasing rate of deformation as the test proceeds, and of the curve becoming less steep than at the start.

In order to examine this hypothesis, as compared with that of the work-hardening of the test-pieces, the two deformed specimens were turned down to their original diameter and re-tested at the same temperature as before. In both cases it was found that the rate of deformation was much greater than just before the test was interrupted, as is shown in the dotted portion of curves I and II (Fig. 16).

On the grounds, therefore, of the small number of blows, and of the possibly misleading nature of the results, it was felt that the type of test adopted by Herschman and Basil was unsuitable. The use of cylindrical specimens was therefore discontinued.

As an alternative, tests were carried out on specimens shaped like half a bearing as shown in Fig. 17. The brass shell or mould was not tinned, the white metal being keyed in by means of small holes drilled into the sides of the semi-circular groove. After casting the white metal, the brass mould was fastened to the anvil. As a result of many preliminary tests, the actual indenter finally took the form of a case-hardened steel rod, 1·25 in. long and 0·33 in. in diameter, on to which the hammer of the machine fell. With an indenter such as this, immersed up to its horizontal diameter, the angle of indentation remains constant. Therefore the amount of deformation produced in one test is *strictly comparable* with that produced in any other test on the same machine.

CASTING PROCEDURE.

The following casting technique was used exclusively in all the work described, with the exception of that done in the few tests carried out on specimens cast in tinned moulds.

A definite weight of new metal (20 grm. in the case of alloys 1, 2, and 3, and 25 grm. in that of alloys 4 and 5) was melted under charcoal in a small crucible in an electric furnace, and its temperature measured by means of a copper–Constantan thermocouple. For mould temperatures above 18° C. the brass shell was heated in a small oven to the required temperature. When the melt was at the casting temperature, the mould was taken from the oven, a small " dozzle " placed on top, the contents of the crucible vigorously stirred with a graphite rod in order to prevent segregation, and the alloy poured into the mould until a head of metal 0·25 in. high was formed. The mould was then allowed to cool in air. When cool the brass block with the white-metal casting was removed, the feeder head filed off, and a small hole drilled along the top edge for the thermocouple. The specimen was then ready for testing.

DESCRIPTION OF TEST.

With these specimens, the problem of chilling by contact with the anvil is much less than in the case of the cylindrical specimens, so that the hard asbestos plate was replaced by one of mild steel. In the centre of the latter was fastened a small steel block to which the brass mould was secured, bringing the test-piece to the middle of the furnace.

The indenter rod was then inserted along the groove in the specimen, a small projecting upper lip of bearing metal on each side of the indenter helping to keep it in position. This was re-enforced by two light springs,

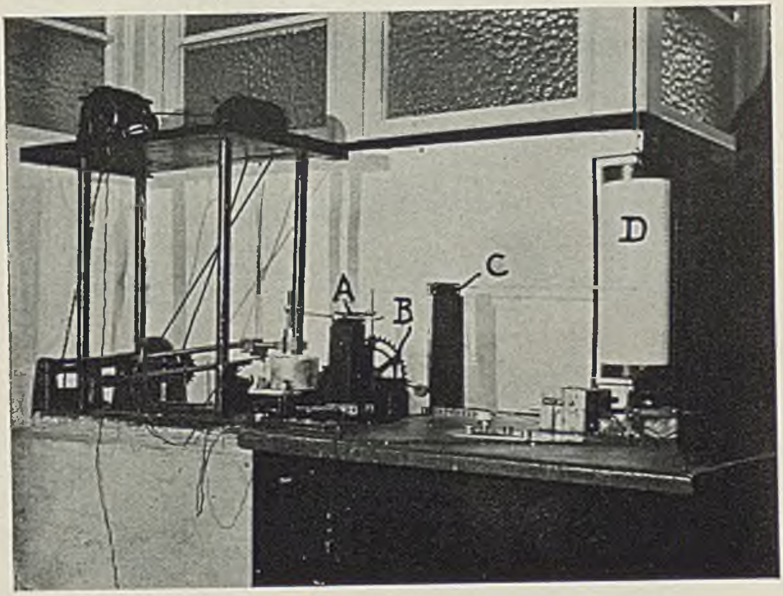


FIG. 15.—Pounding Apparatus.

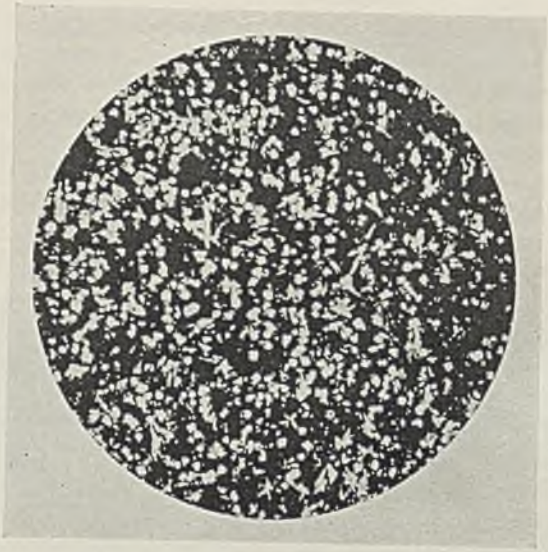


FIG. 22.—Alloy No. 2. Casting Temperature 450° C. Mould Temperature 18° C. × 100.

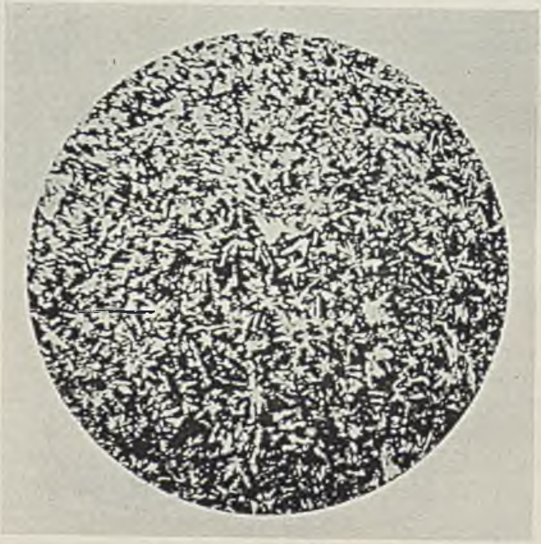


FIG. 23.—Alloy No. 2 + 1% Cadmium. Casting Temperature 450° C. Mould Temperature 18° C. × 100.

Structures of Alloy Cast in Brass Shell.

PLATE VI.

FIG. 24.—Alloy INC after Pounding. × 500.

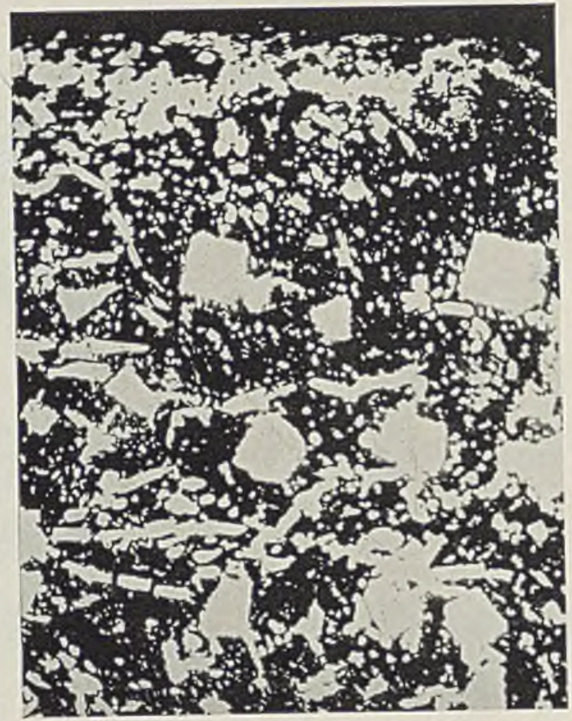
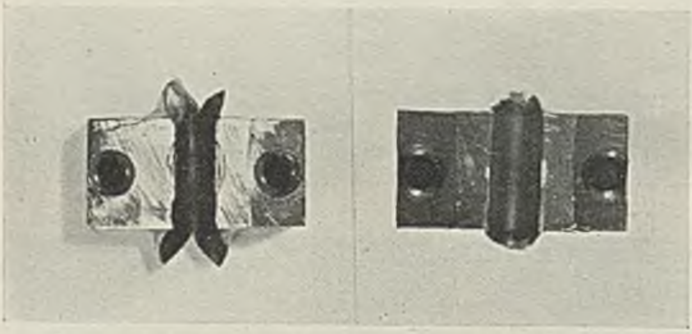


FIG. 25.—Alloy II after Pounding. × 250.



Alloy No. IV. Alloy No. I.

FIG. 26.—Linings after Pounding.

which were stretched from the base-plate to the ends of the indenting tool. The projected horizontal area of the bearing was 0·248 in.^{2}.

After some trials, the energy of the blow was fixed at 0·44 ft.-lb. per blow, being the equivalent of a 6½-lb. hammer falling 0·8 in. As before, for all tests above room temperature the pounding was started 30 minutes after the test temperature had been attained, 100,000 blows being then given.

TESTS ON TINNED SPECIMENS.

Since bearings are almost invariably tinned on to the brass or steel shell, tests were carried out on four castings in tinned moulds. Samples of alloy No. 1, cast at 300° C. into a mould at 100° C., when pounded at a temperature of 200° C. gave considerable variations in the rate of deformation in the four tests. This trouble was almost certainly due to variations in the adhesion of the white metal to the brass block. After the pounding test had been completed each specimen was removed, when it was possible to correlate the resistance offered in the test to the extent of the adhesion. In the case of the smallest amount of deformation it was shown that the adhesion had been effective over the whole area of contact.

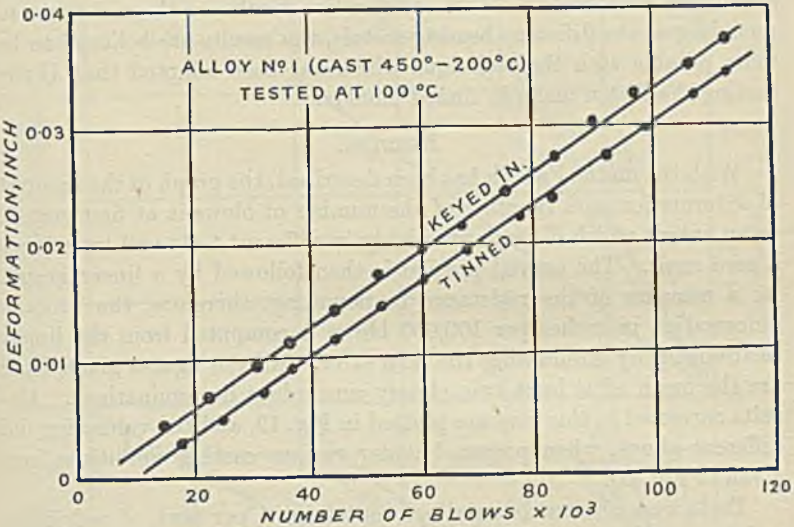


FIG. 18.—Tinned Lining and Keyed Lining.

It is not improbable that the low pouring temperature employed may have exercised a considerable influence in giving the poor results of some of these tests. In another set of comparative tests as between tinned and keyed-in specimens, the results of which are shown in Fig. 18, the casting temperature was therefore increased to 450° C. and that of the mould to 200° C. Using these conditions, the tinning appeared to be perfectly satisfactory in all cases. As will be seen, the graph of deformation is practically linear, and almost the same as regards rate of deformation in the two sets of determinations.

In view then of this proof that the deformation under the conditions of these tests was the same for tinned as for keyed-in test-pieces, coupled with the possibility of erratic results arising from imperfect tinning at the lower casting temperatures, it was felt preferable to employ the keyed-in specimens and to abandon the practice of tinning. Since the aim of the work was to obtain comparative results on the resistance to pounding of the different bearing metals, the results are believed to be more reliable with the technique which has been adopted than if the castings had been made in tinned moulds.

RESULTS.

With the method which has been described, the graph of the amount of deformation as a function of the number of blows is at first curved to an extent which differs appreciably in different tests and introduces a zero error. The curved portion is then followed by a linear graph. As a measure of the resistance to pounding, therefore, the average deformation in inches per 100,000 blows is computed from the linear relationship by eliminating the zero error. All the figures given later are the mean of at least two, closely concordant determinations. Results corrected in this way are plotted in Fig. 19, and the values for the different alloys, when prepared under various casting conditions, are given in Fig. 20.

Tests were also made on alloys containing 1 per cent. of cadmium, and on a specimen of alkali-hardened lead (LA). These are recorded in Table XVIII, and may there be compared with results for INC and II.

TABLE XVIII.

Alloy.	Casting Conditions.	Deformation (In. per 100,000 Blows) at the Following Testing Temperatures.			
		18° C.	100° C.	150° C.	200° C.
INC	300°–100° C.	0·0047	0·012	0·046	...
	350°– 75° C.	...	...	0·012	...
ICd	400°– 75° C.	0	0·004	0·008	...
II	350°– 75° C.	...	...	0·009	...
IICd	400°–100° C.	0	0	0	0·001
LA	500°–200° C. Aged for 6 days	0·010	0·018	0·025	...

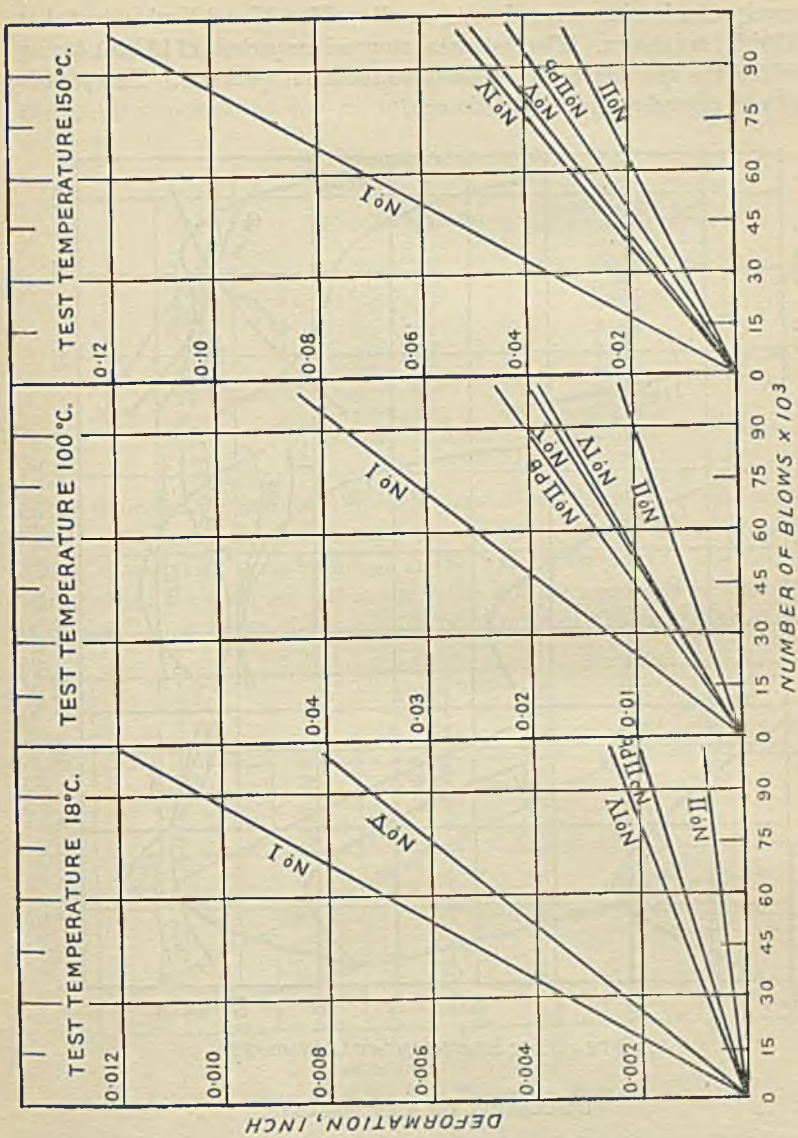


Fig. 19.—Alloys Cast at 300°–100° C. and Tested at Different Temperatures.

Effect of Interrupted Pounding.

In an actual bearing, periods of rest interrupt those of pounding during service. The extent, if any, to which these rests affect the behaviour of the metal is clearly one of some interest, and in Fig. 21 the results of a few interrupted tests on alloys Nos. II and V when tested at 150° C., are shown. The tests were stopped for periods of 12 hrs., during which the specimens cooled down to room temperature. The periods of rest caused no important change.

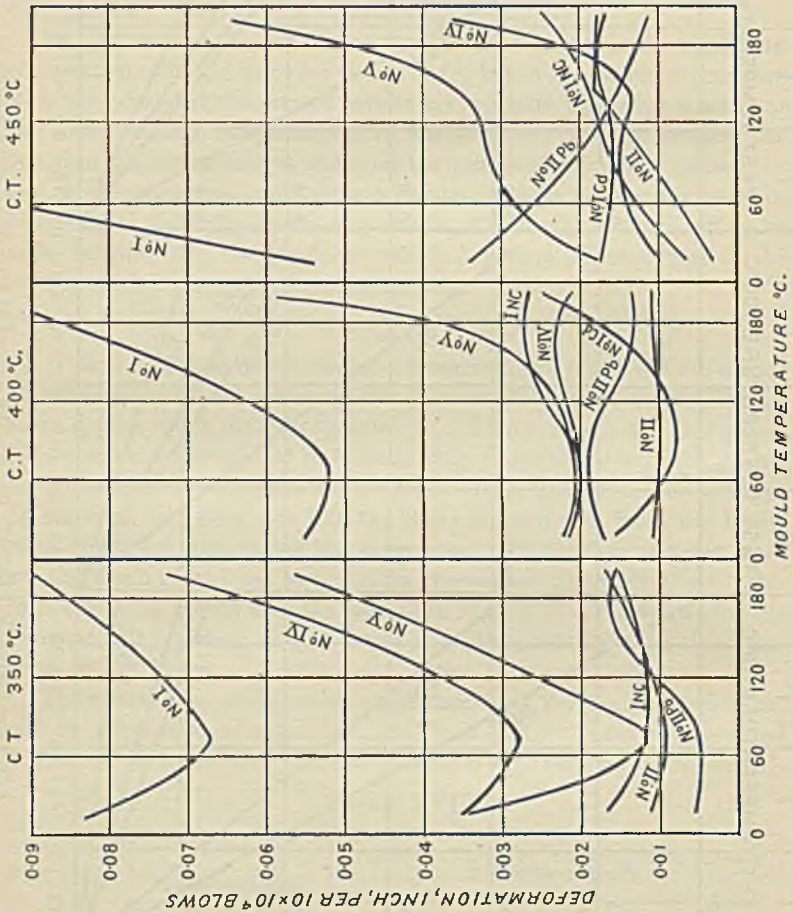


Fig. 20.—Tests at 150° C.

Discussion of the Results.

From an examination of Figs. 19 and 20 it is possible to draw up Table XIX giving the optimum resistance to pounding of the various alloys. The good qualities in this respect of No. II and the great resistance offered by No. IICd are very much in evidence. It is also to be noted that No. INC is very satisfactory when cast at 350°–75° C.

Considering the effect of the casting and mould temperature on the results for No. II, it will be seen that, when tested at 150° C., the greatest deformation is given by the test-piece cast at 300° C. and the least when the metal is poured at 450° C. into a cold mould. The casts at the lower temperatures into cold moulds showed cold lapping, to which the poor results under these conditions may be due. An additional possible cause of variation is to be found in the wide differences in the micro-structure of the samples, but so far it has not been possible to discover any correlation between these and the results of the pounding tests.

Table XIX.

Alloy.	Casting Conditions, ° C.	Deformation (In. per 100,000 Blows) at 150° C.
I	400°– 75°	0·052
INC	450°– 18°	0·007
ICd	400°– 75°	0·008
II	450°– 18°	0·003
IICd	400°–100°	0
IIPb	350°– 75°	0·005
IV	450°– 18°	0·010
V	350°– 75°	0·012
LA	500°–200° C. Aged	0·025

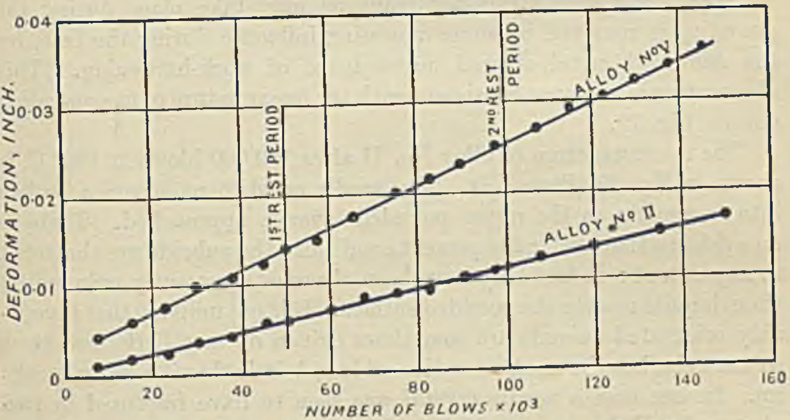


Fig. 21.—Effect of 12-Hr. Rest Periods on Tests at 150° C.

Unless the yielding stress of the material is exceeded, no permanent deformation will result from pounding, and since alloy IICd has completely resisted the hammering (Table XIX), its yield-point should be higher than that of any of the alloys. This is fully confirmed by the results given in Part II of the present paper (p. 74) and the same relative generalization may be applied to alloys ICd and I. Figs. 22 and 23 (Plate V) make it evident that the addition of 1 per cent. of cadmium to alloy No. II enormously increases the amount of the needle constituent at the expense of the cuboids.

The normal structure of alloy INC (450°–200° C.) may be seen in the *lower* part of Fig. 24 (Plate VI). The upper portion of this photomicrograph shows, in section, the appearance of the deformed surface layer of the alloy after pounding with 100,000 blows at 150° C. The break-up of the fine needle network into small particles is apparent. This effect is not due to any chilling by the metal core during casting, for examination of the upper undeformed portion of the lining showed that it had the same structure at the surface as in the body of the alloy. A similar casting of this material was also sectioned and examined after a standard pounding at 18° C. The microstructure was exactly similar to Fig. 24. Scratch tests with the Ball sclerometer made along the sectioned faces of these specimens gave the following results :

Resistance to Scratching, Alloy INC.

	Pounded at 18° C.	Pounded at 150° C.
At pounded surface . .	42 kg./mm.^{2}	41 kg./mm.^{2}
Inside	42 ,,	41 ,,

Apparently such strain-hardening as may take place during the pounding is removed by some annealing influence during the test, for the deformed metal showed no evidence of work-hardening. This observation is of course consistent with the linear nature of the pounding curves, Fig. 19.

The microstructure of alloy No. II after 100,000 blows at 150° C. is shown in Fig. 25 (Plate VI). The needle constituent becomes broken into fragments as the upper pounded layer is approached. There is no evidence that under the present conditions the cuboids are shattered to any extent : in fact they have been observed apparently unimpaired though quite near to the pounded surface. It is not unlikely that favourably orientated cuboids are sometimes driven down a little into their soft matrix, but the needle constituent is so brittle that it readily breaks up. In one case a needle crystal was seen to have fractured in two places where it became pounded against the sharp edges of two adjacent cuboids.

Cracking.—Most of the deformed test-pieces showed signs of cracking at the two ends immediately beneath the indenter. In all cases, however, these cracks were confined to the extruded portions and were never, as far as could be determined, propagated into the main body of the specimen.

Although there was a considerable amount of deformation in samples of alloy No. I no cracks were produced in this material. No. INC cracked slightly, but not as much as No. II for instance. All the other alloys showed some evidence of cracking, the extent of which was in general proportional to the total amount of deformation. In Fig. 26 (Plate VII) photographs of deformed specimens of alloys No. I and No. IV, both tested at 150° C. are given. The total amount of deformation was about the same in each case. Alloy No. V behaved very similarly in this respect to No. IV.

In order to ascertain whether there were any cracks just below the surface of the test-pieces, many deformed specimens were etched electrolytically in a dilute solution of nitric acid, but no fissures were ever revealed.

JOINT DISCUSSION ON PAPERS NOS. 673, 674, 675, AND 676 (BEARING METALS).

The President: These four papers will be discussed together. The work which they represent has been rendered possible through the activities of the International Tin Research and Development Council, of which Mr. D. J. Macnaughtan is the Director of Research. The last three papers report work carried out in Professor F. C. Thompson's metallurgical laboratories in the University of Manchester, and I will ask Professor Thompson, therefore, to open the discussion.

Professor F. C. Thompson,* D.Met., B.Sc., M.Sc. (Member): There is probably no big group of engineering alloys about which so little is known with certainty as the bearing metals. Until comparatively recently one felt on fairly safe ground in the old belief that these materials must have a duplex structure, but some of the more modern developments have cast a doubt even on that hypothesis. This fact must be taken into consideration in connection with the papers under discussion. They represent what is definitely preliminary work which had to be carried out to obtain some basis line which would enable future modifications to be quantitatively judged. It must also be remembered that this work in its present stage is, on the whole, of a technological rather than of an academic character, although this does not, perhaps, apply to the paper by Dr. O'Neill and Mr. Kenneford, which represents a very important contribution to the general question of the hardness measurement of soft materials, and moreover, it does not wholly apply to Mr. Macnaughtan's paper.

Certain types of cracking, particularly in aeroplane bearings, have been ascribed for some time, by manufacturers and engineers, to fatigue. There was really no reason to doubt that conclusion, but it was very difficult, if not impossible, to visualize the manner in which the fatigue was set up, and Mr. Macnaughtan's contribution is important in that he has provided, I believe for the first time, a plausible explanation of the stress conditions to which these fatigue cracks are due. Whether Mr. Macnaughtan's explanation is correct or not, he has shown that it is possible to provide, on perfectly rational grounds, an explanation of these fatigue cracks. That is a matter of the greatest importance in connection with further work, because it means that it is to the hardness aspect of the properties rather than to the ductility that special attention must be given.

Three lines of investigation on these materials now clearly suggest themselves: (1) on the fatigue properties; not necessarily directly, because it is possible to get very clear indications now by an indirect method; (2) the thermal properties, since clearly on these depends to a large extent the temperature which will be attained in the bearing in service, and consequently, the mechanical properties of the white metal at those service temperatures; (3) the question of the anti-frictional characteristics—this may, or quite possibly may not, be of great importance, but it is obviously a factor which must be borne in mind.

The papers by Messrs. Arrowsmith and Greenwood represent work which at its present stage is mainly of a preliminary and exploratory character; but already that work has led to useful results, particularly in connection with the very valuable effect of the addition of small amounts of cadmium. No claim is made, however, for credit for the introduction of this alloy.

Since the work on the tensile properties which is recorded in Mr. Arrow-

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* Professor, Department of Metallurgy, The University, Manchester.

smith's paper was done, it has been carried much further, and these properties have now been measured in some detail at temperatures up to about 175° C. Those who have had experience in dealing with such materials will realize, however, the difficulty of making measurements of yield-point and elastic limit. I am not, in fact, satisfied that there is an elastic limit, but something of the nature of a proof stress can be determined. Investigations on the specific heat, thermal expansion, and conductivity are practically completed, and those aspects of the work may be of very considerable interest.

If the papers are read with care, it will be agreed that they contain a large amount of interesting information. It needs, perhaps, to be sorted out, and, in fairness to the authors, I would point out that the necessity for drastic condensation in the presentation of the papers—very properly, from the point of view of the Institute—is one reason why the t's have not been crossed and the i's dotted a little more completely.

In conclusion, the position, as I see it, is that this basis work has been more or less completed. The normal characteristics of these materials are now known, and we are, therefore, in a position to attempt to improve them, either by heat-treatment or by the addition of other suitable materials.

Mr. A. J. Murphy,* M.Sc. (Member): It has been felt for some time that, considering the large tonnage of tin consumed annually in this country and throughout the world for anti-friction purposes, this Institute has been somewhat remiss in the small amount of attention it has devoted to the subject. It is pleasing, therefore, to see this leeway being made up to some extent.

These papers are, in a way, propaganda, but so long as the contributions sponsored by the International Tin Research and Development Council maintain the standard set to-day, even the most academic of our members will not complain that they are unsuitable for presentation before the Institute.

As Professor Thompson implied, practice with regard to bearing metals is far in advance of theory. Mr. Macnaughtan's paper is a very interesting movement towards reducing this gap between theory and practice. It is difficult to decide in which direction progress can most usefully be made. He is concentrating on considerations of fatigue because one of the most remarkable problems with white metals recently has been that particular form of failure by apparent fatigue-cracking found in the connecting-rod bearings of aero-engines and road-vehicle Diesel engines. A difficulty is encountered immediately, however, in comparing the results obtained in practice with the values of fatigue strength, tensile strength, and hardness. This is well illustrated by the case of the alloy containing approximately tin 92, antimony 4, and copper 4 per cent. There is no doubt whatever that this is one of the most successful bearing metals for thin linings in connecting rods, and yet, judged by its Brinell hardness, fatigue strength, tensile strength, and behaviour in pounding tests, it would rank extremely low in the list of available materials.

A careful distinction must be made between thin and thick linings in the selection of white metals. Whereas the linings of aero-engine connecting rods are usually only of the order of 0·02–0·04 in. thick, those in marine Diesel engines are frequently above ⅜ in. in thickness. The latter present quite a distinct problem, and the soft, very high tin content white metals are not the most successful in these heavier bearings.

It is often not realized how severe are the stresses which can arise from the differential contraction between the white metal and the shell on lining. An opportunity to observe dimensional changes resulting from this cause arose recently in connection with the re-lining of a semi-cylindrical cast-iron

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shell. The outer and inner curved surfaces of the shell were concentric, and had the respective diameters 14½ and 11 in., the thickness of the iron being 1¾ in. The shell had been machined, when lined with a soft white metal having a Brinell hardness of 20–25, to fit in an outer housing, and it was desired to re-line it with a harder white metal, with a Brinell hardness of 30–35. The old white metal was run out, the harder white metal cast in, and the bearing was bored to size, leaving a lining ⅜ in. thick. It was found that the shell was now loose in its housing. As this could not be tolerated, it was necessary to re-line the bearing, and on this occasion careful measurements of the shell were taken at various stages. Midway along the bearing the external diameter of the shell before lining was 14·495 in. After lining and boring to leave 0·5 in. thickness of the hard white metal the external diameter across the horns was 14·449 in., a reduction of 0·046 in. There was little doubt that this contraction was due to internal stresses resulting from the lining. The existing shell had to be used, and no alternative white metal was permissible, so that it was necessary to find some way of relieving these internal stresses. Immersion in boiling water for 2 hrs. had no appreciable effect on the dimension concerned. In order to overcome this difficulty it was necessary to perpetrate what must be regarded as a metallurgical heresy, namely, to hammer the bearing along the centre of the lining. In general, this is, of course, a practice not to be recommended, but it was justified in the present instance because it was the only practicable way to restore the dimensions of the shell. On first hammering the lining the horns opened out to 14·494 in., *i.e.* an expansion of 0·045 in., but on resting for ½ hr. they closed in again to 14·484 in. A second hammering caused an expansion to 14·495 in. followed by a contraction to 14·485 in. on resting several hours. After a third hammering to expand the shell diameter again to 14·495 in., the white metal was bored to the finished size, and the correct dimensions were maintained during the period of several days for which the bearing was kept under observation. A very careful examination of the lining failed to reveal any sign of damage, such as cracking or loss of adhesion. When the fairly robust character of the shell is remembered, this experience emphasizes the magnitude of the contraction stresses which can be set up, and indicates that they may easily form an important factor in the performance of a bearing in service.

Mr. Macnaughtan has referred to the suggestion that the superiority of copper–lead over tin-base bearings in some cases might be connected with the presence of a brittle film between the tin-base lining and the shell. The evidence at present available, including that in the present papers, is, I think, not sufficient to discount that possibility completely. There are cases where it is fairly certain that a bearing which has gone into service with perfect adhesion has lost that adhesion at a later stage without any cracks appearing on the surface. When comparing copper–lead with white metal linings, it has to be remembered that the fatigue-strength of annealed copper is approximately 4·5 tons/in.^{2}, whereas that of white metals is about 1·8 tons/in.^{2}. It may be that this is the important factor deciding the superiority of copper–lead in thin linings.

Mr. J. CARTLAND,* M.C., M.Sc. (Member): I have studied these papers with very great interest, and I have also had the benefit of being in close touch with the International Tin Research and Development Council since its inception. I welcome the papers particularly because until the present time the Institute of Metals had neglected the important subject of bearing metals. I mention that rather strongly because in the fifty-four volumes of the *Journal* already published there have been only six papers which can

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* Director, Fry's Metal Foundries, Ltd., London.

be directly connected with bearing metals. A great deal of valuable work, on the other hand, has been published elsewhere, particularly in America by the American Society for Testing Materials and by the Bureau of Standards and other bodies.

Mr. Macnaughtan and his collaborators are to be congratulated on getting down to the fundamentals of this problem, and Mr. Macnaughtan gives an admirable exposition of the requirements of a bearing metal and the advantages of low-temperature melting-point bearing metals, with which I am in complete agreement.

The breaking up of bearings by fatigue-cracking, with the well-known "crazy pavement" effect, occurs as described by Mr. Macnaughtan on p. 37, but the question arises as to whether this is fatigue or not. The evidence on that point seems to be that in practice bearings in failing present exactly the same "crazy pavement" appearance as the rings which were tested by Stanton in 1930 and subjected to alternating flexure from the outside and to no internal loading. There it was obviously a case of fatigue, and the conclusion is therefore reached that the bearings, having a similar appearance, are also fatigue failures.

Murphy, in his lecture to the London Local Section, attributed these failures to the presence of a brittle tin–iron compound between the white metal and the steel; the evidence for that seems to be that Stanton did not find similar breaking up with bearings lined with copper–lead, and that copper and steel or copper and iron form a solid solution. There is no doubt that when white metal is cast on to steel this brittle tin–iron compound is formed; that is proved by the work of Hoare and of Jones and Hoare described in papers presented to the Iron and Steel Institute; but there is no definite chain of evidence connecting that brittle compound with the fatigue failure. The evidence is only circumstantial. It seems a definite issue which we ought to clear up if possible in this discussion. If the brittle tin–iron compound is to blame, the solution of our problems lies in attacking that. I had one or two promising lines of attack on that assumption, but if the tin–iron compound is going to become unfashionable as a bogey I do not wish to waste time in pursuing it!

We all thought on those lines, and the main factor which seemed to change the situation was Mr. Macnaughtan's visit to America! Apart from that, however, I think that there has been a gradual accumulation of evidence that similar fatigue-cracking takes place in bearings in which flexure is definitely excluded. I see a number of users, and I get a few instances of the sort of thing which happens. Two occur to me at the moment. In one case an electric traction engineer has bearings where he is confident there is no flexure, and yet he sees "crazy pavements" regularly. In the other, a marine Diesel engineer is sure that before he gets from London to Flamborough Head his bearings resemble a jigsaw puzzle, but they have no flexure. Asked whether he took the bearings down when he got to Glasgow, he said, "No, because if I did the pieces would fall out, and I should not be able to put them back!"

Mr. Macnaughtan starts out to explain these failures on the basis of a rigid shell, and to do this he has to explain tension in the white metal. He does that under five headings: (1) flexure. That is agreed; (2) also includes flexure, because that is the one where the adhesion of the white-metal coating is imperfect; In (3) he explains that when a bearing is subjected to pressure which causes permanent deformation, and that pressure is removed, it leaves tension. I am unable to follow his explanation there; perhaps he will enlighten me on that subject; (4) is the friction of the oil on the surface of the white metal, which is agreed, but which is very small. The important one, to my mind, is (5), which is the tension due to the difference in contraction between the white metal and the steel on cooling, the difference in the coefficient of contraction about which Mr. Murphy has just spoken.

I do not think that we need look very much further than that for our explanation. I suggest that when white metal is poured at about 360° C. into a steel shell heated to about 200° C. and is then cooled to room temperature from that resulting temperature, there is very considerable tension left in the white metal, and later, when that white metal is subjected to repeated hammerings in use, that tension is relieved in the form of cracks. Can failure of this type properly be classified as fatigue ?

A very simple illustration of the great tension due to that contraction can be obtained by casting white metal on to thin steel strip. On cooling to room temperature, the white metal and steel strip will be found to be bowed upwards with a distinct curve, with the white metal on the concave side; this curvature is, incidentally, a good test that adhesion has taken place.

With Mr. Macnaughtan's remarks on micro-examination I am in complete agreement, and I have had a good deal of experience in industrial practice. I have examined a great number of bearings with an internal combustion engine manufacturer who was troubled with these fatigue cracks. The cracks appeared to bear no relation whatever to the structure; only in one case did they start on a cube face or seem to follow a cube face, and there was evidence, although I would not be positive on this, of the cracks starting from the surface and not from the bottom.

With regard to the improvements suggested, from the arguments which I have just brought forward I think that it seems clear that the greatest improvement towards overcoming the trouble would be to use a steel shell, if that were possible, of the same coefficient of expansion and contraction as the white metal. The addition of the cadmium is very interesting. The laboratory tests seem to prove the great possibilities of this, and I refer not only to Mr. Macnaughtan's paper, but also to all the others. I think that the case is so well made out from a laboratory point of view that it justifies practical trial, and one or two important users are already, on my recommendation, trying it out in their own work.

Had time permitted, I should have liked to discuss the other three papers in detail. They represent really important fundamental work, a basis from which we can start and a tabulated list of figures on which we can work and which will remain as a standard.

The PRESIDENT : Regarding Mr. Cartland's reference to the Institute's alleged neglect of bearing metals, I would say that the Institute was fully alive to the importance of the subject. It is the members and others who write papers and send them in to us who have neglected bearing metals, and not the Institute itself !

Mr. R. CHADWICK,* M.A. (Member) : The investigations described cover a very wide field, and, I hope, represent only a beginning of the scientific study of a very interesting group of alloys. It is perhaps premature, therefore, to complain that the authors have not been able to correlate their results and formulate any outstanding conclusions.

What impressed me about the investigations was that the problem was really one concerning the behaviour of the alloy composing the bearing under small amounts of cold-work, for in its early life the bearing is subjected to battering involving surface deformation until it takes up the contour of the shaft, and either this deformation or alternate fatigue stressing would produce cold-work in the bearing. A direct investigation of the effect of cold-work on some of the alloys, therefore, might have yielded interesting and informative

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results, because the alloys behave on rolling in much the same way as the eutectics discussed by Mr. Pearson at the last meeting of the Institute.

Part I forms the bulk of the investigation under discussion, and presents a somewhat formidable mass of data on indentation tests. It deals almost exclusively with material in the cast condition, and I was surprised, therefore, to find that the authors described the deformation as viscous flow. The cast alloys must be in an unstrained crystallized condition, and the stress-strain curves reproduced in Part II show perfectly definite yield-points. Such a condition is very different from the cold-worked condition in soft alloys, in which true viscous flow may occur under low loads. In alloy I in the cast condition I could detect no creep after 2 days under a tensile load of 1 ton/in.^{2}, *i.e.* the creep rate was less than 2×10^{-7}/in./in./minute, whilst after 80 per cent. cold reduction it showed an elongation of 5 per cent. in 1 hr., representing a creep rate of 10^{-3} in./in./minute under the same load. The word "creep" should be reserved for such deformation under small loads, whilst deformation under high loads might more properly be referred to as flow, and the deformation as plastic.

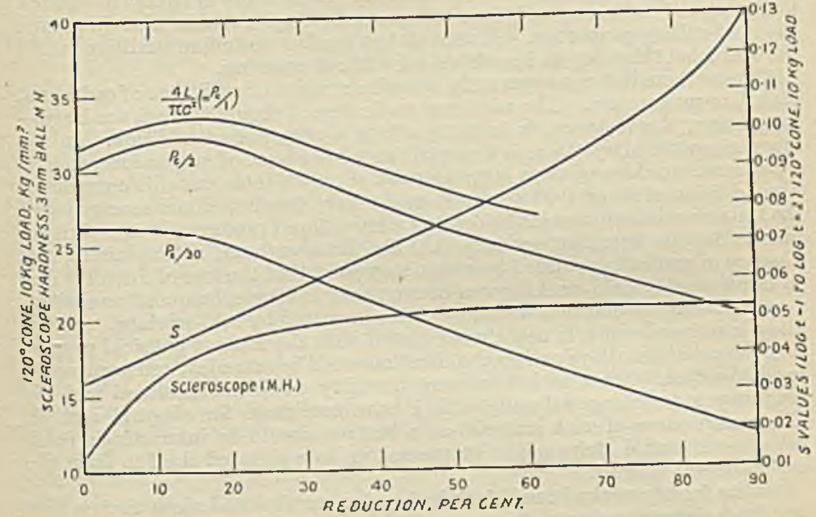

Fig. A.

Hargreaves' method of analysis, originally employed to examine the effect of cold-work, has here been employed on a series of cast alloys. I applied this analysis to cast and cold-worked alloy I, and on two samples showing a ratio $\frac{S \text{ cast}}{S \text{ rolled}}$ of 3 : 1, I obtained a ratio of rates of creep $\frac{R \text{ cast}}{R \text{ rolled}} > 5000 : 1$, which demonstrates the advantage of direct creep measurements over indirect indentation methods. I noted the one case in which Mr. Kenneford and Dr. O'Neill gave some values of rolled alloys in Table IV. I was not able to confirm the S value given for rolled alloy 1 (see Fig. A) and the log t/log d curves obtained were not straight lines except in the case of the cast alloy.

It is suggested that limiting creep stress may be estimated from Meyer graphs, but indentation necessarily involves deformation, and limiting creep stress must always be below the yield-point of the material. The direct measurement of limiting creep stress would have presented no difficulties.

I was interested in the results obtained by the authors by scleroscope testing. In the case of alloy I, I found that the effect of cold-rolling was a steady decrease in cone hardness as measured on a loading period of 30 seconds, but when the load was applied for approximately 2 seconds an initial increase in hardness due to cold-work was noticed. Roughly parallel curves were obtained using ball indentation. The scleroscope gave a normal roll-hardening curve. Cone hardness and scleroscope values are plotted in Fig. A, which illustrates the great importance of the rate of testing, and qualifies the idea that these alloys are softened by cold-work.

In Part III the authors made what I thought to be a notable discovery: the addition of cadmium to alloy II suppressed the cuboids of antimony solid solution, and the alloy obtained, although harder and less ductile (according to Table XVI), yet withstood pounding to an increased extent. I found that on cold-rolling alloy II, cracking commenced on the edges of cuboid inclusions. Quite small cadmium additions suppressed these cuboids and improved the cold-rolling properties. A correct but smaller cadmium addition might have enabled this alloy to be cold-rolled without cracking.

The authors did not apparently examine a range of additions of cadmium, nickel, or magnesium. The additions made were, I thought, much too large—magnesium, for instance, is in many alloys a very potent addition. In the magnesium–tin alloys there is a eutectic at 2·3 per cent. of magnesium, so that 1 per cent. would produce a large amount of brittle inter-metallic compound. The addition of about 0·01 per cent. might have toughened and strengthened the tin-rich solid solution in the bearing alloy without producing this embrittlement. In his introductory remarks, Mr. Macnaughtan, in explaining the absence of cracks in pounded bearings, suggested that the loss of ductility due to hardening by cold-working was counterbalanced by subsequent annealing. I suggest that the ductility would be rather increased by cold-working. A cast alloy is not one which is usually associated with the highest physical properties. Most of the alloys under consideration could be extruded, and some could be cold-rolled. After such treatment ductility would be increased and the tendency to cracking reduced; this I have confirmed for alloys I and II. The examination of such material as a bearing should be interesting; cold-rolled or extruded strips might be pressed on to a serrated shell to form the experimental bearing.

In its freshly worked condition the bearing metal would show viscous flow to a high degree, and would exaggerate the effect of the flow observable, for instance, in cast alloys at high working temperatures. It may be that such properties to a small degree would be an advantage in the early life of a bearing, because it would thereby accommodate itself to the shaft without the intense local stress formed on the surface of a less yielding alloy; in other words, the deformation would be below instead of above the yield-point of the alloys, *i.e.* viscous instead of plastic. Self-annealing would subsequently slowly reduce the physical properties more nearly to those of the rigid cast structure, but would not perhaps entirely eliminate the dense structure and greater toughness produced by the fabricating process.

In view of Mr. Murphy's observations on the hammering of bearings, I may mention that I hammered some cast bars of alloys I and II, machined off the surface, and compared the impact strength both before and after annealing with that of machined cast bars. The hammering appeared on the whole deleterious, and it seems probable that slight surface cracks were produced. Using blows of regulated intensity it might be possible, however, to produce the requisite cold-working without this accompanying surface damage.

Professor D. **Hanson**,* D.Sc. (Vice-President): This series of papers is not only important from the practical point of view, but also extremely interesting, in that Mr. Macnaughtan has attempted to analyze what happens in a bearing and what leads to failure. His arguments in favour of fatigue stresses as a source of cracking certainly make out a *prima facie* case for considering them as important. The conditions in bearings, however, are very complex. There are not only alternating stresses imposed on the lining, but also alternating stresses which may vary very greatly in the mean value of the cycle of stress; there are shock stresses and another type of stress to which I consider that possibly sufficient consideration has not been given: that is steadily applied prolonged stresses. In what respect may these steadily applied stresses contribute to the failure of the bearings?

From Mr. Macnaughtan's analysis, there are quite clearly certain factors that may set up prolonged stresses in a bearing, stresses which, if they are not entirely constant at any rate do not vary sufficiently to be regarded as fatigue stresses. For example, the stresses due to the flow of the oil, which he has worked out, are of that type, imposing a steady stress on the lining. Although the tentative figure at which he arrives is only 90 lb./in.^{2}, in the case of a low-melting-point metal such as tin and its alloys, in the absence of positive evidence I am not prepared to believe that even such a low stress might not be important at high temperatures.

What appears to me to be, however, the most important factor imposing steady stresses on the bearing is that referred to in (5) in Mr. Macnaughtan's paper—the contraction stresses between the tin and the shell, which may impose very high stresses that are acting all the time. It seems to me that under some conditions, and perhaps under many conditions, met with in service the bearing may be subjected to what may be called creep stresses, and therefore creep phenomena may enter into the failure of the linings.

From this point of view, it would be important to study still further the type of crack which is formed, particularly at its beginnings. Mr. Macnaughtan refers to the lack of information on the nature of these cracks. He states that they do not show any definite relation to the structure of the alloy, but I suggest that the subject has not been fully investigated. The metallography of bearing metal as a rule consists of etching in such a way that the intermetallic compounds are well distinguished from the matrix; but, if creep stresses cause cracking, the most probable seat of the cracks is the grain boundaries within the matrix itself. A new technique is needed to reveal the matrix structure. It is necessary to know just where the crack begins, and to discover this special means have to be adopted: present evidence is far from conclusive.

The "crazy pavement" appearance to which Mr. Cartland referred, and which Mr. Macnaughtan mentioned, although not in those words, and the falling out of pieces of metal, are characteristic of the type of cracking which occurs under creep stresses. The weakness under low stresses acting for a long time tends to develop at the boundaries, and a rather large series of connected cracks tends to form, which surround the grains and might very well lead to the falling out of pieces, so that the evidence which has been adduced in support of fatigue stresses might also conceivably be consistent with the existence of failure by creep.

The tin alloys are fairly ductile, but under the action of very prolonged stresses it is conceivable, by comparison with other materials, that they would crack with very low elongations indeed. In my own work on aluminium which had elongations of 30, 40, or even 50 per cent., creep cracks began with elongations as low as 4 per cent., so that they have in that respect some of the

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characteristics of fatigue cracks, in that they commence with very little general elongation of the material. I do not suggest that fatigue actions are not important, because Mr. Macnaughtan has shown that they are; but I suggest that he should include in his analysis the possibility of failure under the prolonged action of a relatively steady stress, because I do not regard the stresses set up by thermal reactions as of the nature of fatigue cracks at all. The number of repetitions in the life of a bearing is relatively small, and the phenomena could scarcely be classed as fatigue phenomena.

On the question of remedies, it is quite likely that the one which would be right to counteract fatigue cracks would also be right to counteract creep cracks. A stiffening of the solid solution of the matrix by suitable alloying constituents, such as antimony, cadmium, bismuth, and so on, is important, as well as the provision of some sort of scaffolding of harder constituents such as the copper–tin constituent; but if the failure is by creep, we must know it, because it may be that the action of these different alloying metals will have different effects on creep and fatigue, and an investigation which was confined to fatigue alone might just fail to reveal the correct alloying element.

Mr. Macnaughtan makes comment on the use of Brinell and tensile tests as having a bearing on fatigue properties. I have no definite data bearing on the question of fatigue in relation to tensile and Brinell tests, but I have data which show clearly that ordinary tensile and Brinell tests are not a sufficient guide to the behaviour of tin alloys when subjected to prolonged creep stresses. The order of the different alloys may be reversed, and quite a wrong impression may be obtained of the creep strength on the basis of short-time tensile or Brinell tests. At Birmingham University there is being carried out a large series of creep tests on tin alloys, and I hope that the information which they will give will add very greatly to our knowledge of these materials; for, while the short-time tests already carried out are essential, I feel that with a metal which can flow under relatively low stresses at ordinary temperature they are only a small part of the whole tale, and that creep tests on tin and its alloys are going to be far more important to the engineer than the short-time Brinell and tensile tests used at present.

Mr. H. Sutton,* M.Sc. (Member): This is indeed a very opportune time for the study of tin-rich bearing metals, particularly as bearing performance is closely connected with the subject of lubrication, and recent research work on lubrication and lubricants appears to have been very fruitful.

Mr. Macnaughtan refers to connecting rod and main crankshaft bearings of internal combustion engines as having to face conditions more severe than those of any other important class of bearing. In the case of aircraft engines it is rarely found that main bearings fail, unless the shaft flexes badly. When failure does occur, it is usually of the big-end bearings, and on the top side, generally immediately under the connecting rod. It is agreed by all that the conditions are exacting. The present tendencies to increase revolutions and compression ratios have produced a long succession of failures of big ends. There would seem to be overwhelming evidence that the cracks are associated with fatigue. In my own experience, the first stage of the breakdown appears to consist of superficial cracks. As those occur in the top half where some flow occurs, they may possibly be associated with surface cracking under compression with the surface possibly in tension, as suggested by Mr. Macnaughtan. Such surface cracks would tend to propagate further under the influence of flexure, which is very difficult to avoid in practice.

I was interested to notice that in Mr. Greenwood's pounding tests no

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cracking within the bearing itself was observed by the author. There, I think, the backing of the bearing was very rigid and strong.

I find myself at some variance with one remark in Mr. Macnaughtan's paper, where he refers to the "superior merits of tin-base alloys, particularly at elevated temperatures." I feel that the temperatures at which tin-rich bearings operate satisfactorily are, to say the least, moderate.

I was pleased to see reference made in the text to the fact that friction is an important source of heat. It was recently stated by R. Dean Averns in a paper presented to the Institution of Automobile Engineers that the temperature of the oil leaving a big-end bearing is known definitely to be much lower than that of the bearing itself, which would seem to indicate that friction in the bearing is an important source of heat. Heat reaches the bearings by way of the piston and connecting rod, and also by way of the oil, and some of our engines work with oil temperatures up to 100° C.

From practical experience it would seem that the strength of the layer of white metal, from the point of view of resistance to deformation and displacement under working conditions, is greatest when the layer is very thin. That fact appears to have been overlooked by a good many engineers.

The influence of carbon particles in the oil seems to be worthy of some attention. To me it would appear that particles of carbon are worked into the surface of the metal and remain firmly embedded there. It is known that white-metal bearings can operate comfortably in an engine which has its crank-case full of relatively dirty oil, whereas, for instance, lead–bronze bearings require a very clean and well-filtered oil. I have the impression that white-metal bearings in engines have an appreciable quantity of carbon embedded in their surface. Are they really improved by free carbon in the oil? It is believed that running in with particular types of oil is of benefit in some instances. The influence of carbon appears to me to be worthy of careful consideration.

From my own point of view, an alloy containing about 0·6 per cent. of nickel would have been of great interest if included in the series. It is one of which we have had considerable experience, and perhaps one which has been generally fairly successful. I do not see the II Ni alloy in the series subjected to pounding tests by Mr. Greenwood. As the No. II seems fairly good in this respect, tests of the II Ni would appear to be worth while.

Mr. A. H. **Mundey** * (Member of Council): The causes of failure in bearings have been very thoroughly diagnosed by Mr. Macnaughtan and his coadjutors. Not only has Mr. Macnaughtan diagnosed the trouble, if not completely at any rate most suggestively, but he has also suggested remedies which are very important both to the manufacturer and to the user.

I have never been entirely happy in attributing the trouble to the hard tin–iron compound at the junction of the white metal and the liner, because, although it is agreed that that compound does exist, I have seen it withstand such extraordinarily difficult stresses without breaking that I have felt that in all probability it was made a convenient whipping boy but was in fact not guilty. I must not take up time by giving instances, but I have seen cases where it has resisted the most severe stresses without cracking.

I should like to refer to one point to which Mr. Arrowsmith directs attention. Twelve years ago, Cartland, Bissett, and I submitted a paper to the Institute which was really a review of the white metals in existence and generally used at that time. We reported a very large number of tensile tests, and we did so with a sort of apology, because it was generally said that engineers did not want to know anything about tensile tests in bearing metals.

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Do we agree with that to-day? I think that apology twelve years ago was unnecessary.

We made some mistakes, however. Metallurgists have become very much wiser in twelve years. We reported no elongation on certain of those alloys, and I should like to explain that. In order to make the results absolutely comparable, we cast the whole series of test-pieces in 1-in. bars and machined them down to 0·564 in. and tested them. We did the very worst thing for getting good results, and we obtained little, if any, elongation. We did not claim, however, for the metals qualities which they did not possess, and it is gratifying to find that those self-same alloys have been giving good service; although failing now under the very severe duty put on them in extreme cases, it should be borne in mind, and should be a comfort to the engineer, that they are perfectly serviceable for general practice, and it is only in the extreme cases of high stresses and temperatures that these enhanced properties are required.

With the addition of 1 per cent. of cadmium, and possibly nickel, I am in entire agreement. I hope that this will be pursued, because it is strongly to be recommended that the engineer should be supplied with material of higher fatigue limits.

With regard to substitutes, one thing has not been mentioned. It is possible to get substitutes for the tin-base bearing metals which would have certain high properties in general service, but there is another question which I wish the metallurgists would bear in mind. We have to consider sympathetically the man who has to make the bearing in very difficult and adverse circumstances, to run in a new bearing in difficult conditions at sea or in a field workshop behind the lines. He needs something which is easy to work, which is reliable, and which he can be sure will give him good service. With the substitutes proposed up to the present it is not easy to get good adhesion and to make a good and reliable bearing straight away.

I was very interested in what Mr. Murphy said about hammering; but I do not like to hammer a bearing. I feel that the hammered bearing which he describes has started to wear out before it is really taken into use, and that is a pity.

Mr. H. L. EVANS,* M.Sc.Tech. (Member): My interest in this field has centred in the research and development of certain cadmium-base bearing alloys.† In the earlier stages of the work I became quite familiar with the peculiar form of cracking mentioned in these papers. Fortunately, it is now less frequent, but I fully endorse the authors' view that contraction stresses are mainly responsible.

In metalling semi-cylindrical bearing shells, a measure of the degree of contraction is obtained by the resultant "pinch" across the horns of the shell. We have found with cadmium-base alloys that prolonged annealing, at a temperature where the metal presumably possesses a fair degree of viscous flow, considerably relieves the pinch and results in much greater freedom from fatigue-cracking in service. I consider that although the annealing may not entirely eliminate the stresses, it does tend to dissipate them from regions where unavoidably unequal cooling has caused them to be localized, and I think that that is of considerable importance.

I am of opinion that localized stresses are important in other ways in the production of these fatigue cracks. Contrary to Mr. Macnaughtan's findings, my experience, entirely, of course, on cadmium alloys, has shown that the location and direction of the cracks are related intimately to the structure, although incidentally I am in agreement with him that they commence at the

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† Work undertaken on behalf of Electrolytic Zinc Co. of Australasia, Ltd.

surface and not at the bond. It seems to me that fatigue stresses, in such a material with constituents of widely differing properties, must necessarily be influenced by the size, shape, and distribution of the hard constituent particles, thus giving local concentration of stress. Obviously if these particles are extremely fine the metal approximates too closely to a homogeneous material to discharge effectively its diverse functions; but, short of this state, it would appear desirable to have the hard constituent particles as small, as rounded, and as uniformly dispersed as possible.

I should like to take Mr. Macnaughtan gently to task in connection with his statement that cadmium-base bearing alloys present much greater difficulties in casting on steel or bronze liners than do tin-base alloys. This was the case to some extent in the earlier stages, but the development of suitable bonding alloys has eradicated that completely. The shear of bond test described by Stanton (reference No. 1 in Mr. Macnaughtan's paper) gives very consistent values about 6 tons/in.^{2} on our standard cadmium-base alloy metalled on S14 steel shells. National Physical Laboratory figures for this test on two test-specimens recently submitted were 6·66 and 6·51 tons/in.^{2}, respectively, which it will be agreed are much greater than may be obtained with tin-base alloys.

The question of the type of work which is necessary to produce these cracks is interesting. I have here specimens of shells which have been submitted to the Stanton rolling fatigue test carried out at the National Physical Laboratory. The test results show that both shells withstood 15 million reversals of stress at a stress of 18·9 tons/in.^{2}.* The small circular pieces were removed by trepanning after test, but in neither case could the cadmium alloy be detached from the steel disc. Incidentally, the very fine cracking which may be observed in the thin bearing metal lining does not resemble in any way the tesselated-pavement appearance which is quite typical of the fatigue-cracking. Whether there is any difference in this respect between cadmium-base alloys and tin-base alloys I cannot say, but it is at least a point of interest.

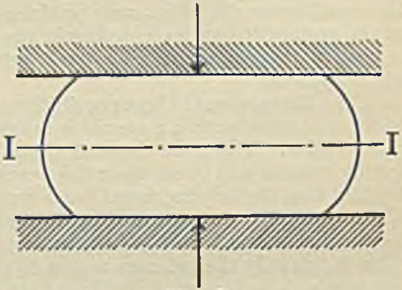

FIG. B.

Mr. R. W. Bailey,† B.Sc., Wh.Sc. (Member): I have not much experience of the kind of cracking discussed, because the bearings with which I have most to do are under fairly steady load. One or two cases have occurred, however, and Mr. Macnaughtan has shown how difficult it is to find an explanation, as, for example, when he mentions that the cracking in the case of a connecting-rod big-end bearing is directly under the rod itself, where the flexure is very small. On consideration it seemed that a possible explanation might be found for the cracking, or at least factors which contribute to it might be identified, even when compression stresses exist.

As the bearing metal is attached to a metal shell at one side and the loading is applied through a film of lubricant at the other, a state of stress exists in the white metal which is not quite what is given by the paper. For example, a short cylinder of metal when compressed deforms as shown in Fig. B. At the ends of the cylinder frictional constraint prevents the lateral

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* Range of stress on the inner surface of the steel shell.

† Research Department, Metropolitan Vickers Electrical Co., Ltd., Trafford Park, Manchester.

spread of the material which occurs towards the middle I–I. Bearing metal is under conditions approximately similar to those applying to one half of the cylinder, the plane I–I corresponding with the bearing surface. At the bearing surface the loading is applied by the pressure of the oil film with negligible lateral constraint from the film, whereas at the other side the bearing metal is attached to the shell or base metal. The freedom for lateral displacement of the bearing metal, both elastic and plastic, will be greatest at the surface, and diminish to a negligible amount where it joins the shell. It seems very likely, therefore, that the lateral pressure in the bearing metal is not constant, but that it varies radially through the thickness from possibly quite a small value at the bearing surface to a value at the shell which would be practically the same as the oil pressure. In that state of stress the surface material is under shear stress which depends on the magnitude of the oil pressure being ½ (oil-pressure–lateral pressure), and as the journal goes through its cycle the oil pressure and lateral pressure vary, causing a state of variable shear stress at the region of the bearing surface. This is repeatedly applied, and therefore the conditions exist which may produce ordinary fatigue of the bearing metal at the surface region, except that in the case of ordinary fatigue the material is usually under tension and a crack develops and spreads under the repeated stress applied.

Thus, there seems to be a possibility of a condition here which is equivalent to what obtains when a material is fatigued, although the stresses are entirely compressive. When the journal comes to rest and the bearing cools, large tensile stresses will be set up in the bearing metal during the cooling, owing to the fact that the bearing metal has a very much higher coefficient of expansion —something like twice that of steel—and it appears likely that these may give rise to actual cracks in the fatigued bearing metal. Once a crack is started, there is not only the pressure acting at the bearing surface, but also a varying pressure acts in the crack itself, so that the conditions are doubly favourable for its spread into the metal.

The explanation given appears to be a feasible one of why cracking can occur where there is a compressive stress and negligible flexure, as exists in the case of many bearings. It also indicates that if this effect is to be got rid of, a sufficient lateral stress must exist at the bearing surface. Without making any estimate of the magnitude of the lateral stresses, it is fairly obvious that as the bearing metal becomes thinner, the lateral stress at the bearing surface becomes larger. A thin lining or film of bearing metal under oil pressure will have lateral stresses in the metal which are not very far from uniform and of the order of magnitude of the oil pressure; the shear stress in this case would disappear and the fatiguing action at the surface of the metal would therefore not exist.

It is necessary to question whether the varying load on a bearing being associated with a varying rate of heat generation might have some bearing on fatigue fractures. The oil film is continuously delivering energy, but at a varying rate, and therefore at the surface of the metal there may be variations of temperature very much larger than might be imagined. An estimate of that effect, however, shows the variation of temperature of the metal to be less than 1° C., so that this factor is of no consequence.

Referring to the paper by Kenneford and O'Neill, the subject of the flow or creep of bearing metals is of considerable importance from a practical point of view in the case of high operating temperatures, and the results of their indentation tests are of interest, particularly if they can be correlated with creep as it is more commonly understood. The cone test lends itself very well for this purpose, because it may be taken that with varying depth of penetration the stress distribution in the metal may be regarded as similar.

The results of tensile creep tests on steels, particularly when the double logarithmic method of plotting is employed, as adopted by Norton in the U.S.A., show that at the same temperature the creep rate is proportional to $(\text{stress})^n$, or, if $r =$ creep rate, $f =$ tensile stress, and a and $n =$ constants,

$$r = af^n \quad . \quad . \quad . \quad (1)$$

It is extremely probable that such a law may be applied generally to metals with constants a and n appropriate to a specific case. It is necessary to bear in mind that creep is due to shear stress, and in a tensile test, of course, the shear stresses will be directly proportional to the stress f. In the case of the cone indentation test, under a constant load the shear stresses will be inversely proportional to the area of the base circle of the conical indentation.

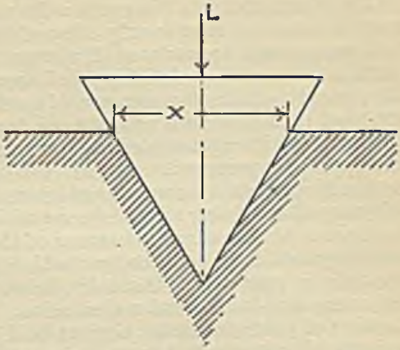

FIG. C.

If $t =$ time, and $x =$ diameter of impression, it will be seen that in applying equation (1), $r \propto \frac{dx}{dt}$, $f \propto \frac{1}{x^2}$, and therefore

$$\frac{dx}{dt} = \frac{ab}{x^{2n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

where a relates to the material as in equation (1) and b is a constant which depends on the form of the cone and the stress distribution in the material, which may be taken to be the same, for a given apparatus. Integrating (2) gives

$$\frac{x^{2n+1}}{2n+1} = abt$$

$$x = [(2n + 1)\,ab]^{\frac{1}{2n+1}}\, t^{\frac{1}{2n+1}} \quad . \quad . \quad . \quad (3).$$

Evidently the relation (3) corresponds with the expression $d = ct^s$ used by the authors. It follows that:

$$s = \frac{1}{2n+1} \text{ or } n = \frac{1-s}{2s} \quad . \quad . \quad . \quad . \quad (4),$$

and $[(2n + 1)ab]^{\frac{1}{2n+1}} = c$, from which it will be found that:

$$a \propto \frac{c^{2n+1}}{2n+1} \text{ or } a \propto sc^{\frac{1}{s}} \quad . \quad . \quad . \quad . \quad . \quad (5).$$

It is of interest to apply relation (4) to the authors' tests. Common values of s appear to be 0·03–0·07; these give values of n of 16·1–6·7, respectively. Tensile creep tests on carbon and low alloy steels give values of n of 5–8, and in austenitic steels it has higher values, of the order of 10–15. There is thus interesting correspondence in the order of magnitude of n of creep tests on steel and those deduced from values of s obtained in indentation tests on bearing metals.

Irrespective of values, it may be taken that the existence of the relation $d = ct^s$ in indentation tests indicates the corresponding existence of the relation (1) for tensile creep tests. Research should enable the results of one test to be interpreted quantitatively in terms of the other.

Mr. Macnaughtan (*in reply*): In view of the short time available, it is possible for me to refer to only a few of the points raised in the discussion.

I very much appreciated Professor Thompson's remarks. It is clear, I think, in view of the relatively small amount of basic knowledge that is available, in spite of the vast amount of testing of bearings that has been carried out, that it is important to carry out fundamental investigations. It was in the hope that it might contribute towards stimulating such investigations that this paper was prepared.

Mr. Murphy raised a number of interesting points, one of the chief being the difficulty of imagining that white metal of higher strength would be better in the light of the excellent behaviour of the alloy containing about 4 per cent. antimony and 4 per cent. copper, which is a material that has comparatively low fatigue properties. Actually, however, this alloy fails by cracking in the severe conditions under discussion. Further, although there is little in the way of published data, a great deal of work has been carried out in the research laboratories in America, where it has been found, in special tests which simulate the conditions in service that produce failure by cracking, that this alloy is not so satisfactory as alloys in which the antimony content is increased, and which have higher fatigue-resistance, as is shown in the paper.

Mr. Murphy also commented on the brittle layer at the bond. The manner in which, in many cases, cracks, after proceeding downwards from the surface of the metal, turn off and proceed laterally well above the tin-iron compound, makes one wonder whether the presence of this compound does not actually strengthen the bond. In any case, the fact that in a large number of instances the cracks spread laterally well above the bond, rules out the explanation that failure is primarily due to the brittleness of the layer at the bond.

Mr. Cartland referred to the difficulty of understanding point (3) in my paper in connection with tension stresses in the metal. I tried to think of every way in which tension stresses could be produced, and this appeared to be one of them. In view of the large amount of testing by indentation, it is surprising that there is so little precise information concerning what happens in the metal when, for example, it is indented by a Brinell ball. I am inclined to think that there is bound to be tension around the indented area.

The chief point with regard to an alternative explanation is that raised by Professor Hanson, who referred to creep stresses. One of the difficulties in the way of such an explanation is the fact that these failures are liable to occur in a comparatively short time. The number of cycles of stress to which bearings in an internal combustion engine may be subjected is rather surprising. With a speed of 3000 r.p.m. there will be 180,000 pulsations of pressure in an hour and nearly 2 million in 10 hrs. The fact that quite a number of these failures occur in a few hours is, therefore, not inconsistent with the view that the cracking is due to fatigue, whereas the time is inadequate for creep phenomena to become of predominant importance.

CORRESPONDENCE.

Mr. H. N. Bassett * (Corresponding Member to the Council for Egypt): Mr. Macnaughtan's paper, although of a general character, is very interesting, and from personal experience I can confirm much of what the author says in relation to cracking of white-metal linings, not in connection with compression ignition engines, however, but in the axle-box brasses of railway-wagon stock.

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The loading is of the order of 250–350 lb./in.^{2} projected area, but as the actual bearing surface is not the whole of the projected area of the bearing, but considerably less in many cases, the actual loading is often of the order of 400–500 lb./in.^{2}. The metal is of the composition tin 50, lead 38, antimony 10, and copper 2 per cent. Over a period of several years I have examined quite a large number of brasses in which cracking has taken place. In most cases the metal had spread to some extent under the load (and the effect of heating), and the cracks were opened in a few instances $\frac{1}{16}$ in. or more. In some brasses small sections of white metal had fallen out completely, and in many cases the adhesion was destroyed entirely over a considerable area of the brass. I formed the opinion that the cracks began on the wearing surface and progressed downwards through the metal, which is normally upwards of $\frac{3}{8}$ in. thick, but which in the brasses examined was rarely more than $\frac{3}{16}$ in. in thickness, even when no spreading had taken place.

I have not seen any instances of a crack turning sideways, as suggested by Mr. Macnaughtan. I agree that the cracks are due to fatigue arising out of wide variation in normal pressure, which in the case of wagon stock sometimes comes about through gross overloading, and inequalities in the track.

From the point of view of the railway engineer, I am not sure that failure by pounding is not more important than failure by cracking, for in the case of connecting- and coupling-rod ends, for instance, failure by pounding means that an exaggerated clearance is developed on the pin, which causes knocking and sometimes fracture of the brasses. The metal may spread to such an extent as to close the oil hole more or less completely, and entirely to obliterate the oil grooves, leading to heating and failure of the engine. On the "Great Bear," the late Mr. Churchward's Pacific locomotive, the white-metal facing of the side of the axle-boxes in the bogie near to the wheel boss on either side had to be substituted by phosphor-bronze because the white metal squeezed or pounded out. There was no question of failure by cracking, but it was due purely and simply to pounding or squeezing.

Mr. Greenwood, who has contributed an excellent paper on pounding tests, would be interested to see the paper by Lynch * on the same subject, which I believe to be the earliest work recorded on resistance of white metals to pounding. It is interesting to note that Mr. Greenwood found that when adhesion of the white metal to the brass block was good, the degree of deformation was lower than when the contrary was the case. This confirms my own deductions as to the prime reason for the spreading of white metal in carriage and wagon brasses, which is inadequate tinning before metalling. I am glad to have support from an entirely independent and unrelated source.

The effect of cadmium on high-tin base metals is obviously very different from its effect on lead-base metals, especially in its suppression of the cuboids and the increase which takes place in the acicular constituent. It would be useful if some data could be given on the wear-resisting properties of these cadmium-bearing high-tin metals, because it has been found generally that too fine a structure in a white metal of the usual type does not give good results. The addition of cadmium refines the structure very much, and suppresses the cuboids to a considerable degree, on which it is conventional to say that the load is carried, the acicular constituent merely serving as a sort of felt to prevent segregation of the cuboids during cooling. One would expect, therefore, to find that a structure from which the cuboids were largely absent would be less satisfactory than one of the usual kind.

The effect is also different in relation to the physical properties, for according to Ackermann † the lead–antimony–cadmium, and the lead–tin–

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* *Proc. Amer. Soc. Test. Mat.*, 1913, **13**, 699.

† *Metallwirtschaft*, 1931, **10**, 593.

antimony–cadmium alloys have lower elastic limits than the corresponding alloys without cadmium. Table XVI in Mr. Arrowsmith's paper shows that the addition of 1 per cent. of cadmium increases the yield-point of the tin-base alloys considerably.

I should like to add how glad I am to see these papers. At Zürich in 1931 I asked whether some papers on white metals could not be obtained; these are the first to appear, and I trust that they are the forerunners of a series.

Dr. R. Genders,* M.B.E. (Member): The subject of bearings has hitherto lacked analytical study, and Mr. Macnaughtan's paper—aptly somewhat speculative—will greatly assist future work by directing attention to a number of important features. From a consideration of the stresses imposed on a working bearing, it would appear unlikely that tensile stresses of appreciable magnitude could be produced directly in the white-metal layer. Such stresses could undoubtedly result from the conditions described, as annular tensions, but an appreciable amount of plastic flow by compression must be assumed. Except during the initial running-in of a bearing the amount of plastic flow must be minute, since even on partial seizure it is not necessarily extensive. Production of tension in the bearing surface is thus probably confined to other causes, such as elastic distortion of the liner or thermal stresses due to the different expansibilities of bearing and liner. The importance of the latter factor, which is thought to be predominant, is clearly emphasized by the author. In this connection it would be of interest to know what would be the result of the use of an aluminium alloy liner, the thermal expansibility of aluminium being near that of tin.

The manner in which the network of cracks is formed in the bearing has so far been discussed only speculatively, and the hypothesis advanced by the author does not appear to be supported by any evidence that the cracks occur successively. If the mechanism suggested were responsible, it would be expected to lead to a characteristic pattern of cracks, different from the random network actually found. It is suggested that the appearance of cracked bearings may rather imply the simultaneous initiation of cracking at a large number of points. This would be consistent with the effect of thermal stresses, and the deepening of the cracks would follow repeated alternations of temperature in conjunction with compressive working stresses.

In considering bearings from the metallurgical point of view, it is probably important to bear in mind that the properties of a thin layer of white metal on a relatively hard supporting mass may be different from those measured on the metal as a thick specimen. It is well known, for example, that, in the testing of thin strip metals, the results of dynamic hardness tests, and to some extent those of static tests, are much influenced by the hardness of the support. Consequently a difference in the hardness of two bearing metals may not be reflected in a difference in working behaviour; and it is interesting to note that reference has been made to the working superiority of a relatively soft bearing alloy by Mr. Murphy in the discussion of this paper. It is thus possible that an approximate relative guide to the behaviour of a bearing metal in service might be most readily obtained by the study of thin specimens supported on harder materials.

Mr. H. H. A. Greer,† J.P. (Member of Council): My long experience of buying metals which have been in use for many years and which have white metal on their bearings, makes me conclude that a bearing made of bronze or manganese–brass, which is first tinned over, and then has the white metal run on to the tinning, shows splendid results, and is free from cracking after

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* Research Department, Woolwich.

† Glasgow.

many years of wear. I consider that the combination of the bronze or brass and the white metal is far more efficient than the steel bearing with the white metal on the top of it. It would be interesting if the Copper Development Association would collaborate with the Tin Research and Development Council on this important matter.

I am not satisfied that the entire absence of lead in some of our white metals is altogether advisable. Many of the old railway white metals which were in axle-boxes contained 3–4 per cent. of lead, and this, I believe, served a useful purpose, and did not soften the bearings to any great extent. The trouble about lead is that it is so low priced that producers who aim at cheapness—both in white metal and in bronzes—are apt to put it in as an adulterant or cheapener; but in certain cases it serves a very useful purpose if kept within its proper percentages.

Mr. E. J. **GROOM** *: Concerning the possible adverse effects of a copper content above 4·0 per cent. my experience with white-metal shells of approximately 1·0 mm. thickness cast direct on to steel, and analyzing approximately 7 per cent. antimony and 8 per cent. copper, leads me to disagree with the findings of Boegehold and Johnson, and Smart. The bearings in question are those on the big end of the connecting rod of a high-duty automobile engine, and run at an average working temperature of 85° C. A white metal of this composition has been used for this purpose for some years, and has proved very satisfactory. I shall be very interested to see the results of an investigation of the problem by Mr. Macnaughtan and his colleagues.

With regard to the addition of other elements to tin–copper–antimony alloys, do these additions increase the sensitivity of the alloy to variations of casting temperature, and so on, and what is the effect of continual and prolonged remelting such as occurs in practice?

Mr. W. E. **HOARE**,† B.Sc. (Member): The few remarks I have to make are stimulated by the oral discussion rather than by the substance of the papers themselves.

I was particularly interested in the brittle layer of iron–tin alloy, which was mentioned by three of the speakers. In normal practice (tinning and casting temperatures below 496° C.) the alloy consists of $FeSn_2$, usually in the form of a narrow fringe of small crystallites. In the past, this small quantity of alloy has covered a multitude of sins of none of which, in my opinion, it was guilty.

I have had some experience of the manufacture of white metalled big-end and main crankshaft bearings for high-speed internal combustion engines, in a works where the greatest care was taken over the initial tinning of the shell. In some cases as long as 30 minutes would be devoted to the fluxing and rabbling operations, naturally resulting in a relatively heavy alloy layer; heavier, in fact, than I have seen in any other practical case. It is, I think, significant that bearings failures were practically non-existent on these engines; and, apart from adverse running conditions, those which did come to our notice were due to absence of the alloy coating at the local point of failure, and not due to an increase of amount. Figs. 5 and 6 of Mr. Macnaughtan's paper indicate quite clearly that the alloy layer is quite innocent of the production of tesselated fatigue-cracking.

In the light of Professor Hanson's remarks, and as a general consideration, I would suggest that the behaviour of a Babbitted footstep bearing would be worthy of investigation, inasmuch as fatiguing forces would be absent, whilst

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steady loads would be applied to procure exaggerated creep effects. I understand that an investigation along these lines is in progress in America.*

Dr. W. D. Jones,† M.Eng. (Member): The work of Drs. Kenneford and O'Neill would appear to show that the copper–tin needles in a tin-base bearing alloy are harder than the antimony–tin cubes; I have always imagined the opposite to be the case. When such bearing metals are examined after considerable use, it is quite common to find antimony–tin compounds broken or even completely chipped out, whereas copper–tin needles are almost always unbroken.

G. A. Nelson ‡ states that "CuSn needles are very ductile, as shown by their ability to be bent backwards and forwards several times before breaking. They are easily scratched by the needle. The SbSn cubes are the hardest of all constituents, being very brittle and shattering with pressure by the needle."

O. Bauer and O. Vollenbruck § show that the Brinell hardness of a copper–tin alloy of approximately the CuSn composition is of the same order as the hardness of copper. H. Heape ‖ apparently reaches a similar conclusion.

Mr. H. W. Russell ¶: This paper is particularly valuable because of its ability to stimulate further thought and inquiry into the causes and prevention of bearing failures. Experience indicates that cracks are the primary cause of failure. Poor adhesion between the white metal and the liner or bearing back is a contributing cause, as it probably permits cracks to form more readily, and will undoubtedly hasten complete failure after cracks start to form.

Among the causes that tend to produce the tension which seems necessary to form cracks, the thermal stresses set up during cooling are mentioned. It is possible that the practice, at one time common, of peening the white metal with a hammer served to relieve or even reverse these stresses. Thin steel-backed bearings, which are made by casting the white metal on a flat sheet which is subsequently bent to form a bearing half, should be relatively free from stresses due to contraction in cooling.

Stresses resulting from thermal changes during service will consist not only of those that are due to a difference between the coefficient of expansion of the white metal and the liner, but also of stresses in which the liner plays a negligible part. These stresses are due to non-uniform heating of the white bearing metal. The temperature of a given portion of the white metal may, in certain conditions, be in unstable equilibrium, an increase in temperature resulting in changes which increase the rate of heating, and hence magnify the increase in temperature; thus a temporary or permanent hot spot may be formed. As operating conditions vary, this spot may appear and disappear repeatedly.

To illustrate how such a local hot spot may give rise to tensile stress, consider, for simplicity, instead of a bearing, a flat sheet of white metal alone, all originally at the same temperature: Now let heat be applied to a circular portion of the surface, rapidly heating a disc or short cylinder of the metal. The expansion of the heated disc will be restricted by the outer cool metal, which, as a rough approximation, may be considered rigid. If the strain in the disc is more than it can absorb elastically, flow will occur, resulting in an increased thickness of the disc.

Now let the temperature of the disc and the outer metal become the same. Then, either because of lateral contraction of the disc or expansion of the

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* J. R. Conelly, *Amer. Soc. Mech. Eng. Advance Copy*, **1933**,

† Assistant Lecturer in Metallurgy, Sir John Cass Technical Institute, London.

‡ *Metals and Alloys*, 1932, **3**, 168–170.

§ *Z. Metallkunde*, 1924, **16**, 426–429.

‖ *J. Inst. Metals*, 1923, **29**, 467.

¶ Battelle Memorial Institute, Columbus, Ohio, U.S.A.

"hole" tensile stresses will be set up, tending to open cracks the volume of which will be roughly equal to the volume represented by the previous increase in thickness of the disc. This mechanism will form a network of cracks which start from the surface, where the temperature was the highest. Tensile stresses due to other causes will, of course, contribute to the formation and propagation of these cracks.

Experience with large thick slabs of copper has demonstrated that intense and rapid local heating will cause cracks. Depending on the shape of the slab and the shape of the portion heated, a network of small cracks or a single wide crack can be formed, in spite of the high ductility of the copper. A white bearing metal that has a high coefficient of expansion and which is unable to withstand large strains may be expected to crack under less intense local heating.

Dr. **Carl E. Swartz** * and Dr. **Albert J. Phillips** † (Member): Mr. Macnaughtan is to be congratulated on his discussion of the requirements of a bearing metal for severe service.

The statement is made (p. 36) regarding cadmium bearing alloys: ". . . but at the present time their general merits as bearing materials have not been evaluated, and they present much greater difficulties in casting on steel or bronze liners than in the case of the tin-base alloys." For most of the cadmium-base alloys suggested, this statement is true. During the past year, however, there have been numerous tests conducted in the United States by the makers of automobile, aeroplane, and Diesel motors in which the new cadmium-base bearing alloy, marketed under the trade name of Asarcoloy No. 7, has been used. This bearing metal ‡ which is an alloy of approximately 1·35 per cent. nickel in cadmium, forms a strong chemical bond easily and directly with the various steels used for backing the liners. The bearings have shown themselves to be satisfactory for the duties required of a bearing in the modern, high-speed, high-compression motor operating at elevated or normal temperatures. The alloy has been adopted by several manufacturers for duty where other types of bearings have failed to stand up.

In addition to the various requirements of a bearing alloy mentioned by the author, there is one property of white-metal bearings which in some cases may be considered a requirement. That is, the "soft matrix-hard inclusion" type of microstructure. With this type of microstructure the supporting constituents are the discontinuous phase. Consequently, with the modern type of pressure lubrication in which the bearing is being continuously flushed with oil, solid particles are more easily washed from the bearing surface than where the reverse type of structure is found. In the latter type solid particles lodge in the soft phase, which is discontinuous, acting as a series of pockets. If these particles are abrasive, as hard carbon, silica, &c., often are, an excellent lap or hone is made which wears down the journal.

In addition to failures due to fatigue-cracking, it now appears from Sparrow's work § that many failures attributed to fatigue are caused by the momentary increase in the tangential force (shear ?) between the journal and the bearing surface when and where the oil film fails to support the load. If

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‡ Properties discussed by Swartz and Phillips: *Proc. Amer. Soc. Test. Mat.*, 1933, 33, (II), 416–425; also *Amer. Inst. Min. Met. Eng. Preprint*, 1933 (Contribution No. 55).

§ S. W. Sparrow, "Recent Developments in Main and Connecting Rod Bearings," *J. Soc. Automotive Eng.*, 1934, 35, 229–237.

this type of failure is shown to be important, a new reason for a stronger more ductile bearing alloy is at once apparent.

Mr. H. STEVENS,* B.Sc. (Member): Mr. Macnaughtan has based much of his argument on the fundamental assumption that bearing metals are subjected to fatigue stresses which are mainly responsible for the failure of bearings. Whilst the assumption may possibly be justified, it is doubtful whether there is, in the present state of knowledge, sufficient evidence to reach conclusions so drastic as the author's. The distribution of stresses in a high-speed bearing is exceedingly complicated, and, possibly, the most likely type of fatigue stress is a shear stress cycle, caused by fluctuations in speed, of which the maximum and minimum values would be positive.

In a well-made bearing carrying a high-speed shaft possibly the pressure of the shaft on the white metal would be one of the greatest stresses, and this, acting in one direction, combined with the shearing stresses caused by the revolution of the shaft, acting in another direction, would be applied throughout the working life of the bearing, and may therefore be an important cause of failure.

It is possible that cracks formed at the surface between the bearing metal and shaft would have oil forced into them, and this may act as a medium for the hydraulic transmission of the pressure of the shaft to the walls of the crack. This pressure of the oil on the walls of the crack would tend to make the latter still larger, and, since it may act during the working life between the start of the crack and final destruction of the bearing, the walls of the crack may be subjected to a continuous pressure forcing them further apart. In this case the limiting creep stress at the working temperature would have to be taken into account.

It appears, therefore, that while there may be much justification for the use of bearing metals having comparatively high fatigue limits, at the same time, the limiting creep stress should be taken into consideration and, consequently, the most useful metal may be one having a good combination of fatigue limit and limiting creep stress.

Mr. MACNAUGHTAN (*in reply*): A notable feature of the discussion is the recognition by several speakers, including Mr. Mundey, of the excellent service given by white metal bearings, even at high temperatures and under severe loads. It is only in certain extreme cases, and particularly under the special conditions of loading that arise in big-end bearings, that failure by cracking demands further immediate investigation.

It is clear that investigation has to be concentrated on the cracks that form at or near the lubricated surface. These cracks spread through the thickness of the white metal, and the subsequent peeling of the tesselations, important as it may be as the immediate cause of failure, is no more than the consequence of the cracking.

The discussion has naturally pursued the query, raised most definitely by Professor Hanson, as to whether these cracks arise from fatigue due to repeated stress or from creep caused by the long-continued action of steady stress. The rapid incidence of the trouble in severe cases and its complete absence after long periods in less severe cases may point to either of these two causes; but the fact that the loads on big-end bearings pulsate seems definitely to point to fatigue.

That flexure may be important, at least as a contributory cause of the cracking, has been brought out clearly by several speakers and notably by Mr. Sutton. It can scarcely be doubted that a rigid support for the white

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metal contributes in high degree to success, but, on the other hand, Mr. Cartland and others have confirmed that the "crazy pavement" type of fracture occurs where flexure must approach the minimum, and this has been indicated previously by Ricardo. The cracking occurs where the normal pressure is most severe, immediately below the connecting rod.

Much of the discussion has turned on the possible mechanism of this peculiar type of cracking, and interesting contributions have been made by different speakers. Whereas I have expressed the view that the cracks arise from wide variation of normal pressure coupled with longitudinal and circumferential tensions, Mr. R. W. Bailey puts forward an interesting argument for an alternative theory that failure is due to variation of shear stress applied tangentially. The action of such shear stresses is illustrated not only in Fig. 13 but also in Fig. 3 of my paper; and consideration of these diagrams seems to indicate that such shear stresses would act rather around the zone of maximum normal pressure and not immediately within it. On this account particularly, the action of such shear stresses appears to be inadequate to explain the tesselation, which shows no tendency to distribute itself in a ring. The discussion, in my opinion, does not appear to have provided any satisfactory alternative for the view that cracking is directly due to variation of radial pressure associated, in all probability, with longitudinal and circumferential tension. The view that tension is essential to the process is supported by different speakers, who have endorsed also the idea that tension may arise from thermal contraction. The examples they have cited which show how tension may be produced in different circumstances are of considerable interest and value in this connection.

Although radial pressure varies during each application of load, the circumferential and longitudinal tensions probably act steadily or vary less frequently, and it follows that the action in cracking may be a combination of fatigue and creep. Alternatively, it has been suggested that the white metal may be heated and cooled by the oil that flows over its surface—which oil certainly must vary in temperature during each loading. It is interesting to learn from Mr. Bailey that an estimate of the range of variation of temperature caused by this effect is only of the order of 1° C., indicating that the action is of only minor importance.

The observations made by Mr. Murphy and others on the effects of hammering the white metal after casting are of special interest, indicating that contraction and tension may arise from causes other than cooling, and that compressive stresses may be produced—to neutralize tension—by bending flat strips to form bearings. It is clear that a field for further investigation lies in this direction and that work of considerable practical value may result.

Alloys with bases other than tin have been mentioned by several speakers and by authors of other papers on this subject: copper–lead by Mr Murphy, and cadmium alloys by Mr. Evans, and by Herschman and Basil. The disadvantages of such substitutes, mentioned by Mr. Mundey, are recognized also by myself; but at the present time, and for the severe conditions of loading in question, these are probably the only substitutes that merit consideration.

As regards copper–lead, Mr. Sutton has pointed out that greater care must be exercised when this material is used, to remove from the lubricating oil any gritty particles that may accumulate; and Herschman and Basil indicate the reason for this: such particles tend to become embedded in the soft constituent which, in this metal, occupies only a small proportion of the exposed surface as compared with the tin- or cadmium-base metals.

That the softer constituent in a bearing metal may serve as a trap for particles of foreign matter in the lubricating oil is, in my opinion, only the least of its advantages. A more important characteristic is the capacity for self-annealing at working temperatures, which capacity counteracts the hardening produced by the cold-work caused by severe pulsating loads. The absence of this capacity in copper-base alloys inevitably carries with it a tendency to harden under severe conditions of loading, and this tends to scoring and eventually to seizure.

As regards cadmium alloys Herschman and Basil, and Mr. Evans, have indicated that improvements have been made to secure better adhesion between the alloy and the liner; but it is believed that those who have experience will endorse my statement that cadmium alloys present greater difficulties in casting on steel or bronze liners. Moreover, it does not yet appear that there is sufficient published data available to modify my statement that the general merits of these alloys as bearing metals have not yet been evaluated.

There can be little doubt that if tin-base alloys can be improved to resist cracking under extreme conditions, their all-round merits as bearing metals will ensure their continued use in severe as well as general service. In the direction of obtaining such an improvement, a number of valuable observations have been made in the discussion.

Mr. Murphy has emphasized the general experience that the ductile tin-base alloy containing 4 per cent. antimony with 4 per cent. copper has given excellent results in spite of its low tensile strength; but the fact remains that under the severe conditions of service now under consideration this alloy admittedly fails by cracking. If the conclusion that cracking is due to fatigue is accepted as valid, the use of a stronger alloy is indicated; and the query then arises, how far ductility can be sacrificed for higher strength. It is of interest in this connection that Mr. Mundey has obtained satisfactory service, as bearing metals, from tin alloys which in the tensile test appeared lacking in ductility. It is probable that this is due to the capacity for self-annealing, which safeguards the metal under practical conditions of service, although it cannot do so during the rapid course of the tensile test. The capacity of tin-base alloys for self-annealing is recognized by different speakers; thus Mr. Chadwick reports that he found softening to occur on cold-working; and Greenwood's results—which were obtained in circumstances more directly comparable with those in bearings—afford evidence that cold-work caused no hardening.

In respect of the development of stronger tin-base alloys, I have given some information on the effect at ordinary temperature of increasing the antimony content while retaining a constant and relatively low copper content. Mr. Groom has mentioned beneficial effects obtained by increasing the copper to 8 per cent.; but these were obtained under conditions that appear only moderately severe, the temperature reached being only 85° C., whereas values up to at least 120° C. are involved among the conditions now under consideration. The influence of copper on the fatigue properties of tin–antimony alloys certainly deserves quantitative investigation; but as a wide variety of such alloys have now been found unsatisfactory in practical service under extreme conditions, a study of tin-base alloys containing other elements, such as cadmium, is perhaps of more immediate promise.

On exploratory tests, likely to be serviceable in such investigations, a number of interesting and valuable comments have been made in the discussion. Whilst it is true, as Professor Hanson has indicated, that short-time tensile or Brinell tests may afford erroneous impressions of creep-resistance, it is believed that such tests may be of value as a guide to fatigue properties: and this view is well supported by results already obtained and compared.

Dr. Genders pointed out that the properties of a thin layer of white metal on a relatively hard supporting mass may differ widely from those measured in test-pieces composed wholly of the white metal under consideration, and this tallies with the view which I expressed that more attention has hitherto been directed to the metallurgy of white metal than to the mechanics of the combination of white metal and liner.

As regards endurance tests, it would appear desirable to obtain data for test-pieces of the simplest type, composed wholly of white metal, but the final test, of course, must necessarily be carried out in an engine, with the white metal and liner subjected to actual working conditions. Between these two extreme types of fatigue test, a selection of intermediates may prove effectively serviceable. In particular, a method of testing thin layers cast on shells appears very desirable, but a satisfactory test of this character has yet to be evolved, although some progress has been made. In the Stanton machine for testing white metal coatings on liners, the essential feature is the simulation of flexure; but, as has been pointed out already, the fundamental requirement is probably the simulation of pulsating pressure. Such a machine would be of value also for testing different materials for liners, the desirability of which investigation, indicated by myself, has received favourable comment from Mr. Cartland, Dr. Genders, and Mr. Greer. The "dummy-engine" type of testing machine developed by the Research Establishment of the Institution of Automobile Engineers, affords a reasonably close approximation to severe conditions of loading in an actual engine; and it is interesting to learn from Mr. Cartland that already bearings coated with the alloy containing cadmium, which I described, are now being tested in actual engines.

Dr. Russell's description of the possibility of cracking being caused by repeated local heating in service, followed by cooling and contraction of the bearing metal, is of considerable interest. If it be the case that slight irregularities of surface result in a thickening of the metal by local heating, and that this thickening increases until the resultant local pressure disperses the plastic metal which subsequently cools and contracts, we must regard the coating of white metal under severe conditions of loading as continually in a state of flux. It may be remarked that the higher range of local variation of temperature contemplated as arising under these conditions is not necessarily incompatible with the smaller range of less than 1° C. estimated by Mr. Bailey on another basis of calculation. If the variations of temperature and stress contemplated by Dr. Russell prove on further investigation to be of large magnitude, the practical importance of plasticity in bearing metals will be more comprehensible: local expansions in a relatively hard non-plastic material in which foreign matter may be embedded in pools of a softer constituent would naturally tend to score the steel journal and, in extreme cases, would lead to further expansion causing seizure.

Dr. Genders commented on the mechanism of the formation of the network of cracks; and I agree that the appearance of the tesselated surface supports the view that cracks have started more or less simultaneously at a large number of points. To me, it appears that the opening of any one crack must necessarily relieve the tension in the surrounding metal, to a distance that is probably proportional to the thickness of the white metal, so that the linear pitch of the tesselations should depend on the thickness of the white metal. Mr. Stevens suggests that oil will be forced in and out of the cracks, tending to accelerate the action; and I agree that this pulsing action is likely to be important after the cracks have developed far enough, and particularly when the tesselations are peeling off the liner; but the initial formation of the cracks must be independent of this action of the oil.

Two features of the discussion, to which so many have contributed, I appreciate in particular: the many suggestions regarding the cause and elimination of cracking under extreme conditions, and the clear indications of the qualities that should be preserved in tin-base bearing metals when these are further improved to overcome cracking.

Messrs. KENNEFORD and O'NEILL (*in reply*): Messrs. Chadwick, Bailey, and W. D. Jones referred to certain points of paper Part I. We are grateful to Mr. Bailey for his most interesting remarks on the correlation of tensile creep tests and cone indenter flow tests. One aim which we had before us in this work was to investigate some single simple test which would evaluate most of the static mechanical properties of soft bearing metals. To this end the cone indenter served the purpose of giving both hardness and flow (S) results, whilst our development of the Mallock test provides ductility values in addition. Now Mr. Bailey takes the required step forward and proposes a quantitative relation between the indenter flow tests and tensile creep tests. The figures which he quotes for steels give support to the expressions which he has developed, and we believe that the latter will also be valid for soft alloys. This belief is based on an examination of the few figures at present available for the lead–tin eutectic.

Results of tensile creep tests (at constant stress on the cross-section during test) upon this alloy were recently published by Pearson.* In discussing his work both Fell and Cook demonstrated that there was a logarithmic relation between creep rate (r) and deforming stress (f). Such a relation, of course, corresponds with the Norton expression for steels mentioned by Mr. Bailey. If we take Fig. D of Dr. Cook's discussion, the slope of the logarithmic graph $r = af^n$ gives a value of $n = 2{\cdot}8$ for the extruded eutectic aged 7 days. Then according to Mr. Bailey:

$$S = \frac{1}{2n + 1} = 0{\cdot}152.$$

Pearson did not perform any identation tests, but Hargreaves reports for ball tests ($L/D^2 = 1$) on lead–tin eutectic, cold-worked 75 per cent. reduction and aged 4 days, that $S = 0{\cdot}155$. This appears to be a promising confirmation of Mr. Bailey's expression as applied to soft alloys.

We do not believe that Mr. Chadwick has demonstrated "the advantage of direct creep measurement over indirect indentation tests." In the example which he gives, the deforming stress in the creep test would enter into the comparison, and furthermore we would refer him to Mr. Bailey's communication above. We consider that it *is* proper to apply the term "creep" to any amount of deformation at constant stress, provided that the increase of strain is simply a function of time; and we did *not* suggest that limiting creep stress might be estimated from Meyer graphs.

It is an interesting point as to whether the tests would have been more representative of practical conditions had they been performed on cold-worked alloys. We did not think that they would, for in the absence of hammer-dressing (which is generally condemned) the main body of the white metal is probably not severely deformed. Actually, we compromised by taking the cast specimens and applying a vigorous surface preparation on emery (as reported on p. 55). Tin alloys are sensitive to such a preparation for a reasonable depth below the surface.

It is, of course, well known that the worked soft alloys creep much more than the cast, and that scleroscope tests give different indications to static ball tests. As regards our results on alloy No. 1 cold-rolled 50 per cent. R.T. compared with Mr. Chadwick's, even if we assume that his casting conditions exactly duplicate our own, we do not consider that the differences are very important. It is true that the $\log t/\log d$ graphs are not very straight on the freshly worked alloys, as ageing changes are actually in progress during the long-time indentations. For this reason the particular S value reported in Table IV is given as 0·175 ±. No tests were made on Alloy II as it cracked badly on cold-rolling.

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* *J. Inst. Metals*, 1934, **54**, 111.

As regards Dr. Jones's point we have remarked on our difficulty in obtaining satisfactory scratch results with the copper–tin needle constituent. We were aware of results already published, and at one stage of the work were inclined to believe that the needles were softer than the cuboids. By increasing the test load, however, to 0·165 kg., we obtained more clear-cut scratches and based our results on them. The copper–tin needles in our alloy definitely could *not* be bent backwards and forwards several times without breaking.

Mr. Greenwood (*in reply*): I am much interested in Mr. Bassett's findings regarding the low resistance to pounding of white metal liners in brass axle boxes where the tinning was imperfect. This is completely consistent with the results which I obtained. I also thank Mr. Bassett for directing my attention to the paper by Lynch, of which I had not previously been aware.

In connection with the wear-resisting properties of high-tin alloys which contain a small amount of cadmium, I have carried out, since the publication of the paper, a certain amount of work which tends to show, though confirmation of this is still required, that the addition of 1 per cent. of cadmium to alloy No. II definitely increases the resistance to wear.

Mr. Sutton is correct in his opinion that the backing to the bearing was very rigid and strong.

Pounding tests on alloy No. II Ni recently carried out yielded results which are similar to those obtained from alloy No. II. So far as the resistance to pounding is concerned, therefore, No. II Ni appears to be definitely inferior to No. II Cd.

SOME PROPERTIES OF TIN CONTAINING SMALL AMOUNTS OF SILVER, IRON, NICKEL, OR COPPER.* 677

By Professor D. HANSON, D.Sc.,† Vice-President, E. J. SANDFORD, B.Sc.,‡ Member, and H. STEVENS, M.Sc.,‡ Member.

Synopsis.

The tin-rich ends of the silver–tin, nickel–tin, and copper–tin equilibrium diagrams have been investigated. With the first, the eutectic occurs at 3·5 per cent. of silver, at 221·3° C.; with the second, at 0·18 per cent. of nickel at a temperature which does not vary appreciably from the melting point of pure tin; with the last, between 0·70 and 0·75 per cent. of copper at 226·9° C. The solid solubility of silver in tin is shown to be approximately 0·02 per cent. at room temperature, increasing to 0·06 per cent. at 210° C. The solid solubility of nickel is less than 0·005 per cent., and that of copper less than 0·01 per cent. at 220° C.

The method of making additions to tin is discussed, and it is shown that no particular difficulties are met with in the case of silver, iron, copper, and nickel.

The influence of additions of these metals on the tensile strength of tin is discussed. A great increase produced by quenching silver–tin alloys is not permanent at room temperature, whilst with the other three alloys quenching has no effect. Additions of iron above 0·4 per cent. are without effect, although up to this percentage an increase of 40 per cent. in the tensile strength is found.

Nickel up to 0·3 per cent. produces an increase up to 2·1 tons/in.^{2}, but further additions have no influence. Copper up to 2 per cent. greatly increases the tensile strength after all heat-treatments investigated.

Silver is shown to refine the grain of tin, but not to prevent grain-growth at high temperatures. The addition of iron above 0·05 per cent. or of nickel above 0·06 per cent. prevents such grain-growth, although below these compositions germination takes place. 0·35 per cent. and more of copper prevents recrystallization of cold-rolled tin at room temperature, but annealing at temperatures from 110° C. upwards produces larger grains than in alloys of slightly lower copper content.

Introductory.

Tin alloys readily with most of the common metals, although, in some instances, small quantities only can be dissolved in liquid tin at tem-

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peratures near the melting point of the pure metal. Intermetallic compounds are freely formed, particularly with metals of high melting point, and some of these compounds have a very definite metallurgical importance. The solid solubility of other metals in tin has been little investigated, and most of the published equilibrium diagrams fail to disclose any solid solubility at all. Even less knowledge is available regarding the influence of added elements on mechanical and other physical properties of the metal. The investigation described in this paper has been undertaken in order to ascertain the effects of alloying silver, iron, nickel, and copper with tin, and special attention has been paid to the constitution and tensile properties. The investigation has been made possible by a grant from the International Tin Research and Development Council, to whom the authors wish to express their indebtedness both for the help received and for their permission to publish the results obtained. In particular, they would like to refer to the interest taken in the work by Mr. D. J. Macnaughtan, Director of Research to the International Tin Research and Development Council.

PART I.—THE CONSTITUTION OF ALLOYS OF TIN WITH SILVER, IRON, NICKEL, AND COPPER.

(a) *Silver–Tin Alloys.*

The work of Murphy [1] and others has shown that the compound Ag_3Sn forms a eutectic with tin. Murphy found that the solid solubility of silver in tin was less than 0·1 per cent. at 206° C.

An accurate determination of the liquidus and eutectic from 0 to 6 per cent. of silver has been made by means of cooling curves. The tin and silver used had a purity of 99·99 and 99·97 per cent., respectively. Cooling curves were taken on 150 grm. of metal, melted in a Salamander crucible and covered with charcoal. The rate of cooling was 1° C. per minute, and this, together with stirring, reduced supercooling to the order of 0·5° C. At least two cooling curves were taken on each alloy, and the maximum difference between duplicate curves was 0·5° C.

From Fig. 1, which shows the tin-rich end of the constitutional diagram plotted from these results, it will be seen that the eutectic occurs with 3·5 per cent. of silver at a temperature of 221·3° C. An accurate determination of the solid solubility of silver in tin has yet to be made, but the results of mechanical tests (to be discussed later) justify the insertion of a tentative solubility line in Fig. 1.

(b) *Iron–Tin System.*

Edwards and Preece[2] found that the compound $FeSn_2$ forms a monotectic with tin and that the solid solubility of iron is less than 0·01 per cent. This was confirmed by Ehret and Westgren.[3] On account of the very low solid solubility, it was not expected that these alloys would be amenable to heat-treatment, and, therefore, no work has been carried out on the constitution.

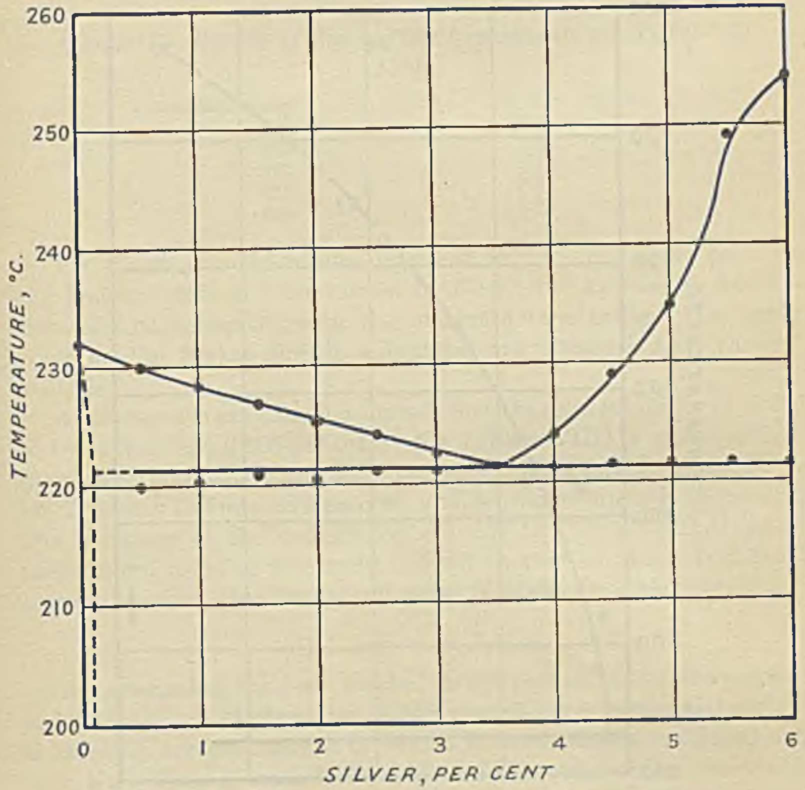

FIG. 1.—Tin-Rich End of the Silver–Tin Equilibrium Diagram.

(c) *Nickel–Tin System.*

Previous workers have agreed that the compound Ni_3Sn_2 forms a eutectic with tin, but have not agreed as to its composition and temperature of formation. The tin-rich end of the diagram has therefore been determined. The materials used were "Chempur" tin and pure Mond nickel shot. Cooling curves were taken on alloys containing up to 2·1 per cent. of nickel, using an iron–Constantan couple for low temperatures and a Chromel–Alumel couple for high temperatures.

In spite of such precautions as slow rates of heating and cooling, inoculation, and stirring, the only arrest found coincided with the melting point of pure tin. Altogether, 28 cooling curves, and 12 heating curves were taken, on varying amounts of metal, at rates varying between 2° and 30° C. per minute. By means of heating curves taken at the rate of 1° C. per minute it was ascertained that the solidus does not vary appreciably from the melting point of tin. Cooling curves having failed, the liquidus was found by segregation experiments. A quantity of metal (about 250 grm.) was heated to 850° C. for 1 hr. (at this temperature about 3·5 per cent. of nickel

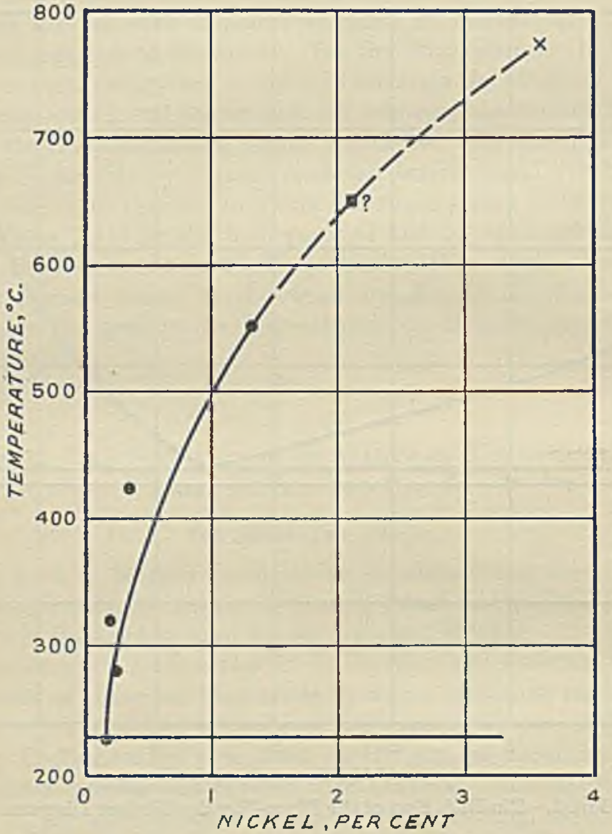

Fig. 2.—Tin-Rich End of the Nickel–Tin Equilibrium Diagram.

would be in solution in the liquid), cooled to a suitable temperature and maintained at that temperature for 24 hrs. The crucible was then lowered carefully into water. The excess solid compound had segregated to the bottom of the melt, so that an analysis of the top layer gave the composition of the liquid phase at the temperature of the experiment. The results are given in Table I.

TABLE I.—*Results of Segregation Experiments on Nickel–Tin Alloys.*

Constant Temperature, ° C.	Nickel in Top Layer, Per Cent.
240	0·18
280	0·23
320	0·19
425	0·31
550	1·29

Fig. 2 embodies the results discussed above. The upper point on the broken line is one determined by Voss,[4] and appears to be substantially in agreement with the present determination. The other point on the broken line is a doubtful one obtained from thermal analysis.

A microscopic examination showed that the solid solubility of nickel in tin is less than 0·005 per cent. Fig 3 (Plate VIII) is a photomicrograph of an alloy containing 0·005 per cent. of nickel, annealed at 228° C. for 7 days. Definite evidence of undissolved compound is present. The markings of the background are due to "dirt" picked up in preparation, it being extremely difficult to prevent this. It demonstrates, however, that the second phase is harder than the matrix.

(d) *Copper–Tin System.*

Agreement has not been reached in the past as to the composition and temperature of formation of the copper–tin eutectic, although it is generally accepted that it is formed between the ε constituent and pure tin. Various workers have placed the composition between 1 and 2·5 per cent. of copper, and the temperature of formation between 225° and 227° C.

Gurevich and Hromatko,[6] as the result of a careful investigation, found that the eutectic occurred at 1 per cent. of copper and at 227·1° C. However, between pure tin and 1 per cent. of copper they investigated only the liquidus, and beyond 1 per cent. obtained only the eutectic points on their cooling curves. Haughton [5] accepted their value for the eutectic composition, but placed the temperature of formation at 227·4° C. In the discussion on Haughton's paper, Rooney gave reasons for supposing that the eutectic composition is less than 1 per cent. On this account, the present authors have made a careful determination of the point.

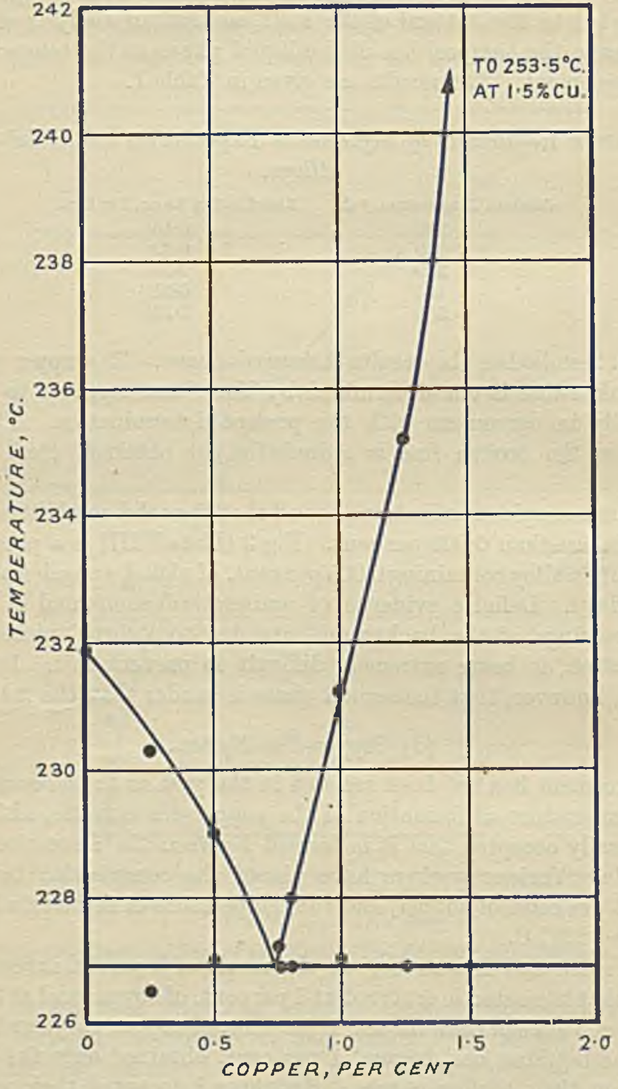

Fig. 4.—Tin-Rich End of the Copper-Tin Equilibrium Diagram.

Alloys containing up to 1·5 per cent.. were made for cooling curve experiments and the compositions confirmed by analysis. Stirring reduced super-cooling to a very small amount and, in the case of the hyper-eutectic alloys, produced definite liquidus points on the cooling curves.

Fig. 4 shows the tin-rich end of the copper–tin equilibrium diagram. The eutectic composition is between 0·70 and 0·75 per cent. of copper and occurs at a temperature of 226·9° C. The figure thus found for the composition is considerably lower than that of Gurevich and Hromatko, although there is good agreement as to the temperature. A comparison of the results of the two investigations shows complete agreement as to the liquidus temperatures of individual alloys. The difference lies, therefore, in the interpretation of the results. Had Gurevich and Hromatko determined the liquidus of the hyper-eutectic alloys, they would have seen that the point on their diagram for the alloy containing approximately 0·8 per cent. of copper lies, not on the falling liquidus line between pure tin and the eutectic, but on the rising liquidus of the hyper-eutectic alloys. With this alteration, their diagram would agree with the one now presented. (See discussion.)

The results of tensile tests on heat-treated alloys indicated that the solid solubility of copper is not as great as was found by Haughton (*viz.*, 0·2 per cent.) and therefore a microscopic determination has been made. Specimens of alloys containing up to 0·21 per cent. of copper were roughly prepared, annealed for 17 days in a salt-bath at 220° C., and quenched in water. Fig. 5 (Plate VIII) is a photomicrograph of an alloy of 0·11 per cent. copper thus treated. That there is an excess of the ε constituent is clearly visible. Finally an alloy containing 0·01 per cent. of copper was annealed at 220° C. for 15 days, quenched and examined. Again an excess of the ε phase was found (Fig. 6, Plate VIII).

The solid solubility of copper in tin is therefore less than 0·01 per cent. at 220° C.; that is to say, is negligible for practical purposes.

Part II.—The Preparation of Certain Alloys of Tin.

The work discussed here involved the addition of several metals of high melting point to tin; a few notes on the method of making the alloys are therefore given. It is fortunate that, in spite of its low melting point, tin has a very high boiling point (over 2000° C.); this made possible the use of high temperatures without an attendant risk of loss by volatilization.

(a) *Silver.*

Silver is readily soluble in tin at 600° C., 6 per cent. dissolving in 2 hrs., while charcoal is sufficient to prevent oxidation. Analysis showed that alloys can be made synthetically with a good degree of accuracy; for example, an alloy intended to contain 6 per cent. of silver, gave 5·94 per cent. on analysis.

(b) *Iron.*

The liquidus of the iron–tin system rises steeply from the melting point of tin to over 1000° C. when 5 per cent. of iron is present. Armco iron, in the form of turnings, dissolves fairly rapidly in tin at 1000° C., charcoal being sufficient to prevent oxidation; 5 per cent. of iron dissolves in 2 hrs., and analysis showed that 4·75 per cent. was present in the cast alloy. On account of the long freezing range (nearly 800° C.), it is advisable to cast such a temper alloy into thin strips to prevent segregation as much as possible.

(c) *Nickel.*

Solid nickel is readily soluble in molten tin at 900° C., up to 21 per cent. having been added at this temperature. Segregation occurs in this series, but severe chilling eliminates this as a source of trouble.

(d) *Copper.*

No special difficulties are encountered in the preparation of tin-rich copper alloys. Copper wire dissolves readily at 600° C., and more rapidly at higher temperatures.

Part III.—The Mechanical Properties of Several Tin-Rich Alloys.

The tests described below were carried out on alloy strips 0·1 in. thick, cold-rolled from 0·5 in. Since the average room temperature is above the recrystallization temperature of pure tin and many of its alloys, the cold-rolled strips were allowed to self-anneal for 15 days before any tests were made. Variations in the speed of testing have a great influence on the ultimate tensile strength of metals of great ductility, and throughout this work the constant rate of strain of $1\frac{5}{32}$ in. per minute was used, this being the maximum attainable. Loads were read to 0·001 tons, and duplicate tests never varied by more than 0·002 tons. The results are shown here as graphs, while the various heat-treatments adopted are indicated thereon.

(a) *Silver–Tin Alloys.* (Fig. 7.)

After the following heat-treatments: (i) self-annealing at room temperature; (ii) annealing at 100° C.; (iii) annealing at 210° C., the addition of silver up to 0·2 per cent. causes a gradual increase in tensile strength up to 50 per cent., although with the last heat-treatment, a maximum strength is found when 0·1 per cent. of silver is present.

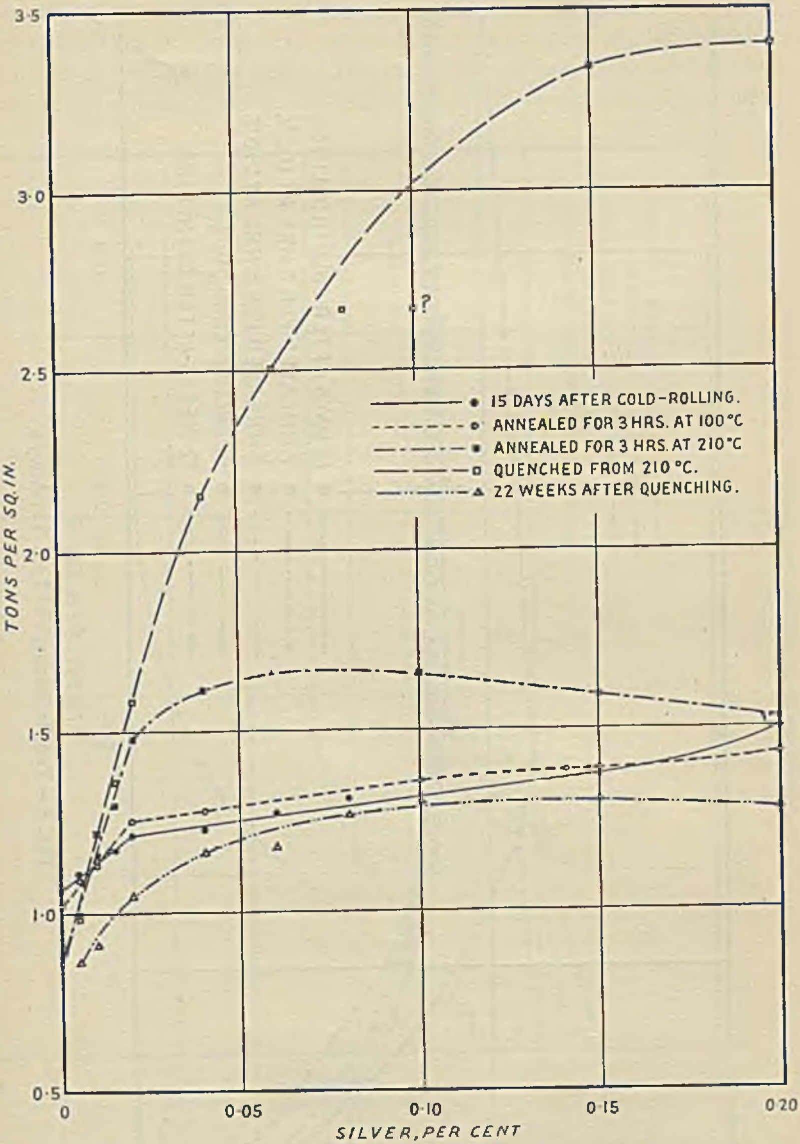

Fig. 7.—Tensile Strength of Silver-Tin Alloys.

The marked discontinuity on these curves, occurring around 0·02 per cent. of silver, is an indication of a limit of solid solubility; the limits thus obtained are shown in Fig. 1.

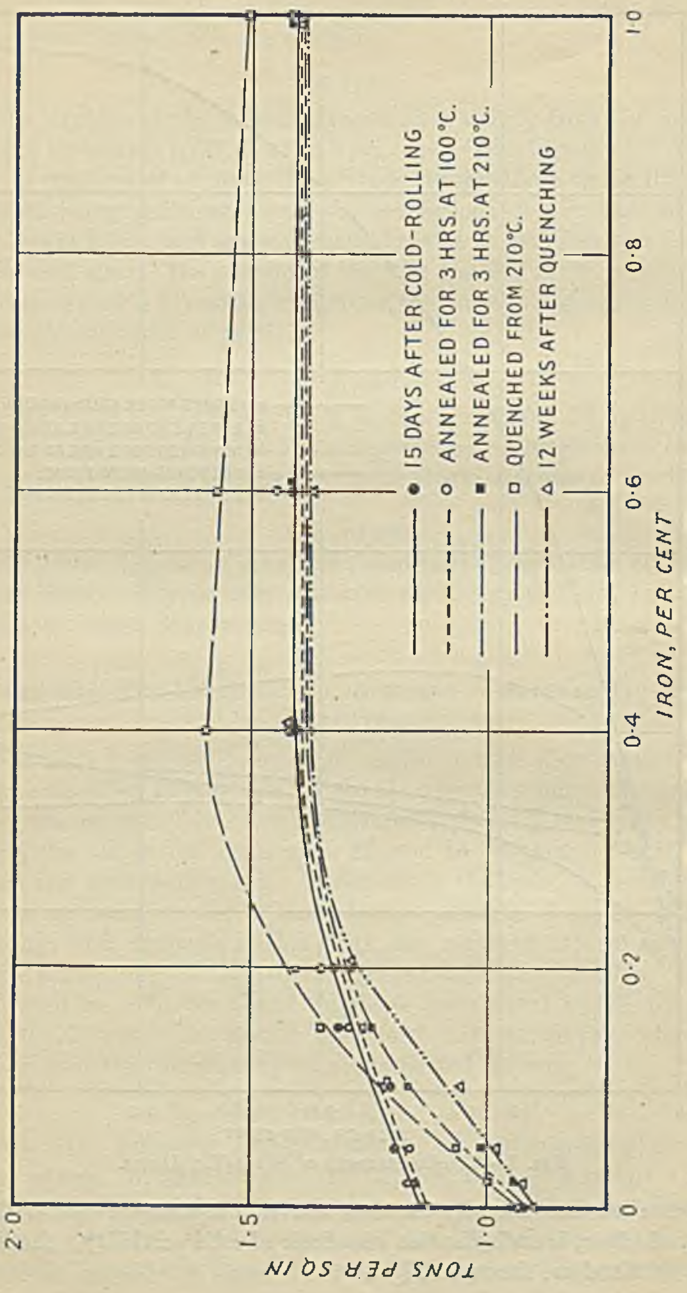

Fig. 8.—Tensile Strength of Iron-Tin Alloys.

After quenching from 210° C. the tensile strength increases rapidly up to 3·5 tons/in.^{2}, when 0·2 per cent. of silver is present, representing an increase of 250 per cent. The curve connecting these results does not show a discontinuity, but attention is directed to the apparently inconsistent results shown by the alloy containing 0·1 per cent. of silver. It is possible that the curve actually shows a discontinuity at 0·07 per cent. of silver, and then ascends to 3·5 tons/in.^{2}. Unfortunately, the effect of quenching is not permanent, since after 22 weeks at room temperature, the enhanced tensile strength completely dis-

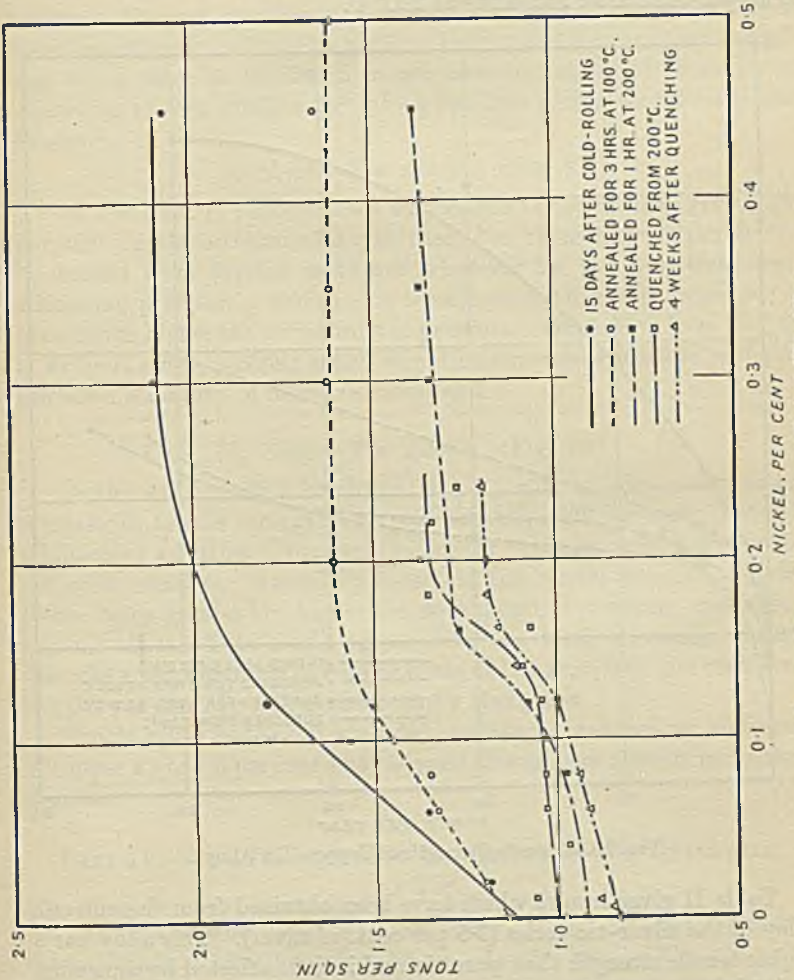

Fig. 9.—Tensile Strength of Nickel-Tin Alloys.

appears, leaving the alloys somewhat weaker than before any heat-treatment.

High-temperature annealing greatly reduces the ductility of these alloys, from an average of 90 per cent. in the self-annealed condition to 40 per cent. after annealing at 210° C.

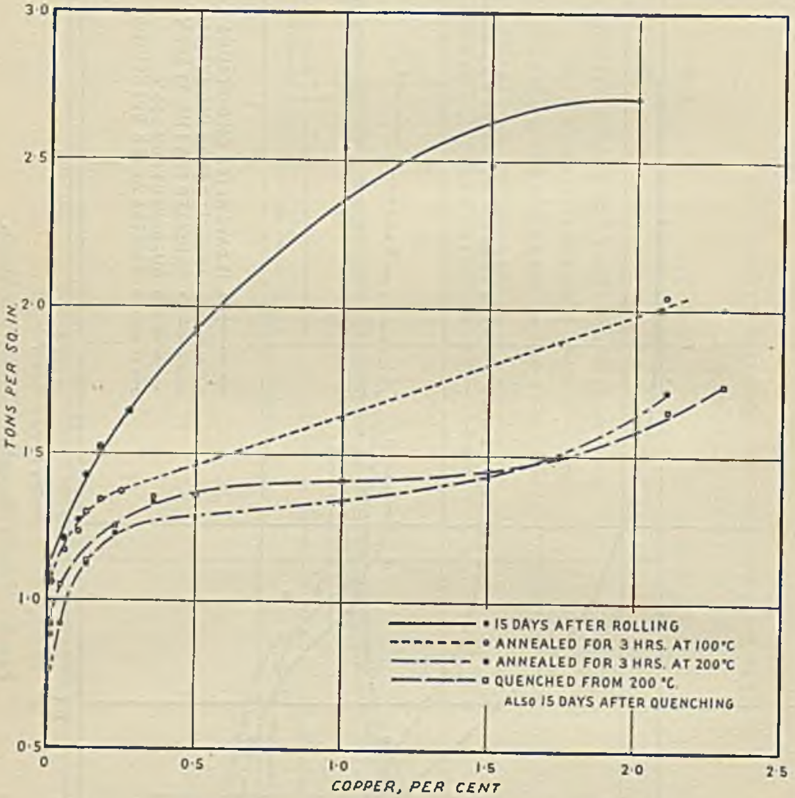

Fig. 10.—Tensile Strength of Copper–Tin Alloys.

Table II gives results which have been obtained from the eutectic alloy of the silver–tin series (3·5 per cent. of silver). This alloy has a higher tensile strength than pure tin and is little affected by annealing at 100° C.

TABLE II.

Condition.	Ultimate Tensile Strength Tons/in.^{2}.
15 days after rolling	3·63
Annealed for 3 hrs. at 100° C. . . .	3·50
Annealed for 3 hrs. at 210° C. . . .	2·34
Quenched from 210° C.	3·70

(b) *Iron–Tin Alloys.* (Fig. 8.)

After the following heat-treatments: (i) self-annealed at room temperature; (ii) annealed at 100° C.; (iii) annealed at 210° C.; (iv) quenched from 210° C., the addition of up to 0·4 per cent. of iron, causes a gradual increase in tensile strength, but further additions have no influence. Quenching causes but a small increase over annealing, which may be attributed to the fact that the solid solubility of iron in tin is very small, a fact which has been shown by Edwards and Preece.[2]

(c) *Nickel–Tin Alloys.* (Fig. 9.)

0·2 Per cent. of nickel causes an increase in tensile strength of 100 per cent. in the self-annealed condition, but there is no advantage to be gained from further additions whatever be the heat-treatment. Annealing produces a decrease in tensile strength, the decrease being greater the higher the annealing temperature. Quenching from 200° C. is without effect, a result which would be expected when the probable low solid solubility of nickel is considered.

(d) *Copper–Tin Alloys.* (Fig. 10.)

In the self-annealed condition, 1 per cent. of copper causes an increase in tensile strength of approximately 120 per cent., but the addition of a further 1 per cent. of copper produces only a further 10 per cent. increase. Annealing decreases the tensile strength, the decrease being greater the higher the annealing temperature; quenching has no effect. This result agrees with the fact, previously stated, that the solid solubility of copper in tin is less than 0·01 per cent. and not 0·2 per cent. as was maintained by Haughton.

The ductility in the self-annealed condition is reduced by additions of copper up to 1·0 per cent., but beyond this amount there is no further decrease.

PART IV.—THE INFLUENCE OF IMPURITIES ON THE GRAIN-SIZE OF TIN.

The experiments described below were carried out on alloy strips 0·1 in. thick, cold-rolled from 0·5 in. In the case of the silver–tin and iron–tin alloys, the ends of the tensile specimens were etched, without previous preparation (this was unnecessary) in dilute nitric acid. With the nickel–tin and copper–tin alloys it was more convenient to use separate specimens; these were cut from strips used for the tensile tests, and were 1·5 in. × 2 in., the shorter length being the direction of rolling; they were etched in a similar manner after the required heat-treatments. In all cases, the grains were counted by the intercept method; *i.e.* the number of grain boundaries crossed in traversing a given length in each of two directions at right angles was ascertained by means of a travelling microscope. The product of the two readings was the number of grains in the area given by the product of the distances traversed. With grain-sizes of the order of 10,000 per cm.^{2}, a distance of 1 cm. was sufficient, but where the grains were large, or where mixed sizes were found, several counts were made over the whole length and breadth of the specimen. In a few cases, where very large grains existed, the intercept method was checked by counting the individual grains on the complete surface of the specimen; complete agreement was always found.

(a) *The Influence of Silver.* (Table III.)

The effect of silver on the grain-size produced by recrystallization at room temperature after severe cold-work is most marked with 0·015 to 0·02 per cent. Between these compositions, a decrease takes place which appears to coincide with the limit of solid solubility and the appearance of a second phase. Further additions of silver cause a small reduction.

Table III.—*Grains per cm.*^{2}.

Silver. Per Cent.	A.	B.	C.
Nil	7,200	8,400	23
0·005	8,300	5,300	28
0·01	8,700	8,700	40
0·015	6,000	10,200	41
0·02	18,100	18,900	53
0·04	19,200	14,800	101
0·06	22,300	...	101
0·08	25,600	...	255
0·10	27,200	17,500	240
0·15	24,600	19,200	240
0·20	24,200	14,400	255

A.—15 days after cold-rolling.
B.—Annealed for 3 hrs. at 100° C.
C.—Annealed for 3 hrs. at 210° C.

Annealing for 3 hrs. at 100° C. causes no increase in grain-size when less than 0·02 per cent. of silver is present, but whereas there was previously a further slight reduction with silver contents above this amount, there is now no change.

Annealing at 210° C. causes a marked grain-growth in all alloys containing up to 0·2 per cent. of silver (the maximum investigated), although additions of silver do cause a slight reduction from 25 grains per cm.^{2} with pure tin, to 250 grains per cm.^{2} when a little more than 0·1 per cent. of silver is present.

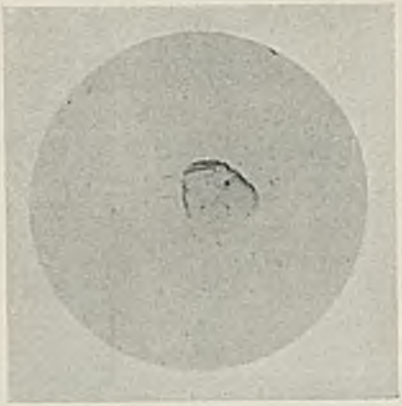

FIG. 3.—0·005% Nickel. Annealed at 228° C. for 7 days and Quenched. × 1000.

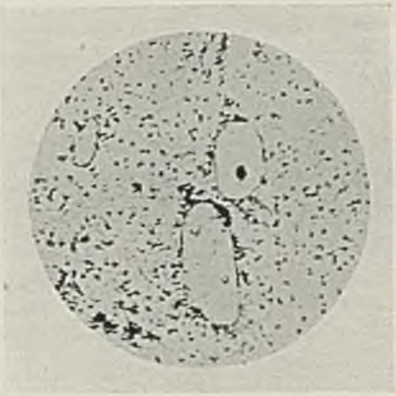

FIG. 5.—0·11% Copper. Annealed at 220° C. for 17 Days and Quenched. × 500.

FIG. 6.—0·01% Copper. Annealed at 220° C. for 15 Days and Quenched. × 500.

[*To face p.* 128.

FIG. 11.—(Above) Equi-Axed Grains Usually Found in Tin Alloys. (Below) Elongated Grains in Copper–Tin Alloy. (0·45% Copper. Annealed at 222° C.)

(b) *The Influence of Iron.* (Table IV.)

Additions of iron up to 0·05 per cent. increase the grain-size of tin, recrystallized after cold-work, from 13,000 to 6000 grains per cm.², but further additions, up to 1 per cent., are without effect.

Table IV.—*Grains per cm.²*

Iron, Per Cent.	A.	B.	C.	D.
Nil	13,500	400	180	55
0·02	10,000	3	3	4
0·05	6,000	2,800	1,400	2½
0·10	6,000	3,300	2,400	700
0·15	6,000	3,100	2,700	1,700
0·20	6,000	2,800	2,200	1,700

A.—15 days after cold-rolling.
B.—Annealed for 3 hrs. at 180° C.
C.—Annealed for 3 hrs. at 214° C.
D.—Annealed for 3 hrs. at 224° C.

Annealing for 3 hrs. at 100° C. causes a slight grain-growth in alloys containing less than 0·05 per cent. of iron, of such a magnitude as to produce a constant grain-size throughout the series, from 0 to 1 per cent. of iron. The grain-growth found to take place in pure tin at 100° C. does not agree with what was stated when discussing the silver–tin alloys, in which series no growth was found in pure tin at that temperature. It is extremely difficult, however, to reproduce the exact conditions of strain and temperature, &c., but it is believed that constant conditions existed throughout each series of alloys.

On annealing at temperatures from 180° to 224° C., germination is found to take place when 0·02 per cent. of iron is present, resulting in the production of grains having areas of 1·5 cm.², while in one case, an area of 8 cm.² was found.

When the iron concentration is more than 0·02 or 0·05 per cent. when annealing at 224° C., the grain-size rapidly diminishes to a figure around 2000 grains per cm.².

(c) *The Influence of Nickel.* (Table V.)

The influence of nickel on the grain-size of tin recrystallized after cold-work, is small. Additions up to 0·15 per cent. effect a slight refining, but beyond this composition there is no change.

Annealing for 24 hrs. at 128° C. causes grain-growth in alloys of low nickel content; with 0·005 per cent. the increase is from 10,000 to 500 grains per cm.². After this heat-treatment the addition of nickel refines the grain, the maximum effect being with 0·06 per cent., beyond which there is no further change; grain-growth is practically arrested at 128° C. by such nickel contents.

TABLE V.—*Grains per cm.*^{2}.

Nickel. Per Cent.	A.	B.	C.
0·005	10,000	560	10
0·01	9,900	1,540	12
0·02	18,100	10,000	1·2
0·04	20,400	6,000	1·2
0·06	30,100	11,500	0·5
0·08	21,000	14,000	114
0·10	18,400	17,500	159
0·12	39,200	13,500	228
0·14	40,800	17,000	1,120
0·16	27,600	17,000	2,370
0·18	28,900	19,000	3,040
0·20	28,900	18,500	3,520

A.—Self-annealed at room temperature.
B.—Annealed for 24 hrs. at 128° C.
C.—Annealed for 24 hrs. at 211° C.

Annealing for 24 hrs. at 211° C. produces grain-sizes of the order of 10 grains per cm.^{2} with 0·005 per cent. of nickel, but compositions between 0·02 and 0·06 per cent. cause germination, resulting in the production of large grains averaging 1 cm.^{2} in size. Beyond 0·06 per cent. a sudden refinement takes place which is continued up to 0·2 per cent. (the maximum investigated), when a grain-size of 3500 grains per cm.^{2} results.

(d) *The Influence of Copper.*

The results obtained from a study of the grain-size of copper–tin alloys are given in Table VI.

TABLE VI.—*Grains per cm.*^{2}.

Copper, Per Cent.	Self Annealed.	24 hrs. at 110° C.	24 hrs. at 222° C.
0·03	4,400	4,400	3
0·04	3,500	3,300	3
0·07	3,000	3,200	100
0·13	5,900	6,800	12
0·17	5,800	7,800	1,700
0·23	11,200	10,100	370
0·25	9,800	9,500	1,600
0·27	7,400	7,200	46
0·35	N.R.	2,100	175
0·45	N.R.	360	116

N.R. = not recrystallized.

The results show that copper exerts a refining action on the grain-size produced by recrystallization at room temperature. With 0·35 per cent. only a portion of the alloy had recrystallized, while with 0·45 per cent., recrystallization had not commenced. This led to peculiar results when the effect of annealing was considered.

Annealing for 24 hrs. at 110° C. has little effect on these alloys, except in those containing 0·35 per cent. and more of copper, *i.e.* those which do not completely recrystallize at room temperature. In this case, elongated crystals are produced instead of the more usual equi-axed ones found in the other alloys. The same phenomenon occurs after annealing for 24 hrs. at 222° C. It seems that these grains are produced by the re-orientation of the original cold-worked structure and not by growth following recrystallization at room temperature; a larger grain-size is produced in the alloy richer in copper than in that which was partly recrystallized before annealing. Fig. 11 (Plate IX) illustrates the difference between the equi-axed grains usually found in the recrystallized tin alloys, and the elongated grains in the alloy containing 0·45 per cent. of copper.

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[1] Murphy, *J. Inst. Metals*, 1926, **35**, 107.
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[4] Voss, *Z. anorg. Chem.*, 1908, **58**, 34.
[5] Haughton, *J. Inst. Metals*, 1921, **25**, 309.
[6] Gurevich and Hromatko, *Trans. Amer. Inst. Min. Met. Eng.*, 1921, **64**, 233.

CORRESPONDENCE.

MR. W. A. COWAN,* B.A. (Member): The authors have carried out interesting and valuable work in investigating the mechanical properties of several tin-rich alloys. A study of the effect of small amounts of other elements in metals is of importance, and many instances are now known of their causing remarkable changes in properties. There has been a dearth of information relating to tin, in this respect, and the present paper increases our knowledge of the effect of additions or of impurities in this valuable commercial metal.

In regard to the physical constitution of the alloys, I am particularly interested in the copper–tin system, work on which was done in this laboratory as reported in a paper by G. O. Hiers and G. P. de Forest entitled "The Eutectic Composition of Copper and Tin." † Whilst the authors do not refer to this paper, the result of the work reported therein agrees fairly closely with the results obtained by Gurevich and Hromatko,‡ to which they have referred. The present authors find that the eutectic has a composition between 0·70 and 0·75 per cent. copper, whereas Gurevich and Hromatko as well as Hiers and de Forest find it to be close to 1 per cent. of copper. Hiers and de Forest obtained differential cooling curves with the use of a special apparatus (described in their paper) designed by Mr. Hiers and myself, following suggestions of Dr. G. K. Burgess, late Director of the U.S. Bureau of Standards. They also made consistent deductions from micrographic examination. Some of the photomicrographs obtained are shown in Figs. A–D (Plates X–XI). These show quite clearly that with the percentage concentration of copper

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† *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1930, 207.

‡ *Trans. Amer. Inst. Min. Met. Eng.*, 1921, **64**, 233.

very slightly below the eutectic composition reported, the structure consists of eutectic with very slight excess of pure tin (or of ζ solid solution), whereas with concentration of copper very slightly above the eutectic composition, the structure consists of eutectic with a small excess of crystals of the ε component.

In the work reported in the present paper it appears that no microscopic examination was made of specimens close to the composition of the eutectic, and the conclusion was reached simply on the basis of time/temperature cooling curves.

In the discussion of the solid solubility of copper at the end of the second paragraph on p. 121, it appears that there may be some lack of clarity in the statements in regard to excess of the ε component. In the alloys on the tin side of the eutectic, the ε component will be present, of course, only as distributed in eutectic formation in the eutectic areas, and with the percentage of copper described there will be a fairly large excess of pure tin (or ζ solid solution), whereas it is only in the hyper-eutectic that there is an excess of the ε component with the remaining structure consisting of the eutectic ground mass. Instead of stating that "an excess of the ε constituent is clearly visible," the following statement might therefore be clearer: This figure shows a eutectic area in which the ε constituent of the eutectic is clearly visible. Both photomicrographs, Figs. 5 and 6 (Plate VIII) are shown presumably as representing eutectic areas, which actually comprise only a small part of the entire structure in alloys of the composition given.

In regard to the solid solubility of very small amounts of copper in tin, the two photomicrographs referred to would appear to indicate that there is practically no solubility, if they represent, as presumed above, the presence of small amounts of eutectic areas in a structure composed largely of excess tin.

The result shown in the diagram giving tensile strength for copper–tin alloys (Fig. 10) is taken as corroborating evidence of the solid solubility of copper in tin being less than 0·01 per cent. This does not appear entirely convincing.

In reporting the conditions of carrying out the tensile strength tests, in regard to the rate of strain per minute, no statement is made as to the length of the specimens. If the rate given of $1\frac{5}{32}$ in. per minute should be taken as $1\frac{5}{32}$ in./in./minute, it appears that the rate of straining would be unusually rapid. However, if the rate per minute is taken as on the entire test length of the specimen, the length should be given in order to designate the rate per inch.

The Authors (*in reply*): We are glad to have Mr. Cowan's valuable contribution to the discussion, and regret that in writing our paper we overlooked the work of Hiers and de Forest on the eutectic composition of copper and tin. We have now carefully studied this work, compared these authors' results with our own, and have come to the conclusion that our results are to be preferred. Hiers and de Forest appear to us to have adopted experimental methods not as well suited as our own to the particular investigation concerned. The main criticism which we offer is that errors due to undercooling of the sample are very likely to arise in Hiers and de Forest's method, and our experience suggests that such undercooling could easily be sufficiently great to account entirely for differences between the two sets of experiments. Undercooling is difficult to avoid in tin–copper alloys, and may easily attain to as much as 8° to 10° C., unless careful steps are taken to avoid it. Undercooling of this amount was actually present in our own experiments until we adopted the practice of stirring together with a slow rate of cooling while the curves were being taken. In our opinion the differential method using a small sample 0·5 grm. in weight in an iron crucible immersed in a large mass of neutral body, together with the rapid rate of cooling adopted (12° C.

PLATE X.

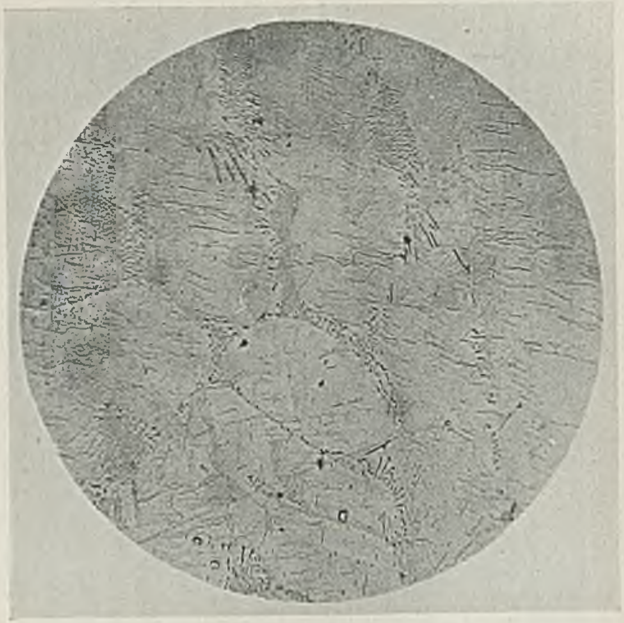

FIG. A.—Copper–Tin Alloy, 0·22% Cu. Slowly Cooled in Graphite Crucible. White areas represent ζ solid solution; half-tone = eutectic. Etched 10% HCl. × 100.

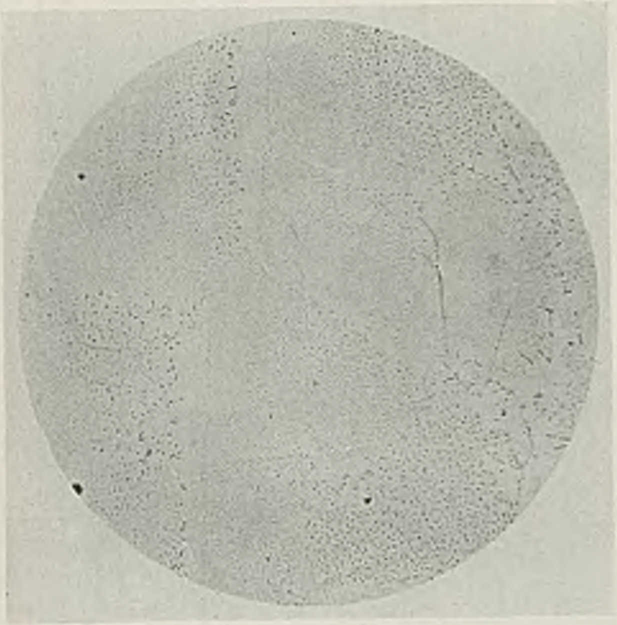

FIG. B.—Copper–Tin Alloy, 0·91% Cu. Slowly Cooled in Graphite Crucible. White areas represent ζ solid solution; dotted areas = eutectic. Etched 10% HCl. × 75.

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PLATE XI.

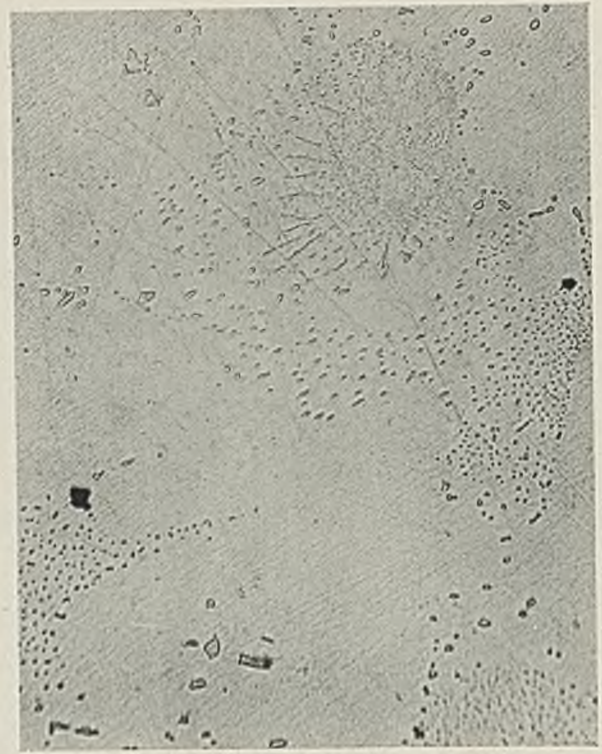

FIG. C.—Copper–Tin Alloy, 0·67% Cu. Slowly Cooled in Graphite Crucible. White areas represent ζ solid solution; dotted areas = eutectic. Etched 1 nitric : 5 acetic : 50 glycerine. × 250.

FIG. D.—Copper–Tin Alloy, Cu 1·04%. Chill-Cast in Open Iron Mould. Half-tone areas = eutectic; grey = primary crystals of ε surrounded by dendrites of ζ (white). Etched 20% HCl. × 450.

per minute as against our 1° C. per minute) are almost certain to lead to serious undercooling, which the differential method adopted might entirely fail to disclose. The rather wide scatter of Hiers and de Forest's results also suggests that a disturbing factor of this character has been operating; the maximum deviation from the mean in our own experiments, was only about 0·25°, whereas Hiers and de Forest found deviations amounting to several degrees.

The use of an iron crucible, even when coated with graphite, may also be criticized, since the graphite usually contains some free iron and this element has a very great effect on the melting point of tin, while the presence of a small amount of iron might easily cause serious errors in the results.

The plotting of a liquidus curve determined under one set of experimental conditions, together with a eutectic line determined under a totally different set, as Hiers and de Forest have done, is to be criticized. If, as we believe, the undercooling had occurred in the determination of the liquidus but not in the determination of the eutectic temperature, a serious error might be introduced. Had Hiers and de Forest determined the temperature of the eutectic in their experiments they might have reached a different conclusion as to its composition. In our experiments, liquidus and eutectic points were found in all the alloys used; the temperature difference between the two points was:

Alloys containing 0·75 per cent. of copper	0·2° C.
Alloys containing 0·8 per cent. of copper	1·1°
Alloys containing 1 per cent. of copper	4·3°

These differences are very small, and we submit that they are evidence strongly supporting the truth of our diagram.

It is somewhat difficult to interpret quantitatively differences between the structures of alloys close to the eutectic composition, and this difficulty becomes insuperable when undercooling effects are present. Indeed, in these circumstances, not only may both primary phases be associated with eutectic in the structure of the alloy, but the eutectic composition may be varied to a very considerable extent, depending on the exact conditions of cooling. The behaviour of aluminium–silicon alloys is an interesting case in point.

On the whole, therefore, we prefer our own determinations of the eutectic composition, and we are further confirmed in this opinion because it serves to clear up the serious objections to the earlier results brought forward by Rooney and by Haughton in the discussion of Haughton's paper in 1921.

Figs. 5 and 6 are intended to show particles of free compound (light etching) in specimens quenched from 220° C.; the spotted background is not eutectic, but imperfectly polished tin, and the imperfections are due to the fact that the specimen was prepared as rapidly as possible after quenching in order to avoid possible changes at room temperature. On consideration, we are inclined to agree with the comments made by Mr. Cowan with reference to Fig. 10. It would perhaps have been more accurate to deduce from the shape of these curves that variations in solubility were very small; we also had in mind that any strengthening effect of copper on tin was so small as to suggest a very low total solubility.

By an oversight, the length of the tensile specimens was not stated; this was about 6 in., the parallel portion being 2·5 in., and the cross-section 0·5 in. × 0·1 in. The rate of straining was 0·4 in./in./minute.

THE CORROSION OF TIN AND ITS ALLOYS. PART I.—THE TIN-RICH TIN-ANTIMONY-COPPER ALLOYS.*

666

By T. P. HOAR,† M.A., Ph.D., Member.

Synopsis.

The tin-rich tin–antimony–copper alloys have been examined with regard to their resistance to corrosion by dilute hydrochloric and citric acids and by various tap-waters. The straight 5 per cent. antimony alloy containing no copper is found to be usually somewhat more resistant to these types of corrosion than alloys containing copper.

Soft water produces tarnishing; hard water gives no tarnish, but may give localized attack if there is much chalky deposit.

I. Introduction.

Tin is well known as a metal distinctly resistant to many types of corroding conditions. It is used in the pure form as a protective coating for steel and for copper, and, alloyed with other metals, it forms useful corrosion-resistant materials such as the bronzes and pewters. In this series of papers it is proposed to make a preliminary survey of the nature and extent of the corrosion which occurs when tin-rich alloys are exposed to various dilute acids, salt solutions, and tap-waters.

The present report deals with the tin–antimony–copper alloys, which are extensively used as pewter. The behaviour of alloys of three different compositions has been examined and compared with that of pure tin.

Two methods of investigation have been used: (*a*) a series of measurements of the change of electrode potential with time of the alloys exposed to corroding media, which gives information as to the state of repair of the oxide-film on the metal surface and hence of the likelihood of corrosion occurring;‡ and (*b*) qualitative and weight-change experiments with specimens partly immersed in various corrod-

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† University Metallurgical Laboratories, Cambridge.

‡ May, *J. Inst. Metals*, 1928, 40, 141; Hoar and Evans, *J. Iron Steel Inst.*, 1932, 126, 379.

ing media, especially tap-waters, which is a state of affairs similar to practical conditions.

II. MATERIALS.

Analyses of the alloys used are given in Table I. Micro-sections of certain cast and cold-rolled alloys are shown in Figs. 1–5 (Plate XII).

TABLE I.—*Analyses of Materials.*

Alloy.	Reference.	Tin, Per Cent.	Antimony, Per Cent.	Copper, Per Cent.	Lead, Per Cent.	Bismuth, Per Cent.	Iron, Per Cent.	Sulphur, Per Cent.
Chempur tin	TP	99·989	0·005	0·0004	0·002	0·0007	0·002	0·001
Tin	TC	99·679	0·225	nil	0·039	0·021	0·010	0·014
Pewter alloys	P 0	95·00	5·00	trace	nil	...	nil	...
	P 1	93·96	5·05	0·98	nil	...	0·01	...
	P 3	91·89	5·12	2·98	nil	...	0·01	...

All the materials were used in the cold-rolled condition. Specimens were cut 6·5 × 2·5 cm., and, except where otherwise stated, were abraded with Hubert IF emery, degreased with carbon tetrachloride, and stored in dry air over calcium chloride for 24 hrs. before the corrosion test.

III. POTENTIAL–TIME MEASUREMENTS.

The technique described in a previous paper was adopted,* so that a rapid survey of the electrochemical behaviour of the alloys could be made. As has been pointed out, a fall of potential with time indicates penetration and/or breakdown of the oxide-film by the electrolyte, which will usually cause corrosion, whilst a rise of potential with time indicates repair of the film and protection of the metal from corrosion. Of course, no indication of corrosion *velocity*, which may be very small even with a film-free metal, can be obtained by the method.

Some of the more significant of the potential–time curves obtained are shown in Figs. 6 and 7, each curve being the average of three concordant experimental curves.

Fig. 6 shows the behaviour of the alloys tested in the cold-rolled condition without abrasion with Cambridge tap-water as corroding medium (*vide infra*, Table II, for analysis). It will be seen that in all cases there is initially a very rapid fall of potential to about — 0·2 to — 0·3 v. on the normal hydrogen scale, indicating film-penetration by the electrolyte; this rapid fall is followed by a slow rise, doubtless because an insoluble corrosion product is being formed so close to the

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* Hoar and Evans, *J. Iron Steel Inst.*, 1932, 126, 379.

metal as to be precipitated in optical contact with it and so lead to film-repair. The general inference is that extensive corrosion is unlikely, and that any which does occur will be of a localized nature at especially weak places in the film which refuse to heal up.

Fig. 7 shows the behaviour of the alloys tested with 0·1*M* citric acid, used as being typical of the organic acids to which tin is exposed in canned fruits. In all cases there is a rapid fall of potential to about — 0·25 v. and no subsequent rise; this, in so acid a solution, undoubtedly indicates the probability of considerable corrosion.

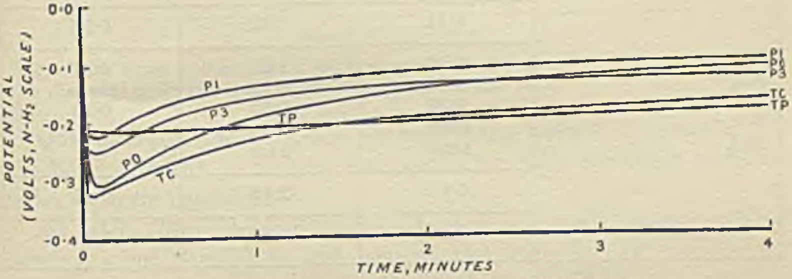

Fig. 6.—Potential–Time Curves in Cambridge Tap-Water.

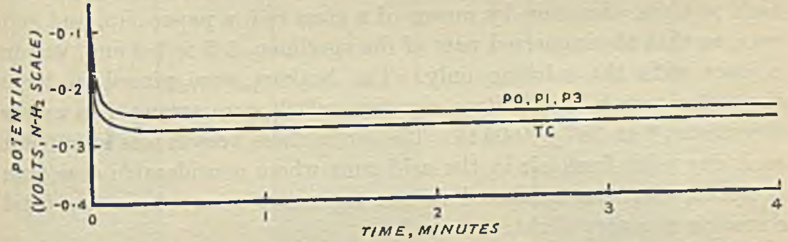

Fig. 7.—Potential–Time Curves in 0·1*M* Citric Acid.

It may be noted that there are no very significant differences between any of the potential–time curves of the alloys and the pure metal, except that P 0 shows a rise of potential rather more rapid than that of the other alloys. Much the same *probability* of corrosion may therefore be expected in all cases except that of P 0, which should be the least liable to attack. This conclusion has been borne out in further experiments which follow.

IV. Partly Immersed Corrosion Tests.

A series of weight-change corrosion experiments on materials TP, TC, P 0, P 1, and P 3 in 0·1*M* citric acid, 0·1*M* hydrochloric acid, and

Cambridge, London, and Birmingham tap-waters was carried out. The tap-waters were analyzed with the following results:

TABLE II.—*Analysis of Tap-Waters.*

	Cambridge.	London.	Birmingham.
	mg. equiv./litre.	mg. equiv./litre.	mg. equiv./litre.
Ca^{++} . . .	4·65	1·54	0·41
Mg^{++} . .	0·08	0·12	nil
Fe^{+++} . . .	nil	nil	nil
Na^{+} (difference) .	0·40	0·76	0·15
	5·13	2·42	0·56
HCO_3^- . . .	4·42	1·21	0·37
SO_4^{--} . . .	0·32	0·59	trace
Cl^-	0·39	0·62	0·19
NO_3^- . . .	trace	trace	nil
SiO_2 . . .	trace	trace	nil
	5·13	2·42	0·56
p_H of water . .	7·4	8·6	7·2

Weighed specimens 6·5 × 2·5 cm., prepared as described, were fixed vertically and symmetrically in uniform straight-sided beakers 8 cm. high × 4 cm. diameter, by means of a glass rod, a paper-clip, and soft wax, so that the immersed part of the specimen, 3·5 × 2·5 cm., was in contact with the solution only. The beakers were placed in large desiccator vessels of 5·5 litres capacity, which were arranged in an air thermostat * at 25° ± 0·05 C. The air in these vessels was swept out each day with fresh air in the acid runs where considerable corrosion occurred, but was unaltered in the tap-water runs where the total corrosion was very slight.

The acid runs were continued for 6 days, after which specimens were removed, washed, and dried. There was very little adherent corrosion product and the weight loss of the specimen may be taken as a measure of the corrosion (Table III). The tap-water runs were continued for some 50 days, when visible attack had occurred; it was not possible in the Cambridge and London water runs either completely to remove the corrosion product or to leave it entirely untouched, and the weight change is therefore little guide as to the amount of corrosion. However, the loss or gain in weight of these specimens with all *loose* corrosion product removed is included in Table III for completeness, and should be considered conjointly with the qualitative description of the corrosion which follows.

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* Evans, *Chem. and Ind.*, 1931, 40, 66, 245.

TABLE III.—*Weight Change of Tin and Pewter Specimens Partly Immersed in Corroding Media*, 25·0° *C.*

Solution.	0·1*M* Citric Acid. 6 days.	0·1*M* Hydrochloric Acid. 6 days.	Cambridge Tap-Water. 50 days.	London Tap-Water. 63 days.	Birmingham Tap-Water. 50 days.
Metal.	mg.	mg.	mg.	mg.	mg.
TP . .	−29·3	−36·1	−0·4	−0·1	+0·2
TC . .	−22·5	−32·7	−0·3	+0·1	+0·3
P 0 . .	−25·5	−17·6	−0·3	±0·0	+0·3
P 1 . .	−27·1	−17·5	−0·3	−0·1	+0·6
P 3 . .	−28·3	−16·5	−0·4	−0·2	+0·6

Mean of duplicates.

The last three columns are semi-quantitative only, and must be considered with due regard to the qualitative description in the text.

Qualitatively, the corrosion showed many points of interest. It will be convenient to present the results for each corroding medium under separate headings.

(a) 0·1M *Citric Acid*, 6 *days.*—There was a very intense attack forming a rut parallel to and near to the water-line in every case, although a very narrow strip in the "meniscus" appeared to be unattacked (Fig. 8 (*a*)). Lower down, there was much less attack, but the whole surface was lightly etched. A small amount of loose black deposit appeared at the water-line.

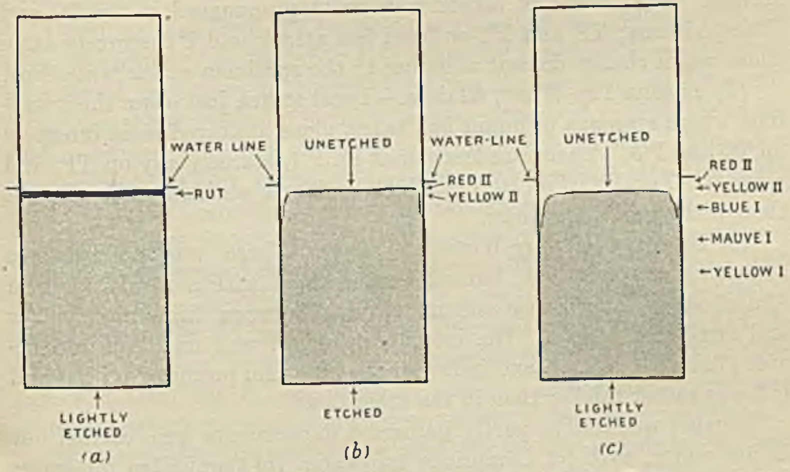

FIG. 8.—Distribution of Corrosion and Interference Tests.
(*a*) Tin and Pewter in 0·1*M* Citric Acid.
(*b*) Tin in 0·1*M* Hydrochloric Acid.
(*c*) Pewter in 0·1*M* Hydrochloric Acid.

(b) 0·1M *Hydrochloric Acid*, 6 *days*.—The whole specimen was evenly etched, except for the part near the water-line, where interference tints indicating a film growing thicker towards the water-line were observed.* This is clearly a secondary film of tin oxides or hydroxides, and it is significant that it is thickest near the surface of the liquid where the oxygen supply is the most plentiful. The interference tints formed a band some 1–2 mm. wide in the case of the tin specimens TP and TC, but were spread out over some 15 mm. in all three specimens P 0, P 1, and P 3, containing 5 per cent. antimony, which it may be noted suffered much less corrosion (Table III). The distribution of the tints is shown schematically in Fig. 8 (*b*, *c*). The main part of the tinted area appeared to be lightly etched, indicating a very porous secondary film formed on it during attack; but the metal beneath the film in the band within 1–2 mm. of the water-line appeared quite bright and unetched, indicating that here the primary air-formed film never entirely breaks down.

(c) *Cambridge Tap-Water*, 50 *days*.—All the alloys except one P 0 specimen showed localized attack just below the water-line (Fig. 9, Plate XIII), and usually a number of minute " pin-holes " over the entire surface. Both forms of attack were most pronounced in the TC and P 3 specimens; TP and P 1 suffered less attack and P 0 scarcely any; there was a chalky deposit adhering to the specimen at the water-line.

(d) *London Tap-Water*, 63 *days*.—Local attack just *above* the water-line, where creepage of liquid had taken place, occurred most intensely on TC and P 3. There was less attack on P 1, scarcely any on TP, and none at all on P 0 (Fig. 10, Plate XIII). There was less chalky deposit than with Cambridge water.

(e) *Birmingham Tap-Water*, 50 *days*.—There was no localized attack on any specimen, but all were covered with a nearly uniform film showing interference colours varying between first-order yellow and first-order mauve. The increase in weight was small but measurable (Table III, col. 6), and indicates that the film produced on P 1 and P 3 was rather thicker than in the other cases.

Further qualitative partly immersed experiments were carried out in hot water, with (*a*) Cambridge tap-water, (*b*) Cambridge tap-water which had been previously boiled and the precipitate filtered off, (*c*) distilled water. Specimens were stood in beakers with 4 cm. immersed,

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* It is well established that a thin transparent oxide-film on a metal surface yields an interference tint depending on its thickness and refractive index, in accordance with optical principles. With any one material, increase of thickness gives successively the colours yellow, mauve, and blue (first order colours), followed by a silvery region (the " hiatus ") and then by yellow, red, and green (second order colours). After this the " overlapping " of the various orders produces results varying from one material to another.

and the beakers, covered with watch-glasses, were placed in a steam-oven which was run each day for 8 hrs. at about 95° C. for 20 days, being allowed to cool over-night. Evaporation was made good with distilled water each day.

The results with Cambridge tap-water were similar to those obtained in the cold, *viz.* local attack just below the water-line and "pin-holing," but, as expected, attack was considerably more rapid. In the boiled water, however, interference tints varying from first-order yellow to first-order mauve and blue, similar to those found with Birmingham water in the cold, were produced over the whole specimen, and very few points of local attack were noticed. Hot distilled water produced no local attack, but gave a similar although thinner film, which did not thicken above the first-order yellow in the case of TP and TC; such a film has also been observed on tin-plate exposed to hot distilled water for a few hours.* Except that all the pewters gave thicker films than TP and TC in the boiled and distilled water, no significant differences in the behaviour of all five materials were observed under hot-water conditions.

V. Discussion.

It will be seen from the foregoing results that the addition of 5 per cent. of antimony to tin (alloy P 0) is usually beneficial from the point of view of resistance to corrosion by the liquids used in this work. There is a slight reduction in the attack by citric acid in presence of air, and a marked reduction in the case of hydrochloric acid. The alloy containing 5 per cent. antimony was also much the least attacked of the series by cold Cambridge and London tap-waters.

The addition of 1–3 per cent. of copper to the 5 per cent. antimony alloy (P 1, P 3) proved detrimental in the conditions investigated. This is perhaps to be expected, since there is extremely little solid solubility of copper in the 95 per cent. tin–5 per cent. antimony alloy;† the copper phase can be seen in the photomicrograph of cast P 3 (2·98 per cent. Cu), Fig. 2, and being a "noble" heterogeneity, may well stimulate attack on the tin–antimony matrix under some conditions.

With regard to the mechanism of attack by the various media, only preliminary observations will be attempted here. It is well known that tin suffers practically no attack by cold dilute acids in the absence of air,‡ owing, no doubt, to its high hydrogen overpotential. The attack by $0{\cdot}1M$ citric and hydrochloric acids in presence of air must therefore be associated with oxygen absorption.

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* Macnaughtan, Clarke, and Prytherch, *Trans. Faraday Soc.*, 1932, 125, 159.
† Tasaki, *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1929, [A], 12, 227.
‡ Mantell, *Amer. Inst. Min. Met. Eng. Tech. Publ.* No. 171, 1929.

Some light is thrown on the corrosion mechanism in citric acid by the following measurements of electrode potential at various points on the corroding metal surface by the method previously developed during a study of the corrosion of iron.* In this technique, a capillary tube is arranged opening on to the metal surface at the point the electrode potential of which is required: through this capillary, liquid connection is made to a standard half-cell, and the e.m.f. of the cell

$$\text{metal} \left| \begin{array}{c} \text{corroding} \\ \text{medium} \end{array} \right| \begin{array}{c} \text{standard} \\ \text{half-cell} \end{array}$$

is then obtained on a valve electrometer. The potentials were measured against a quinhydrone half-cell made up in the same acid as the corroding medium: thus the potential against hydrogen in the same acid could be immediately found without any complication of liquid junction potential, and by a further measurement of the quinhydrone half-cell against a $N/10$ calomel half-cell through a saturated potassium chloride bridge, the potential of the corroding tin was obtained on the normal hydrogen scale. Readings were taken at several points near to the water-line and near to the lower edge of partly immersed specimens, at intervals for 48 hrs. Very concordant results were obtained, and average values are given in Table IV.

TABLE IV.—*Potentials Shown by Tin TC Corroding in Citric Acid Temperature* 18°–20° *C.*

Potentials in (*a*) volts against hydrogen in same acid are printed in italics.
(*b*) ,, ,, normal hydrogen electrode are printed in Roman.

Time, Hrs.	0·1 *M* Citric Acid, p_H 2·14.				0·01 *M* Citric Acid, p_H 2·78.			
	Water-line.		Lower edge.		Water-line.		Lower edge.	
1	*−0·172*	−0·296	*−0·182*	−0·306	*−0·126*	−0·287	*−0·133*	−0·294
2	*−0·168*	−0·292	*−0·176*	−0·300	*−0·127*	−0·288	*−0·136*	−0·297
24	*−0·165*	−0·289	*−0·172*	−0·296	*−0·129*	−0·290	*−0·138*	−0·299
48	*−0·157*	−0·281	*−0·163*	−0·287	*−0·126*	−0·287	*−0·135*	−0·296

Three points of major interest arise:

(1) The water-line potential is invariably some 5–10 mv. more noble than that at the lower edge. There must therefore be a small current of the differential aeration type flowing between the part of the specimen near the water-line and the part lower down. It is probable that most, if not all, of the mild corrosion of the lower part of the specimen can be accounted for in this way. It must, however, be remembered that citric

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* Evans, Bannister, and Britton, *Proc. Roy. Soc.*, 1931, [A], 131, 355; Evans and Hoar, *ibid.*, 1932, [A], 137, 343.

acid causes a very intense corrosion at or near the water-line as well. It is not possible to measure the potential of the metal at the bottom of the " rut " formed by the water-line attack, so that information as to the possibility of a similar differential aeration mechanism applying here cannot be obtained.

(2) The potential of corroding tin in citric acid is considerably less noble than the hydrogen potential in the same acid. Were it not that tin has a particularly high hydrogen overpotential, hydrogen would be evolved; as it is, oxygen is necessary for the depolarization reaction and hence for corrosion.

(3) The potential of corroding tin, in both $0{\cdot}1M$ and $0{\cdot}01M$ citric acid, is about $-0{\cdot}3$ v. on the normal hydrogen scale, whereas the standard electrode potential of tin is given as $-0{\cdot}136$ v.* If therefore tin goes into solution as stannous ions according to the reaction $Sn \longrightarrow Sn^{++} + 2\varepsilon$ the concentration of Sn^{++} near to the metal surface must be very small, being on classical theory given by the equation :

$$-0{\cdot}3 + 0{\cdot}136 = \frac{RT}{2F}\log_e[Sn^{++}]$$
$$i.e.\ [Sn^{++}] = C\,.\,2 \times 10^{-6}\,N.$$

No doubt such calculations can give only qualitative results, but since after 48 hrs.' corrosion the total tin concentration in the solution is of the order of $3 \times 10^{-3}\,N$, there is a very significant discrepancy.

It is very probable that tin ions are removed by the citric acid with the formation of a citrato-complex. This hypothesis will be elaborated elsewhere; here it may be mentioned that an acid such as oxalic, which is known to form stable oxalato-complexes, corrodes tin much more rapidly and at a much lower potential than acids such as citric, and particularly sulphuric acid, where the complexes are considerably less stable. Riley † has recently directed attention to the effect of complex formation on the corrosion of copper and nickel by various acids, including citric acid; his conclusions have many points of similarity to the above views concerning tin.

It is proposed to make further potential experiments with hydrochloric acid. The formation of interference tints suggests that even in this strongly acid medium a certain amount of differential aeration occurs, under conditions of partial immersion.

The two quite different types of attack given by the tap-waters, *viz.* localized attack by the hard Cambridge and London waters, and film-thickening by the soft Birmingham water, are of great interest. Since

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* Lewis and Randall, " Thermodynamics," p. 443. London : 1923.

† *Proc. Roy. Soc.*, 1934, [A], 143, 399.

the film-thickening is also produced by hot distilled water, those waters in which the film does not thicken to interference-tint thickness must contain an inhibitor of the process. It seemed possible that this might be soluble calcium bicarbonate, when present in sufficient quantity, since hot Cambridge water from which bicarbonate and carbonate had been removed by boiling and filtering readily gave the thickening, whereas hot untreated Cambridge water did not. The latter must always contain an appreciable amount of soluble bicarbonate; under the alternate hot and cold conditions of the experiment it is to be expected that absorption of carbon dioxide from the atmosphere would occur during the cold period with consequent re-dissolution of some of the precipitated carbonate.

The hypothesis was verified by a series of 14-day tests with tin TC half-immersed in several mixtures of very dilute potassium chloride, to represent the "penetrating" type of ion present in tap-waters, and calcium bicarbonate, the supposed film-repairing agent. The results are summarized in Table V. It will be seen that increase of chloride concentration increases both the amount of film thickening and the tendency to break down at isolated points. Increase of calcium bicarbonate concentration decreases both the amount of film thickening and the local attack; at 0·005*N* the film remains below visible thickness, as in Cambridge tap-water containing about 0·0044*N*-HCO_3^- (Table II).

TABLE V.—*Effect of Calcium Bicarbonate on the Film-Thickening and Corrosion Produced by a Penetrating Anion* (Cl^-).

Conc. $Ca(HCO_3)_2$ → Conc. KCl ↓	0	0·001*N*	0·005*N*
0	Film: yellow I — mauve I * Attack: none	Film: yellow I Attack: none	Film: invisible Attack: none
0·001*N*	Film: mauve I — blue I Attack: 1 local point, at water-line	Film: yellow I Attack: none	Film: invisible Attack: none
0·005*N*	Film: mauve I — 'Hiatus' Attack: 6 local points, all over surface.	Film: yellow I Attack: 3 local points, 1 at water-line.	Film: invisible Attack: 1 local point, at edge.

* See footnote to p. 140.

PLATE XII.

All specimens etched electrolytically.

FIG. 1.—P 0. 95·00% Sn, 5·00% Sb. As cast. × 750.

FIG. 2.—P 3. 91·89% Sn, 5·12% Sb, 2·98% Cu. As cast. × 750.

FIG. 3.—P 0. 95·00% Sn, 5·00% Sb. Cold-rolled; section. × 1000.

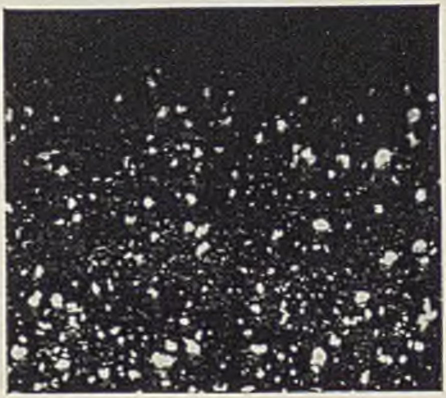

FIG. 4.—P 1. 93·96% Sn, 5·05% Sb, 0·98% Cu. Cold-rolled; section. × 1000.

FIG. 5.—P 3. 91·89% Sn, 5·12% Sb, 2·98% Cu. Cold-rolled; section. × 1000.

[*To face p.* 144.

PLATE XIII.

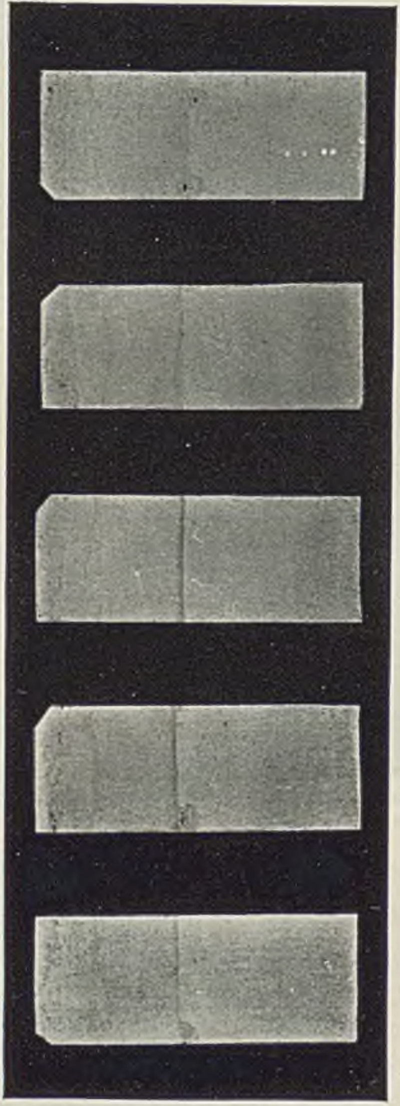

FIG. 9.—Corrosion in Cambridge Tap-Water

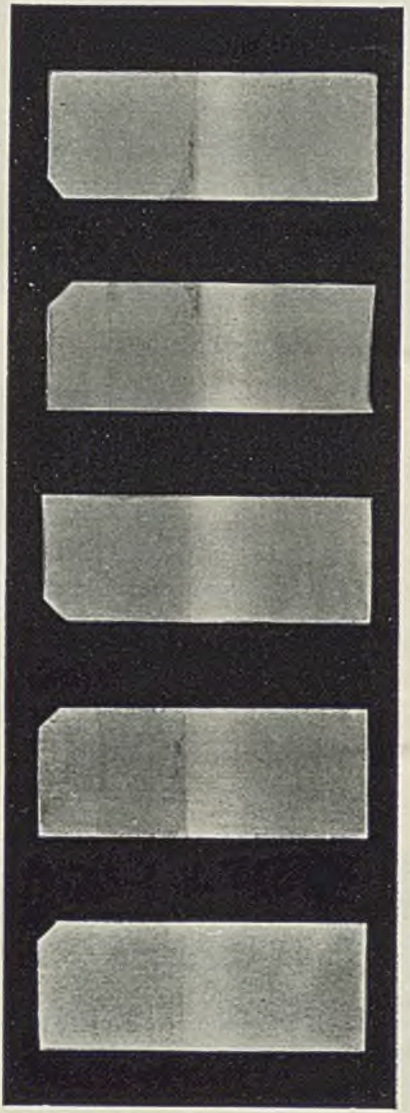

FIG. 10.—Corrosion in London Tap-Water.

Precipitated carbonate is probably mainly responsible for the localized water-line attack found with hot and cold hard waters. Such attack did not occur except when precipitated carbonate was observed: thus a 14-day test of tin TC in Cambridge tap-water run concurrently with the tests of Table V gave only a minute trace of precipitate and no attack. The loosely adherent chalky deposit, found at the water-line of the specimen, might stimulate corrosion either by partly screening parts of the metal from oxygen access and so giving a differential aeration, or by assisting in the loosening of the otherwise protective film by surface tension effects. The "pin-hole" attack, found only in the very hard Cambridge water, may likewise be attributed to the precipitation of minute particles of carbonate all over the metal; the less hard London water gave much less precipitate and no pin-holing.

Finally, the creepage of the London water above the water-line is no doubt due to the high p_H, 8·6, of the water. The carbonate deposit, and the localized attack, was found in the creepage area.

VI. CONCLUSIONS.

This work indicates the desirability of incorporating about 5 per cent. antimony in tin from the corrosion-resisting standpoint, but suggests that the presence of 1–3 per cent. copper as well is deleterious

Tin and its alloys with small amounts of antimony and copper are corroded by dilute citric and hydrochloric acids in the presence of air. The addition of 5 per cent. antimony effects a marked reduction of the corrosion in hydrochloric acid, but is without much effect in citric acid.

Two kinds of attack are found in hot and cold tap-waters. In soft water, tin and pewter tarnish with the production of a visible film of interference-tint thickness. In hard water there is no tarnishing, owing to the film-repairing properties of calcium bicarbonate, but localized attack at the water-line and sometimes elsewhere occurs if a chalky deposit is formed from the water. Nevertheless, if care be taken to remove chalky deposits from a pewter vessel, there should be no attack in hard waters; fortunately such cleaning is likely to be the rule in good domestic practice. The straight 5 per cent. antimony alloy containing no copper proved to be, under the conditions studied, somewhat more resistant to tap-waters than alloys containing copper.

VII. ACKNOWLEDGMENTS.

The above work forms part of a programme being carried out by the International Tin Research and Development Council. My great thanks

are due to the Director of Research, Mr. D. J. Macnaughtan, for many stimulating discussions and for permission to publish.

I am grateful also to my colleagues, Mrs. F. D. Heywood, B.Sc., for carrying out the difficult and tedious photomicrographic work, and to Dr. W. D. Jones and Mr. W. E. Hoare, B.Sc., for the preparation of some of the rolled alloys.

University Metallurgical Laboratories, Cambridge.
March, 1934.

CORRESPONDENCE.

Mr. H. Stevens,* M.Sc. (Member): Comparatively little work has been published on the corrosion of tin and tin-rich alloys. Whilst much work has been carried out on corrosion in general, most attention has been directed to the more reactive metals, the so-called "noble" metals having been somewhat neglected. The present paper forms a welcome contribution to our knowledge of the latter, and it is to be hoped that the investigation will be considerably extended.

In the experimental work insufficient attention appears to have been paid to the preparation of the specimens. It is not clear whether all specimens were cold-rolled to the same extent; it is probable that differences in cold-rolling would leave the specimens in different conditions as regards internal stresses. Probably the pure tin, and some alloys, would recrystallize spontaneously at room temperature; but unless all the specimens had been stored at room temperature for considerable periods it does not follow that they would be free from internal stresses, and as these, if present, may affect the potential, it is better for them to be absent. The precaution of boiling the specimens in water for an hour or so would probably have removed internal stresses.

In the case of mild steel Homer † has shown that lines of abrasion may play a greater part in the progress of corrosion than inclusions in the metal; and, therefore, it is possible that in the case of corrosion of the alloys containing copper, the scratches caused by the emery paper may be as important controlling factors as the excess of the copper constituent.

In the preparation of tin alloys for microscopic examination it is very difficult to prevent the picking up of "dirt" from the emery paper, especially when the finest papers are not used, and, since the inclusions picked up from a Hubert IF emery would be fairly large, they may quite easily play a great part in the corrosion. This would apply particularly to the "pure" tin specimens, and the value of the results would thereby be somewhat diminished.

The preparation of specimens for work on corrosion is of great importance, and in the present paper there are at least three irregularities which may influence the results.

The Author (*in reply*): Each tin–antimony–copper alloy used in the work consisted of strip 0·050 in. thick which had been cold-rolled from ingots 0·3 in. thick; they are, therefore, strictly comparable with each other as regards mode of preparation. It is unlikely that the two varieties of "pure" tin, which were obtained as cold-rolled strip, contained any serious internal

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* Metallurgist, Blakey's Boot Protectors, Ltd., Leeds.

† Homer, *Iron Steel Inst., Second Corrosion Report*, 1934.

stresses, and such stresses as may have remained in the harder cold-rolled alloys may be regarded as inherent qualities of such materials. The comparison of the corrosion of the five materials, therefore, seems to me to be a fair one.

Since all the materials were abraded under as nearly identical conditions as possible, it would appear that Mr. Stevens' second and third criticisms, regarding the possible effects of scratch lines and emery inclusions, are not valid; the alloys of different copper content *do* in fact behave differently, although identically prepared. If scratch lines and/or emery inclusions play important parts in determining the nature and extent of the corrosion, one would expect the differences due to the nature of the materials to be partially masked, and all the materials should suffer nearly similar attack. Yet the copper-bearing antimony alloys always give several well-defined points of attack in the hard tap-waters, whereas the straight antimony alloy containing no copper gives practically *none at all.* Clearly then the scratch lines and/or emery inclusions neither promote corrosion nor mask the effect due to the copper. In the case of the acid corrosion, the initial air-formed oxide film on the metal is very quickly dissolved, and the effect of possible breaks in it due to deep scratches or to emery inclusions cannot arise.

Mr. Stevens rightly emphasizes the importance of a proper preparation of corrosion specimens, a matter which has been repeatedly stressed by workers in this laboratory and others; but he is perhaps unfortunate in terming a uniform method of preparing specimens an " irregularity."

THE INFLUENCE OF PICKLING ON THE FATIGUE-STRENGTH OF DURALUMIN.* 668

By H. SUTTON,† M.Sc., MEMBER, and W. J. TAYLOR.‡

SYNOPSIS.

In order to assist in the detection of flaws, manufacturing defects, and fatigue cracks in aluminium alloy components it has been customary to pickle or etch the components in various solutions, the main etching usually being effected in an aqueous solution of caustic soda. Wöhler-type fatigue tests were made on test-pieces machined from Duralumin bar and the effect of various pickling treatments on the fatigue-strength was investigated.

Pickling Treatment A (2½ minutes in 10 per cent. caustic soda solution at 60° to 70° C.; rinse: 1 minute in 10 per cent. nitric acid, 10 per cent. sulphuric acid) lowered the fatigue limit by 31 per cent., but the reduction was very much less after immersion of the test-pieces in boiling water. After a layer 0·0025 in. thick had been machined off, the pickled test-pieces showed normal fatigue properties.

Pickling Treatment B (2 minutes in 10 per cent. hydrofluoric acid, 10 per cent. nitric acid) lowered the fatigue limit by 15 per cent.

Pickling Treatment C (3 minutes in 10 per cent. sulphuric acid 4 parts, hydrofluoric acid 1 part; rinse: 1 minute in 50 per cent. nitric acid) only lowered the fatigue limit by about 6 per cent. and the reduction was less still, *i.e.* within the limits of experimental error, when the specimens had been immersed in boiling water after being pickled. This treatment appears suitable for pickling new components to reveal macrostructure and defects, or for etching used components for the detection of fatigue cracks, stress-corrosion cracks, &c.

INTRODUCTION.

THE experiments described in this paper were made to ascertain the effect of various etching or pickling processes on the fatigue properties of Duralumin. Pickling and etching treatments have commonly been used on manufactured pieces for the detection of defects of manufacture such as laps and forging cracks, as well as for the detection of fatigue cracks in used components.

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‡ Technical Officer, Royal Aircraft Establishment, South Farnborough.

Professor A. von Zeerleder had drawn the attention of the authors to the harmful effect of pickling treatments on the fatigue properties of high-strength wrought aluminium alloys. Professor von Zeerleder in collaboration with Dr. M. Bosshard had shown * that in material of the Duralumin type the number of stress cycles to fracture in fatigue tests was much reduced after the test-pieces had been given a normal etching treatment in caustic soda solution.

INDUSTRIAL PRACTICE.

Enquiries were made to ascertain details of the procedure followed with regard to pickling of light aluminium alloys at various works. It was found that caustic soda solutions of 10 to 25 per cent. concentration were being used at temperatures from normal to 70° C. and periods of immersion of up to 3 minutes. Usually the pickling in caustic soda solution was followed by rinsing, immersing in nitric acid or nitric–sulphuric acid solutions, to remove the dark slime left on the surface after the caustic soda pickling.

As the pickling in caustic soda solution is more vigorous than the second pickling operation in the acid bath it was decided to employ, in the first experiments, a caustic soda solution in the highest temperature range of those used in industry.

MATERIAL.

The experiments were made on Duralumin bar, ¾ in. in diameter, prepared to British Standard Specification No. 3L1. By arrangement with the manufacturer, the entire consignment (40 ft.) was extruded from the same billet. The material was supplied in the heat-treated and aged condition, in straight lengths which were marked A, B, C, D, and E for identification.

LOSS OF METAL BY PICKLING.

The loss of metal due to pickling was observed in some preliminary experiments by change of diameter and of weight of carefully machined cylinders.

(1) *Samples Pickled for* 2½ *minutes in Cold* 25 *per cent. Caustic Soda Solution, Rinsed, and Cleaned in Cold* 50 *per cent. Nitric Acid Solution.*—The loss of metal as observed by direct measurement was less than 0·00005 in. and the loss of weight was equivalent to removal of a layer 0·00005 in. thick.

(2) *Samples Pickled for* 2½ *minutes in Cold* 10 *per cent. Caustic Soda*

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* Communicated privately to the authors: this information is gratefully acknowledged.

Solution, Rinsed, and Cleaned in a Cold Solution containing 2 *parts Nitric Acid,* 1 *part Sulphuric Acid,* 3 *parts Water.*—The loss of metal as observed by direct measurement was less than 0·00005 in. The loss of weight corresponded to removal of a layer 0·00003 in. thick.

(3) *Samples Pickled in* 10 *per cent. Caustic Soda Solution at* 60°–70° *C. for* 2½ *minutes, Rinsed and Cleaned in Cold* 10 *per cent. Nitric Acid,* 10 *per cent. Suphuric Acid.*—The loss of metal as observed by direct measurement was 0·0003 to 0·0005 in., and that calculated from loss of weight was 0·00094 in.

The results obtained show that the most vigorous of these three pickling treatments resulted in a loss of metal sufficiently small to be negligible from the point of view of reduction of section of the pickled fatigue test-pieces.

In the case of other methods of pickling employed in later stages of the work the diameters of test-pieces were measured before and after pickling for information on loss of metal by pickling.

TENSILE TESTS.

The material was supplied in the form of five bars in straight lengths and marked A, B, C, D, and E.

The results of tensile tests on samples from bars A, B, C, and E are given in Table I. These results indicate that the material is fairly uniform in mechanical properties.

TABLE I.—*Control Tensile Tests.*

Mark.	Diam., In.	L.P. Tons/in.^{2}.	0·1% P.S. Tons/in.^{2}.	0·5% P.S. Tons/in.^{2}.	Maximum Stress, Tons/in.^{2}.	Elongation, Per Cent. on 4 $\sqrt{A}$.
A	0·493	12·8	17·6	18·8	28·0	21·0
B.7	0·494	12·1	17·1	18·9	27·8	23·0
C.19	0·494	12·8	17·2	18·9	28·2	24·6
E.17	0·494	11·9	17·3	18·9	28·1	23·0

FATIGUE TESTS.

Wöhler fatigue tests were made on machined specimens of the type illustrated in Fig. 5.

Pickling Treatment A.

This treatment, intended to represent the most vigorous pickling employed in industry, was as follows:—(1) immerse in 10 per cent. caustic soda solution at 60°–70° C. for 2½ minutes and rinse; (2) immerse in cold 10 per cent. nitric acid, 10 per cent. sulphuric acid (vol.), for 1 minute, rinse, and dry.

The loss of metal resulting from this treatment was 0·00094 in., as observed by loss of weight.

In these and subsequent experiments treatment of specimens for fatigue tests was carried out immediately before commencement of the fatigue tests.

The results of the fatigue tests are plotted in Fig. 1.* The fatigue test results are somewhat irregular, even in the case of tests of material in the unpickled condition. Probable endurance curves have been drawn with reference to the lower values obtained in each series of tests. The fatigue limit of the untreated material at 10 million cycles was ± 10·2 tons/in.^{2}, and that of pickled material ± 7·0 tons/in.^{2}, the reduction in stress being 31 per cent. For material which had received pickling treatment A and subsequent immersion in boiling water for 15 minutes, the fatigue limit was 9·1 tons/in.^{2}, 10 per cent. lower than that of the original material. The maximum stress ranges for which an endurance of ten million cycles may be expected are collected in Table II.

TABLE II.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Pickling Treatment.	Untreated.	Pickled.		Pickled and Boiled.		Pickled and Machined.		
						Fatigue Limit.		Decrease in Stress, Per Cent.
	Fatigue Limit, Tons/in.^{2}.	Fatigue Limit, Tons/in.^{2}.	Decrease in Stress, Per Cent.	Fatigue Limit, Tons/in.^{2}.	Decrease in Stress, Per Cent.	0·005 in. off Diameter.	0·010 in. off Diameter.	
A	±10·2	±7·0	31·4	± 9·1	10·0	±10·5	±10·5	Nil
B	±10·0	±8·5	15·0	...	...	...	...	...
C	±10·4	±9·8	5·8	±10·0	3·8	...	...	...

Samples 0·005 in. and 0·01 in. oversize in diameter, respectively, pickled and subsequently machined to normal size showed the same fatigue limit as the original material (Fig. 4).

Pickling Treatment B.

In view of the fact that etching in hydrofluoric–nitric acid solutions is frequently employed to develop the macrostructure of wrought light aluminium alloys, experiments were made with a pickling bath of that type. The treatment employed was to immerse in 10 per cent. hydro-

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* The letter at each point on the fatigue graphs indicates the bar from which the specimen was taken.

FIG. 6.—Section from Broken Fatigue Test-Piece, Etched. × 200

FIG. 7.—Typical Fractures of Fatigue Test-Pieces. × 2

[*To face p.* 152.

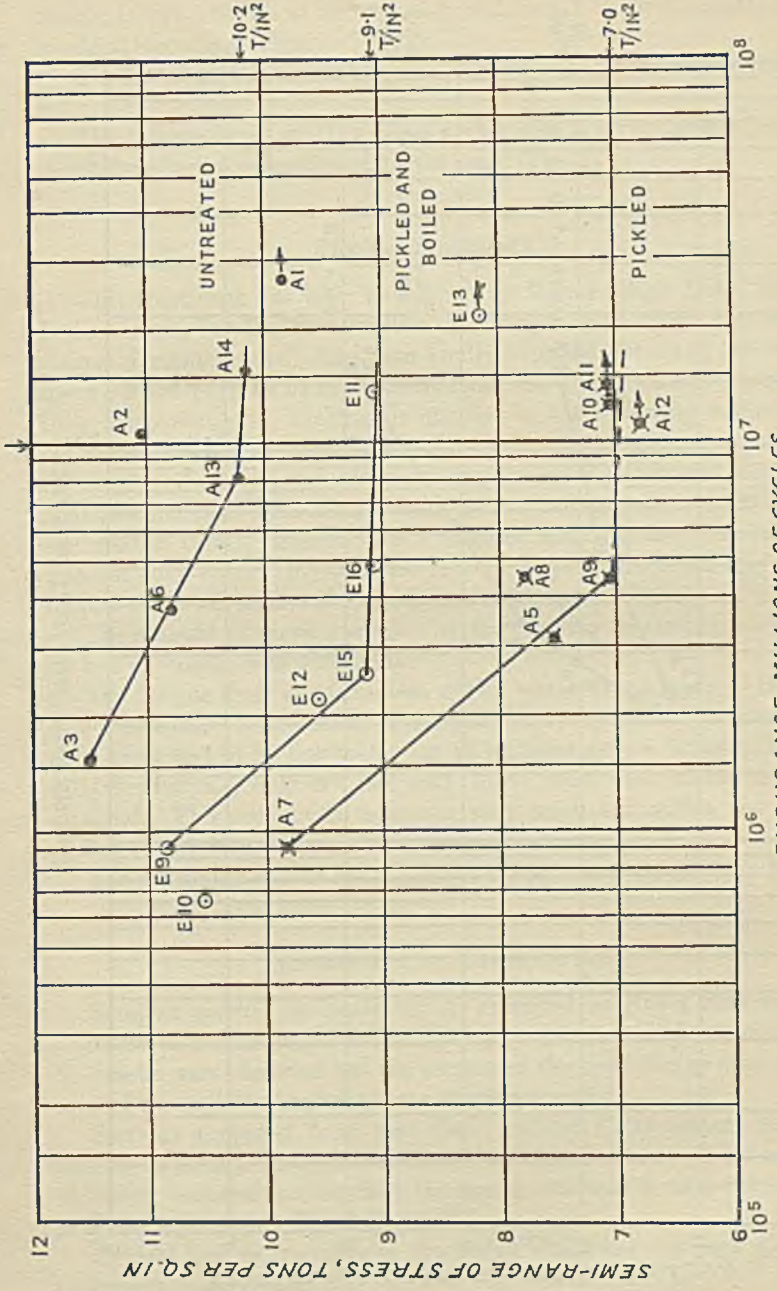

FIG. 1.—Influence of Pickling on the Fatigue-Strength of Duralumin. Pickling Treatment A.

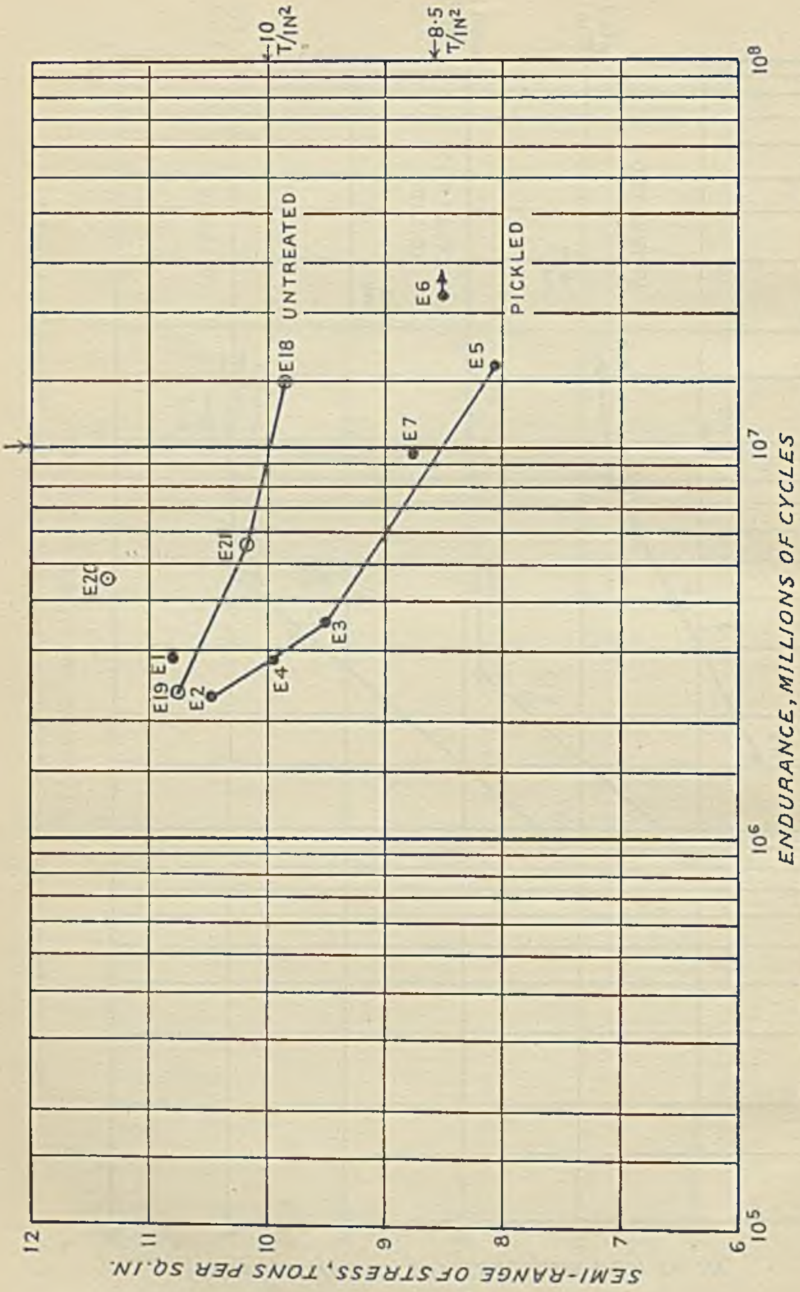

FIG. 2.—Influence of Pickling on the Fatigue-Strength of Duralumin. Pickling Treatment B.

fluoric, 10 per cent. nitric acid solution (vol.) at 20° C. for 2 minutes with constant movement, rinse and dry.

The loss of metal observed by determining loss in weight was 0·00031 in.

The fatigue limit at 10 million cycles was lowered from ± 10 to ± 8·5 tons/in.^{2}, a reduction of 15 per cent. (Fig. 2).

Pickling Treatment C.

This treatment has been developed by Messrs. High Duty Alloys, Ltd., Slough, for the examination of wrought light alloys at various stages of manufacture. The firm kindly supplied details of the treatment for the purpose of the present tests and their assistance is gratefully acknowledged. Pickling is effected in the following manner:—(1) immerse in hot water (boiling water used in the present experiments); (2) transfer directly to a bath containing 4 parts of 10 per cent. suphuric acid (vol.), 1 part hydrofluoric acid, at normal temperature (20° C. in the present tests): immerse for 3 minutes with constant movement: rinse in cold water; (3) immerse in cold 50 per cent. nitric acid for 1 minute; rinse in cold water, wash in hot water and dry.

The amount of metal removed by the pickling treatment, observed by loss of weight, was 0·00033 in.

The fatigue limit at 10 million cycles was lowered from ± 10·4 to ± 9·8 tons/in.^{2}, a reduction of 5·8 per cent. Specimens pickled and then immersed in boiling water for 15 minutes gave a fatigue limit of ± 10·0 tons/in.^{2}, only 3·8 per cent. lower than that of the original material. This amount is, however, very small and within the range of scatter experienced in the tests.

The endurance curves for this series of specimens are given in Fig. 3.

MICROSCOPICAL EXAMINATION.

Samples pickled by treatment A, extended to give a reduction in diameter of 0·0015 in., were subjected to microscopical examination. No cracks were observed but the surface of the specimen as seen at the edge of the sections examined was sharply serrated.

Sections prepared from test-pieces pickled by treatment A after fracture in fatigue tests showed numerous fatigue cracks. Examination of etched sections showed that the cracks followed a trans-crystalline path as illustrated in Fig. 6 (Plate XIV).

Typical fatigue fractures of specimens which had received pickling treatment A are reproduced (× 2) in Fig. 7 (Plate XIV).

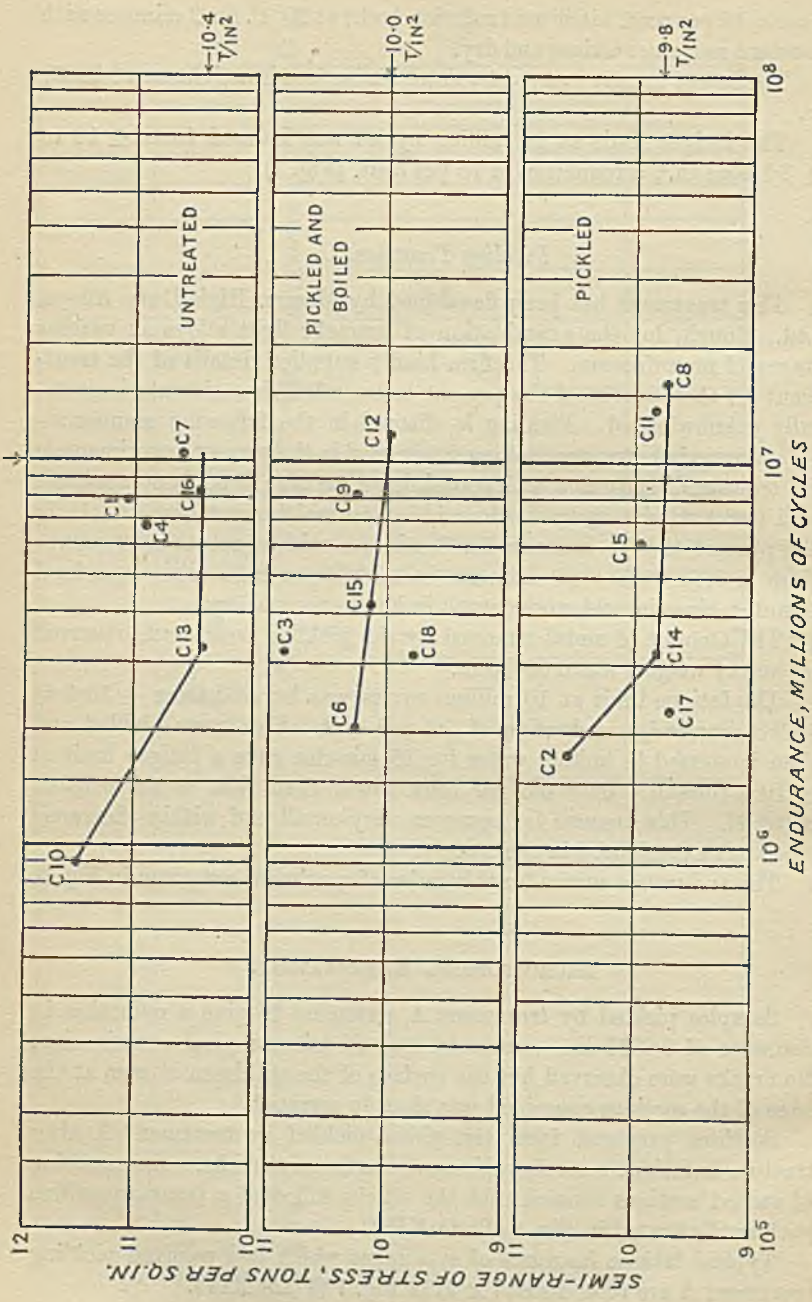

Fig. 3.—Influence of Pickling on the Fatigue-Strength of Duralumin. Pickling Treatment C.

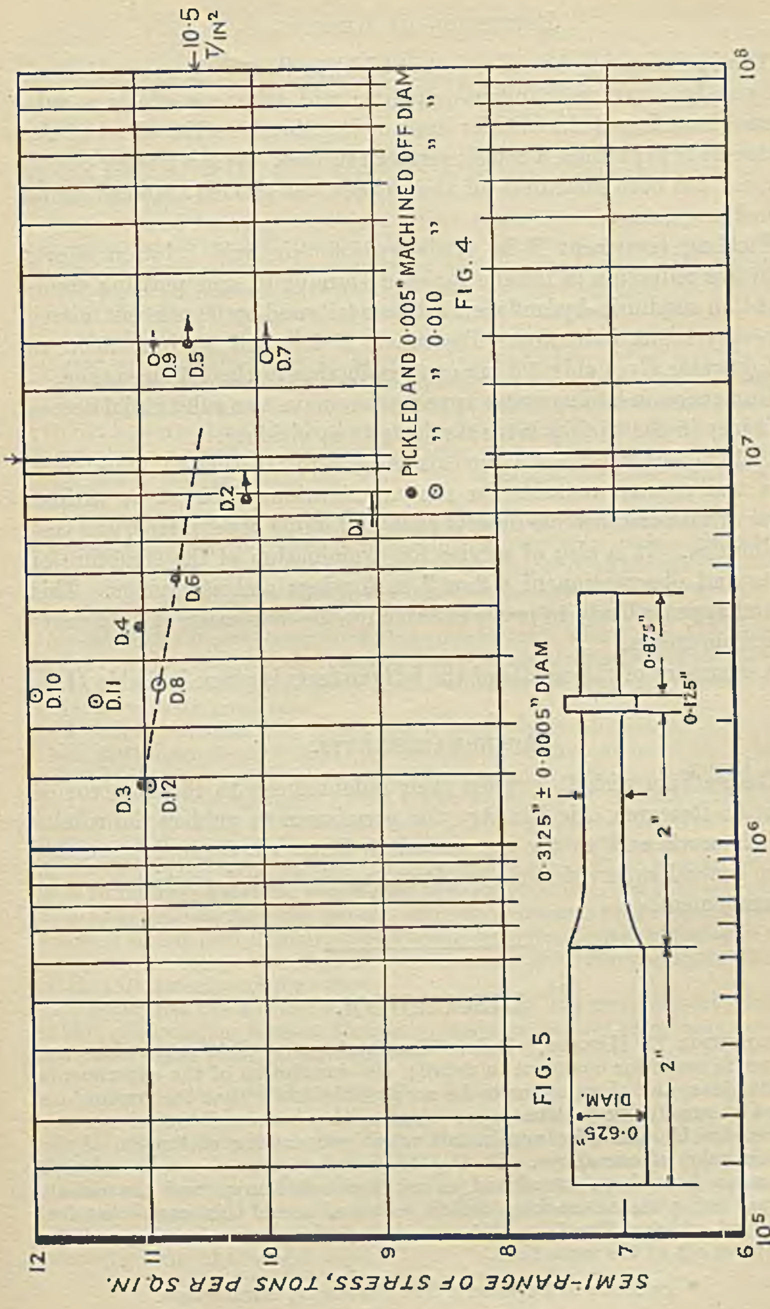

FIG. 4.—Influence of Pickling on the Fatigue-Strength of Duralumin. Effect of Machining after Pickling.
FIG. 5.—Standard Wöhler Test-Piece.

DISCUSSION OF RESULTS.

The investigation has shown that pickling in caustic soda solutions followed by cleaning in nitric–sulphuric acid solutions effects a substantial lowering of the Wöhler limit of Duralumin. The effect of the treatment is to produce a rough, serrated surface. When a layer 0·0025 in. thick has been machined off the surface, the pickled material shows normal properties.

Pickling treatment B in nitric–hydrofluoric acid solution effects much less reduction in fatigue range of Duralumin, and pickling treatment C in sulphuric–hydrofluoric solution followed by 50 per cent. nitric, only very slight reduction. Treatment C followed by immersion in boiling water gives only 3·8 per cent. reduction in the Wöhler range.

Immersion in boiling water appears to remove to a substantial degree the injury in the surface layer resulting from pickling.

Pickling by treatment C reveals the macrostructure of Duralumin parts and appears suitable for the examination of pieces at various stages of manufacture for defects such as forging cracks, laps, and discontinuities. It is also of service for examination of the structure of ingots and observation of "flow" in forgings and stampings. This method appears likely to prove suitable for the inspection of used parts for fatigue cracks.

A summary of the results of the fatigue tests is given in Table II.

ACKNOWLEDGMENTS.

The authors wish to express their indebtedness to the Director of Scientific Research, Air Ministry, for permission to publish the results of their work and to the Aeronautical Research Committee, under whose general supervision the work was carried out, for assistance and encouragement.

DISCUSSION.

PROFESSOR D. HANSON,* D.Sc. (Vice-President): This paper does not offer much scope for comment in detail; the description of the experiments is quite clear, and there seems to be no possible doubt that the conclusions arrived at are justified. The paper is interesting because it introduces one of those troublesome effects in metals which prevent the realization of the intrinsic value of our alloys. During the past few years a number of such phenomena have been introduced to us, the best known and the oldest, perhaps, being season-cracking which requires, as in this case, chemical action, but which differs from this case in that the chemical action and the stress must act at the same time.

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* Professor of Metallurgy, The University, Birmingham.

In the domain of steel some similar instances are found which prevent the realization of the intrinsic values of the material, particularly in the case of fatigue-strength in such things as springs, where the thin, decarburized layer which exists on the surface of the steel may result in a reduction of the fatigue-strength to about one-third of its normal value, whilst irregularities in the surface have also a very important effect. In the same way, steel forgings used in the unmachined condition which contain decarburized skin are damaged by the presence of this weak layer, which is very detrimental when fatigue stresses are present.

In corrosion-fatigue, introduced to us years ago by Professor Haigh, and recently elaborated by Dr. Gough in his Autumn Lecture, chemical actions may also prevent the realization of the intrinsic strength of the materials.

All these phenomena have an important practical significance, and often account for failures which are otherwise difficult to explain.

I should like to make a plea for further study in order that the cause of the one now described may be known. It occurred to me at first that this might be accounted for by the irregularity of the surface which pickling produces, and which results in a reduction in strength in some other materials. I think, however, that the evidence of the paper is quite conclusive, that that is not the case, because heating in boiling water, for example, restores the properties to a large extent but would not, of course, alter the contour of the surface.

The evidence seems to show that, as in some of the other instances which I have mentioned, the effect is confined to a very thin surface layer which differs in some way from the body of the material, and, as the effect is so pronounced under fatigue stresses, it suggests that this layer is weaker. The first guess that one would make would be that the tensile strength or the corresponding fatigue-strength of this surface layer was lower, but it might be due to a very serious embrittlement and practical destruction of the ductility in that layer, leading to an early crack, which would propagate itself, once it had started, with great ease.

I wonder whether the phenomenon might be analogous to that shown when metals are electroplated, particularly in conditions in which a highly stressed coating is produced on the surface, which results in a serious diminution of the fatigue-strength. That rather leads one to consider the kind of possibility which Mr. Sutton must have in mind, that the introduction of gas to the surface layer might set up conditions of severe internal stress in that skin which, when superimposed on the applied stresses, as in a fatigue test or as in fatigue in service, might lead to early cracking. In that connection, it is now known that the penetration of hydrogen, produced by electrochemical action, into aluminium does occur, and occurs with comparative ease; and I would suggest that that may be the most profitable line along which to tackle this question at the outset.

I hope that the authors and the Air Ministry will carry the investigation of this phenomenon further, because it seems to be very important and may have very great practical significance.

Dr. R. Seligman,* F.Inst.Met. (Past-President): I hoped that the authors would exhibit some pictures of the surface of their test-pieces, because to me—as to Professor Hanson—it does not seem at all clear whether this is a mechanical or a chemical phenomenon. Professor Hanson questions the possibility of its being mechanical because on boiling the specimens in water the phenomenon disappears. Does this follow? What I had hoped to see from the photographs was whether boiling in water does not change the surface by removing some of the high points.

* London.

Another point which occurred to me was whether, during the first stage of the treatment, the pickling agent penetrates the surface and is not removed until the boiling process is carried out, so that there may be a combination of chemical and mechanical action, in other words, corrosion-fatigue. This seems possible when the pickling agent is caustic soda and I suggest that the authors might try prolonging the treatment in nitric acid so as to remove the final traces of the pickling agent. In the later processes of pickling caustic soda is not used, and some alternative but possibly analogous explanation would be necessary.

Dr. I. G. SLATER,* M.Sc., Ph.D. (Member): The authors have certainly the distinction of being the first authorities to direct our attention to the effects of chemical pickling on the physical and mechanical properties of non-ferrous metals. Phenomena involved in the acid pickling of steel have been studied by a number of investigators, and Mr. Sutton has himself contributed much information on this subject.

With steels, the embrittling effect produced is shown by a number of physical and mechanical tests; for example, the percentage elongation and percentage reduction of area are much reduced, inferior results with bending and torsion tests are obtained, the fatigue-strength is reduced, and the properties of ductility, as of wire, are seriously impaired, as shown in subsequent drawing operations. These effects in steel have been shown to be mainly of a temporary nature, since by allowing the pickled and embrittled specimens to stand for several days, or by heating to 100° C. for a few minutes, as by immersion in boiling water, the embrittling effects are removed and the original properties of the metal gradually reappear.

It is of interest to compare these observations in the case of steels with those recorded by the authors in the case of Duralumin. The authors' tests are, of course, confined only to fatigue-strength determinations, and, as with the steels, it is observed that the deterioration is essentially only of a temporary nature, and the original properties are restored by heating in boiling water, or at least these properties are nearly restored. I take it that the lack of complete recovery might be explained by the erosion of the surface of the specimen as by etching, as Professor Hanson has indicated.

The effects produced with Duralumin differ from those observed in steels in one rather marked respect. With Duralumin the deterioration is apparently confined to a very superficial layer, something less than about 0·005 in., whereas with steels the effects resultant on pickling may penetrate to considerable depths in the specimen, depending on the severity of the pickling operation. With severe pickling the effects can be discovered at the centre of a bar 1 in. in diameter. We see, therefore, that with Duralumin the mass effect is somewhat different from that with steels. Perhaps longer times of immersion or more severe pickling might show that with Duralumin the effects penetrate deeper than the 0·005 in. or so which has been observed.

With regard to the cause of the deterioration, it is to be presumed that, as with steels, the effects are due to the absorption of nascent hydrogen by the metal, since in the pickling by these processes nascent hydrogen is the initial product of reaction between metal and acid. The authors will no doubt continue their investigations, and it will be interesting and valuable to have their observations on the results of pickling in which they use other forms of test, including the impact test. In further work I suggest that they employ electro-chemical pickling as cathode in some suitable electrolyte, for by that means no attack of the metallic surface will occur, and the effects essentially due to the absorption of hydrogen, if we understand the deterioration as being due to that cause, will be more clearly distinguished.

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

Mr. A. J. Murphy * (Member): This is a very interesting record of experimental results on which we know we can rely absolutely. At the same time, it is a pity that the authors have so rigorously declined to speculate on the theory of the action.

My object in speaking is to direct the authors' attention to a paper on the effects of hydrogen on steel wires recently published by Bardenheuer and Ploum,† who worked with mild steel wires which were charged with hydrogen both by pickling in hydrochloric acid solution without restrainer and also by using the steel as a cathode in the electrolysis of sulphuric acid. They made what is, if correct, a very significant observation, namely that in the wires embrittled by the absorption of hydrogen the original ductility was never completely restored, although all the hydrogen might be removed; also, that the more slowly the hydrogen was removed, as by resting at room temperature for some weeks, the less the permanent damage, whereas if the hydrogen were taken out by immersion in boiling water there was a larger amount of permanent damage. They continued their work with reference to brazing and showed then that if a freshly pickled mild-steel wire were plunged into molten brass the ejection of hydrogen was so violent that there was very severe permanent mechanical damage of the wire.

Bardenheuer and Ploum followed the changes in properties by bending and torsion tests, and advanced a theory—originally proposed, I believe, by Professor C. A. Edwards in his work on the pickling of tinplate—that, being atomic, the hydrogen formed in pickling can diffuse in that form into the steel, but on encountering anything in the nature of mechanical discontinuity, such as the boundary of a non-metallic inclusion, the atomic hydrogen comes out of solid solution and forms molecular hydrogen, which cannot diffuse freely in ferrite. Large pressures can be built up in this way, which these German authors suggest can produce damage by actual mechanical disruption.

Mr. E. Wood ‡ (Member): The academic aspects of this subject have already been dealt with, and I will confine myself to a strictly empirical consideration of one or two experiments which we have carried out during the last week or so, following a visit by Mr. Sutton to our works. In the aircraft industry this etching is very important, and for some time past we have used the hot paraffin and French chalk method on new designs of aluminium alloy components. In case some members may not know of that, it merely consists of immersing the component in hot paraffin or a similar liquid of low viscosity, putting it aside for a few moments to dry, and then immersing it in French chalk. On cooling down, the liquid which had entered the cracks oozes out and shows as a line on the chalk. That was done because we were afraid of the effect of the lowering of the fatigue on such components as pistons, especially on test engines in single-cylinder research work, when etched with caustic soda.

Following the publication of the present paper, Mr. Sutton happened to be at our works, when we told him we were very interested in this process, but that we did not like using strong hydrofluoric acid in the works. He suggested that we should use a solution of 1 per cent. sodium fluoride and 10 per cent. sulphuric acid. This was only a week or two ago, and the holidays have intervened, so that we have not done very much work; but some has been carried out in the laboratory, and from the point of view of fatigue cracks and so on we find that that is quite satisfactory, and we intend to go on with it.

From the point of view of macro-etching, we do not find it anything like

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* Chief Metallurgist, J. Stone and Co., Ltd., Deptford.

† *Mitt. K.W. Inst. Eisenforschung*, 1934, 16, (11), 129–136, 137–140.

‡ Senior Assistant, Laboratory, Bristol Aeroplane Company, Ltd., Bristol.

so good on a forged component as Vilella's nitric–hydrofluoric reagent with glycerine diluent. There again I apologize to Mr. Sutton, because we have only carried out a very few rough experiments, but I think that I could not possibly photograph the macrostructure of a heat-treated specimen after using this reagent. That may be due to the fact that, as we have found before, after heat-treatment, and especially after running in an internal combustion engine, the macrostructure is obscured and cannot be developed.

Mr. C. E. **Stromeyer**,* O.B.E.: Though I have carried out many experiments on fatigue, I am not certain what is really meant in these papers by fatigue. Is the meaning that experiments have been made showing that the failures are due to fatigue or that the fractures are fatigue fractures, and if so what is the nature of the fractures?

I should like to show some results obtained in some fatigue tests which I carried out on mild steel. I obtained comparatively straight lines both for the steel as originally rolled and also for steel which had been boiled in caustic soda; but for the rolled steel I obtained a line the inclination of which represents the modulus of elasticity, 30×10^6. For steel which had been boiled in caustic soda I obtained only 20, showing that the nature of the steel had been altered by boiling, and, what is of great importance, this line is fairly straight, showing that the effect of boiling in caustic soda has penetrated to the very centre of the test-pieces, which were $\frac{3}{8}$-in. square, whereas if the fatigue line had been curved it would mean that the caustic effect had penetrated only a small distance from the surface. These experiments might be continued in the direction of observing both the fatigue stress and the fatigue angle. At the National Physical Laboratory a few days ago I saw a new machine which would enable both these observations to be made. It would be of interest with regard to this subject to ascertain the depth of penetration of the pickling effect.

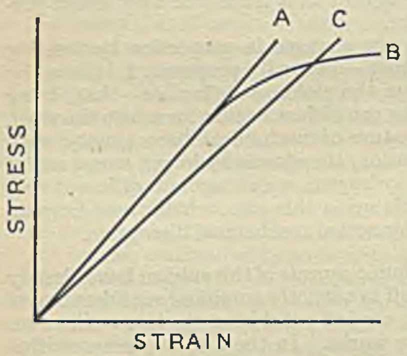

Fig. A.

I started work on the caustic embrittlement question twenty years ago, in 1914, and I have had various curious experiences, one being that the rivet heads broke off. The effect of the caustic fluid, in many cases steam, had gone right through plates 1 in. thick, and the heads of the rivets had broken off on the outside. In one serious case a dozen rivet heads were knocked off. The heads broke off at the top, so that the effect of the caustic fluid had penetrated through 3 in. I cannot imagine that it would have gone to that distance; I think that it was some caustic effect which travelled. There is a possibility that acids may do the same.

Professor F. C. **Thompson**,† D.Met., B.Sc., M.Sc. (Member): A good deal has been said this morning, and properly so, concerning the analogy between the results which the authors have obtained and the results obtained on steel. There is one aspect of the pickling brittleness of steel which has not been emphasized, and that is that with electrolytic pickling the brittleness may be

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* Manchester. † Professor of Metallurgy, The University, Manchester.

almost, if not entirely, removed. Have the authors any evidence of a similar effect in the materials with which they have dealt?

Mr. SUTTON (*in reply*): Professor Hanson referred to the case of steel and corrosion-fatigue. His remarks will be very carefully studied in detail. If we are allowed to do so we shall carry the matter considerably further. We have already done some further work and Mr. Wood has referred to one development; we hope, however, to study the mechanism of the embrittlement.

We agree that irregularities of the surface may be of great importance, and may be the cause of the permanent effect.

The examination of sections of these pickled materials is a matter of great difficulty. The serrations produced on the surface are very small and high-power photography is necessary in order to see anything. With prolonged periods of pickling, however, we see more, and the more detrimental forms of pickling undoubtedly give deeper fissures. I hope that if our further work is published we may be able to show this effect.

It may be that the serrations are the result of damage by hydrogen; for instance, if there is a strong expansion of the material in the surface layer cracking must result, and it may be part of the effect rather than the cause. An increase of volume is usually obtained, I think, when hydrogen is absorbed in considerable quantity. Those remarks bear upon some of the points mentioned by Dr. Seligman.

With regard to prolonging the treatment in nitric acid, I think that would be a very interesting experiment, because it might be possible to remove the most damaged layers by the nitric acid treatment.

Dr. SELIGMAN: I did not mean that; I meant to remove from the surface layer anything which might be causing chemical damage. That was my point.

Mr. SUTTON: That might be so; it might have either of those two effects, and if so it would be valuable, and interesting, of course, from the scientific point of view.

Dr. Slater made some very interesting suggestions. We have studied the pickling of steel, as he said, and we found that short-time pickling operations caused the embrittling effect to penetrate 0·010 in., which is much more than was found in the present case. We are, however, dealing here with relatively short-time pickling operations, and very deep penetration would hardly be expected in those short times.

In further work, we should like to include further tests—impact tests, bending tests, and so on—as mentioned by Dr. Slater and also electro-chemical pickling to escape the embrittlement.

Mr. Murphy referred to the interesting paper recently published by Bardenheuer and Ploum and to a paper previously published by me on pickling of steel.* It was found that the embrittling effect of pickling was rarely removed completely when it could be observed with any degree of accuracy, and in that respect our results were in agreement with those of Bardenheuer and Ploum.

Mr. Wood mentioned a recent suggestion of ours, that sodium fluoride and sulphuric acid should be used instead of a mixture of hydrofluoric acid and sulphuric acid. The handling of hydrofluoric acid in commercial establishments is dangerous, and for shipment to outlying works and places in other countries it would be a great convenience if sodium fluoride and sulphuric acid could be used. I am glad to know that Mr. Wood has had promise of some success on his specimens.

Mr. Stromeyer mentioned some interesting experiences of deep penetration

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* *J. Iron Steel Inst.*, 1919, 119, 179–202.

of hydrogen in steel. We do not know the effect of pickling on the elastic modulus of Duralumin.

With regard to Professor Thompson's remarks on anodic pickling, we have not so far devoted any attention to the electrolytic pickling of Duralumin, but in the case of steel it must be treated with caution. It is possible to get quite severe embrittlement during anodic cleaning of steel in certain electrolytes. In cathodic cleaning in certain alkaline baths it is possible to avoid embrittlement, but in anodic cleaning usually the current densities must be high. It is rather dangerous, in our experience, to assume that electrolytic pickling of steel does necessarily obviate hydrogen embrittlement. It can do so under correct conditions, however.

ELONGATION VALUES OF COPPER AND COPPER-RICH ALLOYS.*

678

By MAURICE COOK, M.Sc., Ph.D.,† MEMBER, and EUSTACE C. LARKE.‡

SYNOPSIS.

A study has been made of the effect on elongation values of dimensional variations in test-pieces of copper and copper alloys in strip form. H.C. copper, 70 : 30 and 64 : 36 brass, 80 : 20 cupro–nickel, and 95 : 5 gilding metal have been investigated, and it has been found that varying the length of parallel portion on 0·5-in. wide test-pieces from 1·5 to 8·5 in. has no appreciable effect on the total elongation values measured on a 1-in. gauge-length. Varying the metal thickness between 0·125 and 0·020 in. does not sensibly affect the elongation, but with metal thinner than 0·02 in. the elongation values decrease with decreasing thickness. With variation in width from 0·25 to 1·5 in. the elongation decreases with decreasing width, the effect being smaller as the gauge-length is increased. Variation in the rate of strain between the limits of 0·06 and 0·55 in. per inch of gauge-length per minute does not appear to affect the elongation values.

The effect of gauge-length on elongation values has been considered in detail for the five materials in the soft condition and for 70 : 30 brass of varying hardness, and a study made of the distribution of elongation along the gauge-length. Values for total and uniform elongation have been obtained and compared with those derived from characteristic formulæ such as those of Unwin, Bach, Bertella, and Krupkowski. The extent of the effect of the local elongation due to necking has been investigated and its influence in connection with the effect of position of the fracture on the elongation considered.

IT is quite generally known that the elongation values obtained in the tensile testing of metallic specimens may be very considerably influenced by the shape and dimensions of the test-pieces used. The present work, which is concerned only with copper and copper-rich alloys in the form of strip material, was undertaken to ascertain the effect of variation in gauge-length on elongation values and the nature of these values. The effect of form of test-specimen on elongation values on other materials in strip form has been studied by several investigators, including Templin,[1] Nichols, Taylerson, and Whetzel,[2] and Kenyon,[3] but no such systematic data on copper alloys in strip form appear to have been

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published hitherto. The effect of thickness, length, and width of parallel portion, rate of extension, and varying thickness on the elongation values has also been examined.

In the course of the investigation, five materials, namely, 70 : 30 and 64 : 36 brass, H.C. copper, 80 : 20 cupro-nickel, and 95 : 5 gilding metal, have been considered. Many of the results obtained are similar for the different materials examined, and it has not, therefore, been considered necessary to reproduce all the experimental results. The effect of thickness, width, rate of extension, and varying hardness has therefore been recorded only for 70 : 30 brass, which serves as a typical example of the materials examined, whilst results obtained with other materials are given to illustrate the effect of varying length of parallel portion and varying gauge-length.

The same procedure for measuring elongation over varying gauge-lengths has been adopted throughout the work. In order to ensure that the fracture occurred approximately at the centre of the parallel portion, each test-piece was slightly reduced in width and tapered towards the centre for a distance of 1 in. each side to the extent of 0·002 in. Each test-piece was marked from end to end of the parallel portion in equal increments of 0·125 in., a Vernier height-gauge reading to 0·001 in. being used for the purpose. After testing, the lengths of the extended gauge-marks of each of the two halves of the test-pieces were measured, as illustrated in Fig. 1, with a travelling microscope, reading to 0·0004 in. In this illustration it will be seen that taking line (1) as the datum line for that half of the test-piece which is to the left of the fracture, the distances *A*, *B*, *C*, *D*, &c., were measured. Similarly with reference to line (6) as the datum line, distances ($F - E$), ($G - E$), ($H - E$), &c., were also measured. Finally the broken halves were placed together, the distance *E* was measured, and the percentage elongations were calculated on the original lengths of ($A + E$), ($B + F$), ($C + G$), ($D + H$), &c. The reduced widths and thicknesses were also measured

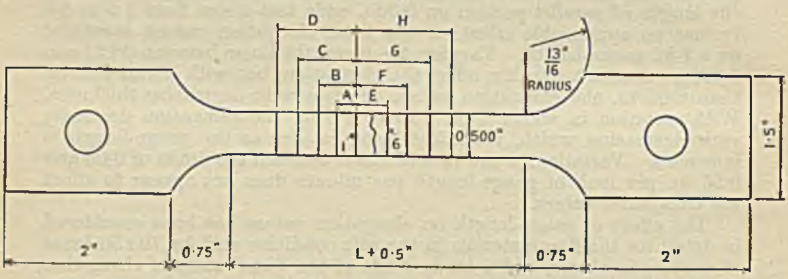

FIG. 1.

microscopically, the percentage reduction of area being then obtained in the usual way.

Effect of Length of Parallel Portion.

Before considering the effect of variation in gauge-length on elongation values, it is necessary to know whether, with a fixed gauge-length, varying the length of the parallel portion has any appreciable effect on the values obtained. In order to establish this point 0·5 in. wide test-pieces of all five materials with parallel lengths of 1·5, 2, 2·25, 4·5, 6·5, and 8·5 in. were broken, and with reference to a gauge-length of 1 in., the percentage elongation values obtained from these tests are illustrated in Fig. 2, from which it will be seen that the percentage elongation in general is not appreciably affected by the length of the parallel portion over the range considered.

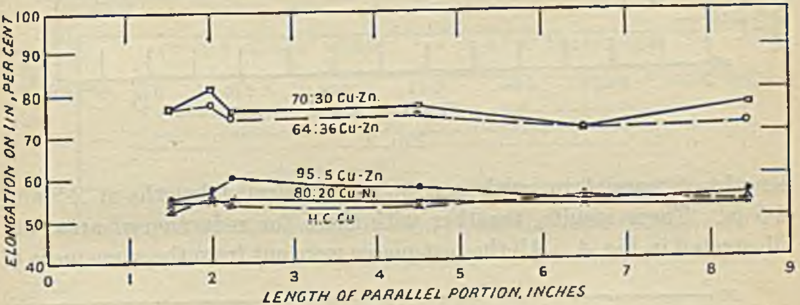

Fig. 2.

Effect of Thickness.

To determine the effect of thickness, 0·5 in. wide test-pieces of 70 : 30 brass with an 8-in. gauge-length were cut from 16 samples ranging in thickness from 0·125 to 0·010 in. The gauge-length on these test-pieces was accurately divided as already indicated into ⅛-in. lengths. Elongation values for all the gauge-lengths ranging from 0·25 to 8 in. were determined, and those obtained on 2-in. gauge-lengths are shown in Fig. 3. The reduction of area and tensile strength values are also shown in this figure. All samples of the series subsequent to the first one were annealed together to ensure uniformity of temper, the tensile strength values indicating that this required uniformity was secured. The results obtained indicate that variation in thickness of the test-piece between the limits 0·125 and 0·020 in. does not appreciably affect the elongation values.

Effect of Width of Parallel Portion.

The effect of variations in width of the parallel portion from 0·25 to 1·5 in. has been determined on test-pieces of 70 : 30 brass with gauge-lengths of 2 and 4 in. with corresponding parallel lengths of 2·5 and 4·5 in. These results, together with those for reduction of area, are illustrated in Fig. 4. All the test-pieces were cut from the same piece of strip, which was 0·06 in. thick. In addition to measuring the elongation of the test-pieces on the maximum gauge-lengths of 2 and 4 in. on the two series of specimens, measurements of elongation were also made

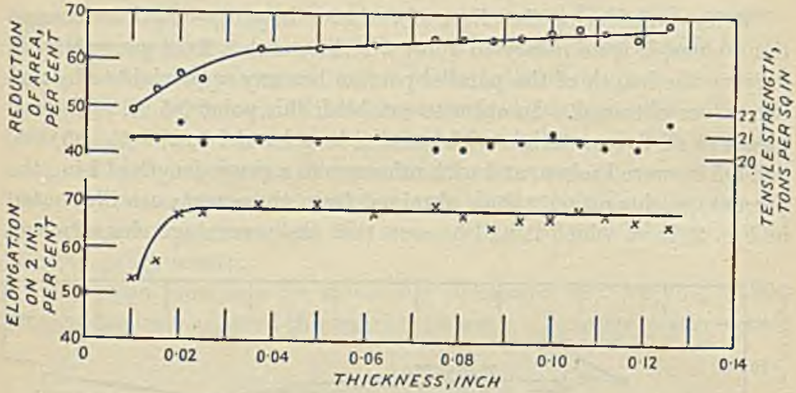

Fig. 3.

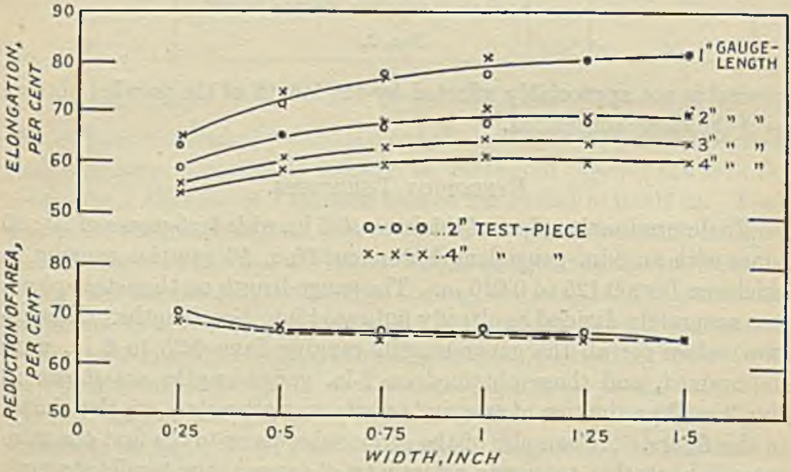

Fig. 4.

on gauge-lengths of 1 in. for both series and on gauge-lengths of 2 and 3 in. on the 4-in. series. The results indicate that the elongation values tend to increase with increasing width, and although for the range of widths considered the actual amount is appreciable, the evidence shows that the curves tend to flatten out rapidly. The curves also show clearly that the effect of width on elongation values decreases with increasing gauge-length. The form of the fracture as the width was increased showed an interesting feature, for with the narrow specimens the break was normal to the axis of the test-piece and deviated from this position in a regular manner as the width increased, until at the maximum width considered, namely, 1·5 in., it occurred at an angle of about 65° to the axis. This observation agrees well with that of Sachs and Stenzel[4] on test-pieces of bronze strip.

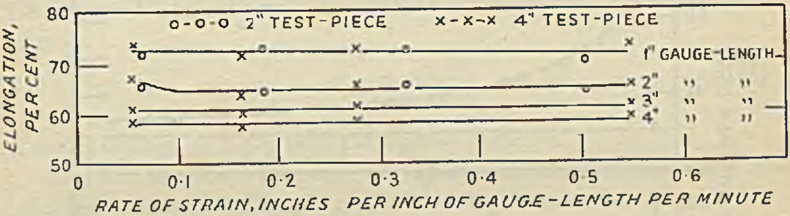

Fig. 5.

Effect of Rate of Strain.

The results of percentage elongation measurements over gauge-lengths of 1, 2, 3, and 4 in. on 70 : 30 brass test-pieces 0·060 in. thick pulled in a tensile machine at different rates are illustrated in Fig. 5. Within the lengths considered, it would seem that the rate of strain has no appreciable effect on elongation values.

Effect of Gauge-Length.

The effect of gauge-length on elongation values was determined on specimens machined to allow of a maximum gauge-length of 8 in. The gauge portion of the test-specimens was 0·5 in. wide and 0·06 in. thick. Each test-piece was accurately marked as already described, the parallel portion being divided from end to end in equal increments of 0·125 in., this enabling a range of gauge-lengths varying from 0·25 to 8 in. to be used. The percentage elongation was then calculated for each of the 32 gauge-lengths, and curves showing these results are given in Fig. 6. The reduced widths and thicknesses were also measured microscopically and the percentage reduction of area was calculated. By reference to the curves in Fig. 6 it will be seen that the percentage elongation decreases

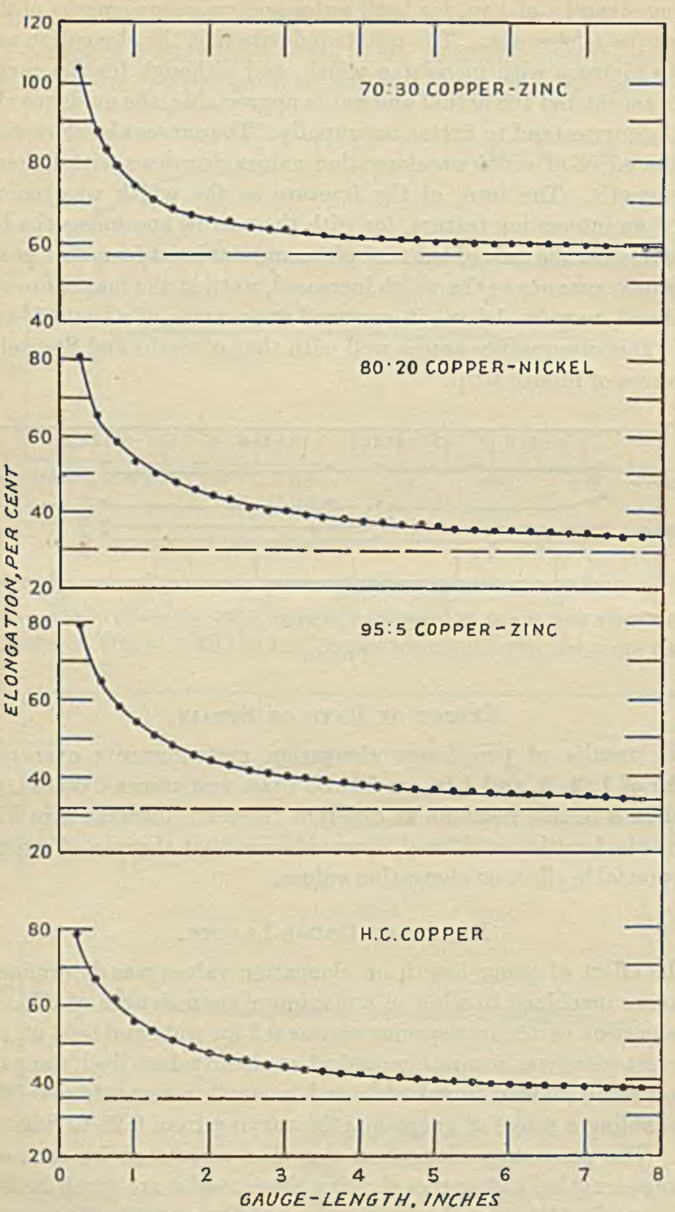
120
100
80
60
40
70:30 COPPER-ZINC
80
60
40
20
80:20 COPPER-NICKEL
80
60
40
20
95:5 COPPER-ZINC
80
60
40
20
H.C. COPPER
ELONGATION, PER CENT
0
1
2
3
4
5
6
7
8
GAUGE-LENGTH, INCHES

Fig. 6.

with increasing gauge-length, the curves tending to become asymptotic to a line parallel to the abscissa.

The effect of shape and gauge-length of test-pieces on elongation values have been the subject of much study, and Barba [5] as long ago as 1880 stated that geometrically similar test-pieces yielded similar elongation values. Unwin [6] deduced the following expression for connecting the elongation with gauge-length :—

$$e = a + \frac{C\sqrt{A}}{L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(I)}$$

e being the percentage elongation on any gauge-length L, a the value of the percentage elongation as L approaches infinity, C a constant for the material under consideration, and A the initial cross-sectional area. This relationship has also been put forward independently by Tetmajer, Tiedemann,[7] and others, In 1902 Bach [8] suggested the empirical formula

$$e = a + \frac{K}{\sqrt{L}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II)}$$

K being defined as a constant for a given material.

In 1922 Bertella [9] proposed an exponential relationship which was later put forward by Oliver [10] in the following form :—

$$e = KL^a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(III)}$$

where e and L are the percentage elongation and gauge-length respectively, K and a being constants for any given material, the former being a function which was found to vary with the initial cross-section.

Later Krupkowski [11] put forward the following relationship :—

$$e = a + \frac{C - a}{km(C - a) + 1} \quad . \quad . \quad . \quad . \quad . \quad \text{(IV)}$$

where e is the percentage elongation, a the value of the percentage elongation as the gauge-length approaches infinity, C a function of the reduction of area, m the quotient of the gauge-length and a function of the initial area, and k a constant for the material under consideration.

According to Krupkowski, if m is the length between gauge-marks expressed as diameter of the test-piece, then $m = \frac{L}{d}$, d being the original diameter of the test-piece if its section is circular and an equivalent quantity if otherwise. Since the experimental work has been confined to rectangular test-pieces, d has been taken as the diameter of a test-piece of equivalent area to that of the rectangular test-piece. In these several relationships only IV includes the reduction of area which occurs when a tensile test-piece is broken.

All these formulæ can be used for obtaining the elongation on any gauge-length from elongation measurements on two different gauge-lengths obtained directly on one specimen. The experimental results are shown in Fig. 6, and a full comparison has been made with these values and those calculated from the several formulæ. Whilst the details of this comparison are not reproduced, a number of percentage elongation values on gauge-lengths of 0·25, 0·75, 2, and 7 in., as calculated from formulæ I, II, and IV, are given in Table I, as well as those actually observed, the latter values on 1 and 8 in. gauge-lengths being used in computing the former. In the same table are included reduction of area, tensile strength, and Diamond Pyramid hardness values, and also the calculated values to which the actually determined curves tend to become asymptotic. Values for total percentage elongation calculated from these formulæ are in excellent agreement with the actually determined values on gauge-lengths above 1 in. for all five materials. Between gauge-lengths of 0·75 and 8 in. the results calculated from the three formulæ agree to within ± 2 per cent. elongation of the actually determined values, with two exceptions, which are 2·8 and 2·9 per cent. On smaller gauge-lengths, however, there is greater divergence between the results obtained from the formulæ and experimentally determined values. In this region the results calculated from the formula of Bach are closer to the experimentally derived values than are those determined from the other two formulæ.

If in the case of formulæ I, II, and IV percentage elongation values are plotted against the corresponding function of the gauge-length, the observed values can be connected by a straight line over the range from 8 in. down to about 1 in. This indicates that between these limits of gauge-length the formulæ are correct in the sense that it is possible to obtain from them values for elongation which are the same as those obtained by direct experimental determination. On the other hand, for a similar range of gauge-lengths, it will be seen by reference to Fig. 7, where the logarithms of percentage elongation values are plotted against the logarithms of gauge-lengths for all five materials in the soft condition, that the lines connecting these experimental points are not straight, and for this reason no results calculated from formula III are given in Table I. The results shown in Fig. 7 do not agree with those of O'Neill and Cuthbertson,[12] who showed a straight-line relationship for soft copper between the gauge-lengths of 1 and 5 in.

Analysis of the four formulæ already referred to shows that as the gauge-length approaches zero the percentage elongation according to formula IV approaches a constant value for any given material, while according to formulæ I, II, and III the percentage elongation approaches

TABLE I.—*Calculated and Determined Elongation Values on Copper Alloys in the Annealed Condition.*

Material.	Total Elongation on 0·25 in., Per Cent.				Total Elongation on 0·75 in., Per Cent.				Total Elongation on 2 in., Per Cent.				Total Elongation on 7 in., Per Cent.				Uniform Elongation, Per Cent.			Tensile Strength, Tons/in.².	D.P. Hardness (10 Kg.).	Reduction of Area, Per Cent.
	Observed.	I.	II.	IV.	Observed.	I.	II.	IV.	Observed.	I.	II.	IV.	Observed.	I.	II.	IV.	I.	II.	IV.			
70 : 30 Cu–Zn	108·0	132·0	101·5	113·5	81·8	82·4	80·1	81·6	67·1	66·9	68·8	67·3	60·3	60·3	60·5	60·3	57·6	51·0	57·3	20·9	65	68·6
64 : 36 Cu–Zn	109·5	123·0	95·6	105·5	77·2	78·5	76·4	77·7	65·3	64·6	66·3	64·9	58·5	58·6	58·8	58·5	56·2	50·2	55·8	21·2	66	65·8
80 : 20 Cu–Ni	81·2	121·5	84·4	89·7	58·4	61·2	58·4	59·7	44·2	42·3	44·6	43·2	34·1	34·1	34·4	34·2	30·9	22·8	30·2	21·3	71	60·0
95 : 5 Cu–Zn	80·0	121·5	84·3	106·5	58·7	61·6	58·8	60·9	44·3	42·9	45·2	43·1	34·9	34·9	35·3	34·8	31·7	23·8	31·4	16·3	59	78·2
H.C. Cu	78·3	114·5	83·6	90·4	61·0	61·8	59·4	60·9	46·3	45·3	47·3	45·9	38·1	38·2	38·4	38·0	35·4	28·2	34·6	15·7	57	61·8

TABLE II.—*Calculated and Determined Elongation Values on Cold-Worked* 70 : 30 *Brass.*

	Total Elongation on 0·25 in., Per Cent.					Total Elongation on 0·75 in., Per Cent.					Total Elongation on 2 in., Per Cent.					Total Elongation on 7 in., Per Cent.					Uniform Elongation, Per Cent.			Tensile Strength, Tons/in.².	D.P. Hardness No. (10 Kg.).	Reduction of Area, Per Cent.
	Observed.	I.	II.	III.	IV.	Observed.	I.	II.	III.	IV.	Observed.	I.	II.	III.	IV.	Observed.	I.	II.	III.	IV.	I.	II.	IV.			
1H	131·5	161·0	115·0	...	131·0	83·6	86·3	82·7	...	79·7	65·0	62·8	65·8	...	63·5	53·0	52·8	53·2	...	52·8	48·8	38·9	48·2	21·2	63	73·3
2H	107·5	129·0	91·7	...	106·7	68·3	68·8	66·0	...	67·9	51·4	50·1	52·4	...	50·5	42·5	42·0	42·4	...	42·0	38·8	31·0	38·4	23·5	97	70·6
3H	93·7	124·0	79·6	...	80·6	60·7	52·4	49·0	...	49·0	31·5	30·0	32·8	...	31·1	20·8	20·4	20·9	...	20·6	16·6	7·2	15·6	26·8	122	57·4
4H	75·6	98·8	69·6	...	63·4	34·6	35·1	32·3	...	33·2	15·2	15·2	17·7	...	16·2	6·6	6·6	7·1	...	6·8	3·2	−5·2	2·4	31·3	151	54·4
5H	64·0	73·1	43·8	67·5	47·5	25·0	24·9	22·8	24·2	23·7	9·8	9·9	11·8	9·7	10·7	3·3	3·5	3·6	2·9	3·7	0·9	−5·8	0·5	35·1	162	49·3
6H	47·2	60·9	30·1	48·8	33·8	17·6	17·3	15·7	17·4	16·5	6·8	6·8	8·1	6·9	6·8	2·3	2·3	2·5	2·1	2·4	0·5	−3·9	0·2	39·2	172	41·8
7H	40·0	43·8	25·8	40·5	27·6	14·6	14·7	13·4	14·4	13·8	5·8	5·7	6·8	5·8	0·2	1·8	1·8	1·9	1·8	2·0	0·2	−3·6	−0·1	40·8	186	35·5

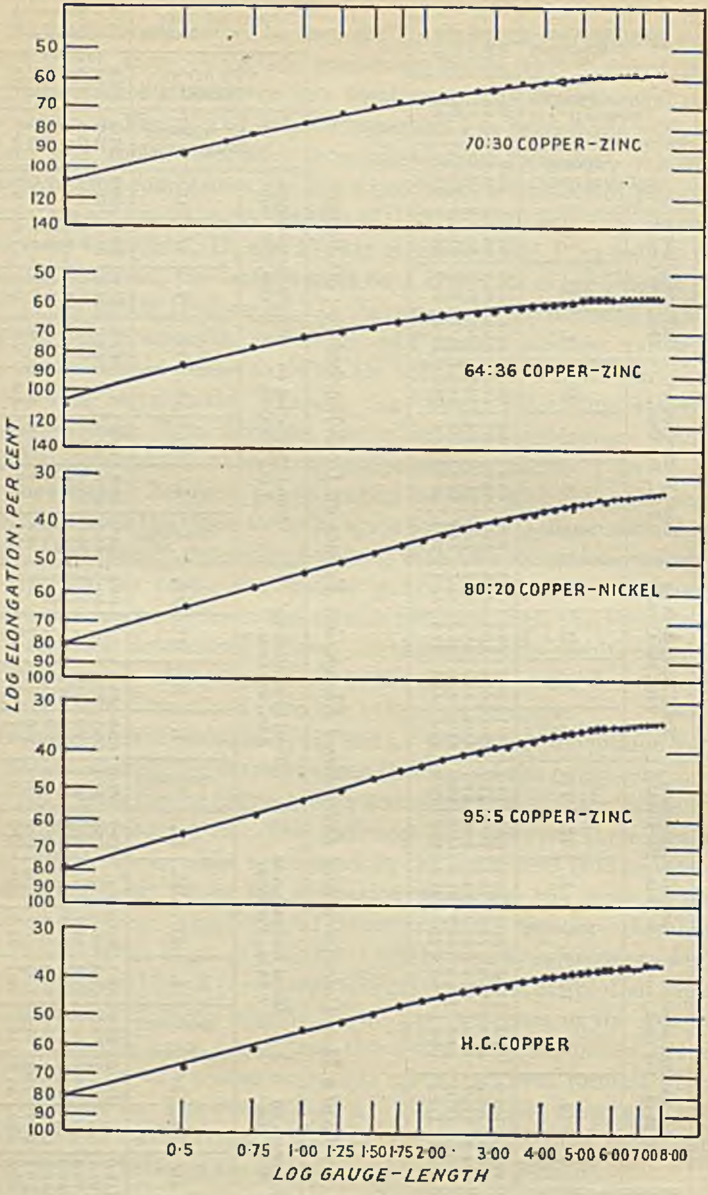

Fig. 7.

infinity. Formula IV indicates that the position at which the curves derived from it intersect the ordinate represent the maximum values of the percentage local elongation. At the other extreme, formulæ I, II, and IV indicate that the percentage elongation approaches a constant value as the gauge-length approaches infinity, whereas according to formula III, as the gauge-length approaches infinity the percentage elongation approaches zero, a condition which is contrary to experience. The constant values indicate for each material the percentage elongation which is independent of the gauge-length and not affected by the fracture. In other words, it represents the maximum value of uniform elongation of the material.

UNIFORM ELONGATION.

The total elongation as measured on broken tensile test-pieces includes the uniform elongation which occurs between the gauge-marks, together with the local elongation due to "necking" at the fracture. This value of elongation is not so characteristic for the material as the uniform elongation which constitutes a more accurate measure of the workability, ductility, or drawing quality. The chief requirements of materials for deep-drawing is the property of being able to withstand a large amount of elongation without local thinning or contraction, in other words, a high value for the uniform elongation. As the gauge-length is increased the effect of the local elongation decreases and the value for the total elongation approaches that of the uniform elongation. It is for this reason that the total elongation figures obtained on comparatively large gauge-length specimens are regarded as a more reliable indication of drawing quality than elongation values obtained on shorter gauge-lengths, because as the gauge-length increases the effect of local elongation becomes increasingly less, as is shown in Fig. 6, until its effect becomes very slight and the value obtained approaches that of the uniform elongation. As already noted, values for uniform elongation can be calculated from the formulæ from measurements of the total elongation on two different gauge-lengths on the test-specimen. Values obtained from equations given by Unwin and Krupkowski are almost identical, and for the different materials considered the average of these values are shown as horizontal broken lines in Fig. 6, being in fact the horizontal asymptotes of the curves. Values calculated from the formula of Bach are lower in each case than those obtained from these other formulæ, as will be seen from the results in Table I.

For the materials under consideration it is possible to determine experimentally the uniform elongation by other methods than that of measuring the total elongation on two different gauge-lengths and then calculating the uniform elongation from one of the several available formulæ. One method suggested by Vietórisz [13] consists of observing the initial position of the maximum load on a load/extension curve. This experiment has been carried out with 70 : 30 copper–zinc, 64 : 36 copper–zinc, 80 : 20 cupro-nickel, 95 : 5 copper–zinc, and H.C. copper, using a specimen with a parallel length of 6·5 in., the width and thickness of the parallel portions being 0·500 and 0·125 in., respectively. The test-pieces were each provided with symmetrical gauge-marks, 2, 4, and 6 in., and intermediate observations were made during the tensile test. The elongations on each of the three gauge-lengths, together with the accompanying reduction of width and thickness, were measured at load increments of, generally, 0·10 ton, the results in the case of the 70 : 30 brass being plotted in Fig. 8.

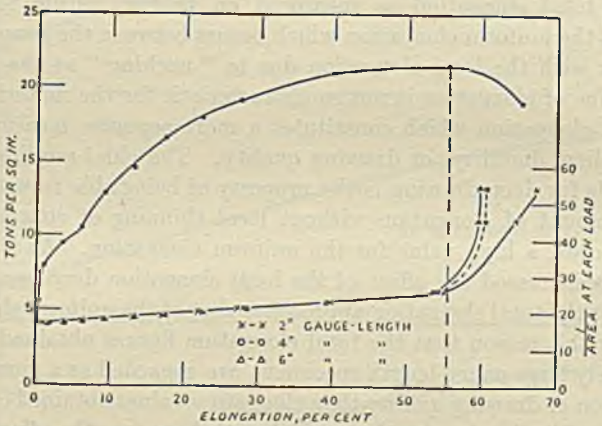

Fig. 8.

The lower curve in this figure was obtained by plotting the reciprocal of the area measured at each load against the corresponding percentage elongations for each of the gauge-lengths considered. By reference to this curve it will be seen that the percentage elongation from the beginning of the test to the point when the maximum load is first sustained by the specimen is independent of the gauge-length, and is therefore inversely proportional to the area at each load. In other words, the curve shows that the percentage elongation increases uniformly from the beginning of the test until the first application of the maximum load. The value of the uniform elongation may be obtained from the load/extension curve by drawing a line from the point indicating the beginning of the application of the maximum load to the abscissa, the value so obtained being strictly true only when the line drawn to meet the abscissa is parallel to that portion of the curve which lies below the limit of proportionality. Values of the maximum uniform elongation were also calculated for each of the samples tested, using the two gauge-lengths 2 and 6 in. and the corresponding percentage elongations, the resulting values being the mean of those derived from formulæ I and IV. In the case of the 70 : 30 brass, this value is represented by a vertical broken line in Fig. 8. For all the materials considered the differences between the experimental values and those calculated did not exceed 3 per cent. elongation.

The maximum uniform elongation may also be determined on one specimen by direct measurements if the gauge-length has been suitably sub-divided. This is based on the assumption that at distances appreciably removed from the fracture the elongation which results is not affected by the elongation caused by necking prior to fracture. It has been stated, however, that the value cannot be satisfactorily derived from measurements of test-pieces taken after fracture, and according to Kuntze and Sachs [14] uniform elongation continues after necking or local elongation has commenced. Haigh and Jones,[15] in a study of tensile tests on lead specimens, considered that for practical purposes it is essential to distinguish between stable distributed, that is, uniform elongation, and local elongation, and stated that an approximate value of the range of stable distributed elongation can be ascertained by measuring the elongation on a short gauge-length far removed from the fracture. The distribution of percentage elongation over the maximum gauge-length considered of 8 in. is shown in Fig. 9, for the five materials studied. These curves were obtained by measuring the percentage increase of each original 0·25 in. length, starting at one end of the parallel portion and passing in 0·125 in. increments through the fracture until the other end of the gauge-length was reached. The horizontal lines drawn through the curves for each of the five materials represent the average of the uniform elongation values calculated from the formulæ of Unwin and Krupkowski, and at distances removed from the fracture more than about 0·75 in. the elongation over the 0·25 in. gauge-lengths approximates to the uniform elongation. Local variations or "necking," of course, occur, and for this reason the method cannot be regarded as constituting an altogether satisfactory means of measuring local elongation, although generally the errors are not large and, as will be seen from Fig. 11, the irregularities tend to be less in magnitude with harder materials.

EFFECT OF POSITION OF FRACTURE.

As previously noted, the effect on the total elongation value of the extension due to local contraction consequent upon fracture decreases with increasing gauge-length, as the curves in Figs. 6 and 10 show.

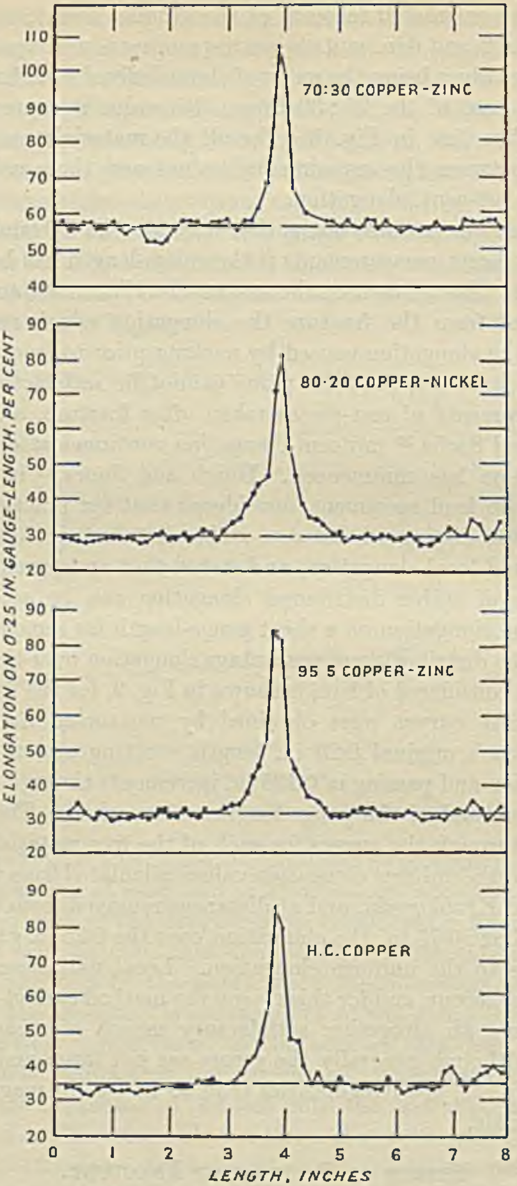

Fig. 9.

How far the extension due to necking extends along the length of the specimen varies with different materials, and for different types of test-pieces, but the evidence which has been obtained in the course of this investigation, as shown by Figs. 9 and 11, suggests that it is very local in character for the materials considered and the forms of test-pieces used. In this connection a point of considerable practical importance emerges with regard to the testing of these materials, namely, the influence of the position of fracture. As already described, total elongation values have been measured on many different gauge-lengths of each of the five materials, and specimens with a maximum gauge-length of 8 in. sub-divided into 0·125 in. divisions have been utilized for determining the effect of position of fracture. On such specimens it is possible to measure the total elongation relative to an original gauge-length of 2 in. with the fracture occurring at various positions between the gauge-marks by the simple expedient of moving the gauge-length relative to the fracture. An analysis which has been made in this manner of the data obtained for the five materials indicates that, provided the fracture does not occur nearer than 0·5 in. to an extended gauge-mark, the value of the total elongation on an original gauge-length of 2 in. is not reduced by more than about 2 per cent. elongation. Specifications commonly require that the fracture should occur within the middle third of the gauge-length, and British Standards Institution specification No. 485, Part 1, 1933, for tensile tests on thin strip and sheet, where flat specimens 0·5 in. wide with a 2·5 in. parallel length and 2 in. gauge-length are standardized, states that the fracture must occur within the middle half of the gauge-length. The results which have been obtained suggest that, for the material under consideration with this form of test-piece, no appreciable effect on the value of the total elongation over an original distance of 2 in. will be observed, provided that the fracture occurs within the middle two-thirds of the extended gauge-marks.

As would perhaps be expected, the data also show that the effect of the position of fracture on the total elongation values decreases with increasing gauge-length. With regard to gauge-lengths less than 2 in., the value of the total elongation rapidly decreases as the fracture approaches one or other of the extended gauge-marks. For the five materials under consideration at a thickness of 0·060 in. using a 1 in. gauge-length, the difference between the total elongation values for a central fracture and one 0·125 in. from an extended gauge-mark is about 8 per cent. elongation. In order to note the effect of the nearness of the radius to the fracture, specimens with a parallel length of 2·5 in. and gauge-lengths of 2 in. were deliberately fractured at various points between the gauge-marks. These observations confirm the finding that the effect of position of fracture on the total elongation, when measured across an original gauge-length of 2 in., is not appreciable unless it occurs within 0·5 in. of an extended gauge-mark, provided that the parallel portions of the test-pieces are 0·5 in. longer than the maximum gauge-length required.

ELONGATION MEASUREMENTS ON COLD-ROLLED 70 : 30 BRASS.

Elongation measurements have also been made on specimens cut from 70 : 30 brass strip, which had been subjected to progressive amounts of cold-rolling. Commencing with material in the soft condition at a thickness of 0·250 in., a series of seven samples was obtained down to a thickness of 0·100 in. with 10 per cent. reductions in thickness between each sample. Test-pieces cut from these were accurately marked before testing and measured microscopically, as previously described.

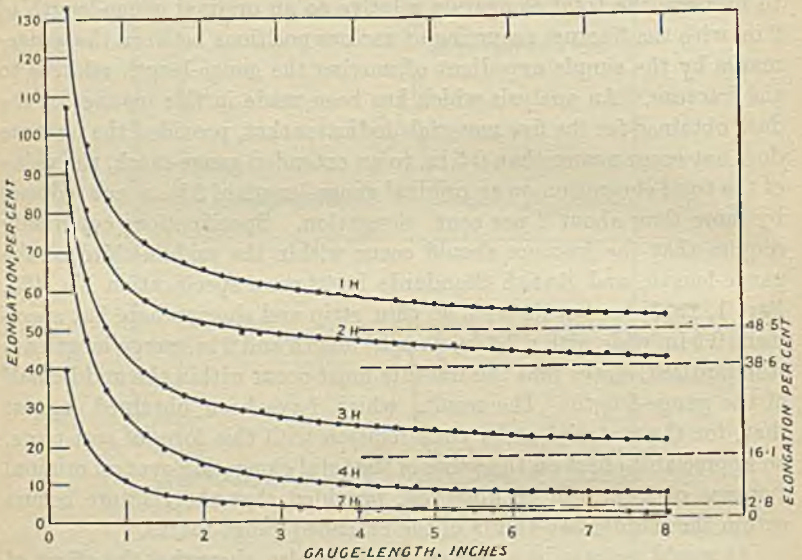

FIG. 10.

The results for five of the samples showing variations in elongation values with gauge-lengths ranging from 0·25 to 8 in. are illustrated in Fig. 10, from which it will be seen, as in the case of the soft materials, that the elongation decreases as the gauge-length increases. The horizontal lines shown in this figure represent the horizontal asymptotes of the curves. Each of these experimental results has been compared with those calculated from the several formulæ, the values both calculated and observed on gauge-lengths of 0·25, 0·75, 2, and 7 in. being given in Table II. For the purpose of calculation observed elongations on gauge-lengths of 1 and 8 in. were used.

By reference to Table II, it will be seen that for gauge-lengths ranging from 0·75 to 8 in. all the calculated values agree to within less than ± 3 per cent. elongation of the observed values, except in one instance, when the value calculated from IV is 3·9 per cent. elongation lower than the observed value of 83·6 per cent. With regard to the values calculated for the minimum gauge-length of 0·25 in., it is of interest to note that while there is a fairly constant difference of about 16 per cent. elongation between observed values and those calculated from formula II, the order of the accuracy of the calculated values derived from I and IV reverses, the values calculated from IV being in excellent agreement with the observed results for the two softest samples, whereas for the three hardest samples the closest agreement is obtained with formula I.

If the observed elongation values, together with the corresponding gauge-lengths, are plotted in a similar manner to the curves shown in Fig. 7, interesting results are obtained. For the softest sample, the points lie on a curve, but with progressive increases in hardness the curves tend to become straight lines. With sample No. 5H, for example, it is possible to connect all points from a 0·25 in. gauge-length to a 5·5 in. gauge-length with a straight line, and in the case of the hardest sample this is possible for the whole range of values from 0·25 to 8 in. gauge-length. Thus it will be seen for the harder samples that as the uniform elongation of the last three is negligibly small, being in fact less than 1 per cent., values for the total elongation calculated from the Bertella relationship, *i.e.* formula III, will be in agreement with the observed values, because the condition exists of zero uniform elongation which is necessary in applying this equation. Values calculated from this equation are therefore included in Table II for the last three samples.

The distribution of the elongation over the total length of the test-pieces is illustrated for five of the samples in Fig. 11, the horizontal broken lines, which are superimposed on the curves, representing the average of the values for the uniform elongation as calculated from formulæ I and IV. As in the case of the soft materials shown in Fig. 9, a certain amount of subsidiary necking takes place on the softer samples. With regard to the position of the horizontal lines which represent the uniform elongation, it would appear in the case of the two softer samples that the calculated values are slightly higher than the observed values, whereas for samples Nos. 4H and 7H the agreement of the experimental values with those calculated is excellent. A similar agreement was found for samples 5H and 6H, which, in order to avoid confusion, are not included in this illustration.

It will be seen from Table II that the uniform elongation values rapidly decrease with increasing hardness, and samples Nos. 5H, 6H, and 7H, which were reduced respectively 50, 60, and 70 per cent. in thickness by cold-rolling, have practically zero uniform elongation. In other words, the material which has been reduced this amount in thickness cannot be stretched without local thinning or contraction.

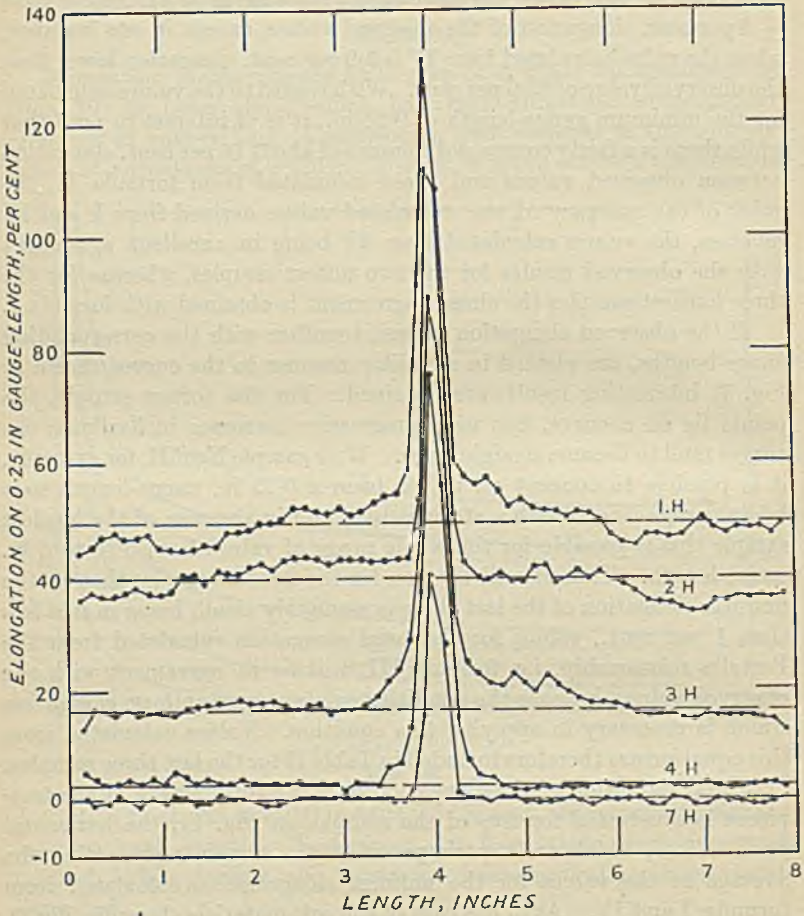

Fig. 11.

Summary.

In the testing of flat test-pieces 0·5 in. wide of H.C. copper, 70 : 30 and 64 : 36 brass, 80 : 20 cupro-nickel, and 95 : 5 gilding metal, varying the length of parallel portion from 1·5 to 8·5 in. has no appreciable effect on the total elongation values on 1 in. gauge-lengths.

If the metal thickness is varied between 0·125 and 0·020 in., the elongation values as measured on specimens of 2 in. gauge-length and 0·5 in. wide in the parallel portion do not appear to be affected, but with metal thinner than 0·02 in. the elongation values decrease rapidly with decreasing thickness.

With variations in width from 0·25 to 1·5 in. measured on specimens 0·06 in. thick, the elongation decreases with decreasing width, the effect being smaller as the gauge-length is increased.

Measurements on specimens of varying gauge-length up to 4 in. show that varying the rate of strain between the limits of 0·06 and 0·55 in. per in. gauge-length per minute does not affect the elongation values.

A detailed study has been made of the effect of gauge-length on elongation values, also of the distribution of elongation along the gauge-length of all five materials in the soft condition, and also for 70 : 30 brass subjected to progressively increasing amounts of cold-rolling. Values for total and uniform elongation have been obtained and compared with those derived from characteristic formulæ, such as those of Unwin, Bach, Bertella, and Krupkowski. Values obtained from the formulæ of Unwin, Bach, and Krupkowski for total elongation on gauge-lengths upwards of 0·75 in. agree extremely well with the actually determined values. Uniform elongation values derived from the Bach formula do not agree with observed values so well as those derived from the other two formulæ. With soft materials it is not possible to obtain from the Bertella formula values for comparison with actually determined values, for it has been found that when the logarithms of percentage elongation values are plotted against the logarithms of gauge-lengths, the lines connecting the experimental points are not straight, or at best can be regarded as straight only over a very limited range of gauge-lengths. As might be expected, the formula is found to be applicable for hard materials which possess little or no uniform elongation.

The extent of the effect of the local elongation due to necking has been investigated, and it has been found that provided that fracture does not occur nearer than 0·5 in. of a gauge-mark, the value for total elongation is not appreciably affected by the position of fracture.

ACKNOWLEDGMENT.

The authors' thanks are due to the Management Board of I.C.I. Metals, Limited, for permission to publish the results in this paper.

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DISCUSSION.

DR. H. O'NEILL,* M.Met. (Member): This paper is particularly interesting to me because it exposes the fundamental limitations of the empirical Bertella Expression III, given on p. 171. A few years ago Mr. Cuthbertson and I examined this logarithmic equation, and found that it held quite well for our particular test-pieces of copper. In our case L never exceeded $7\sqrt{A}$ for the unworked metal, and in discussing the paper at the time of its publication, Mr. Oliver warned us that the expression did not hold if $L > 10\sqrt{A}$.

The present authors are not able to confirm the logarithmic relationship. In the light of the above remarks this is to be explained by the extreme geometrical form of their test-pieces. With the 8 in. gauge-length on their H.C. copper for instance, $L = 46\sqrt{A}$; whilst on the soft 70 : 30 brass, $L = 23\sqrt{A}$. To keep below $L = 10\sqrt{A}$ the gauge-lengths of the copper strip should not exceed 1·7 in., in which case it may be observed from Fig. 7 that the appropriate experimental points would lie sufficiently well on a straight line.

Our object in adopting the Bertella–Oliver formula was to study quantitatively the decrease of "extensibility" $(1 + \alpha)$ and work-hardening capacity as copper was increasingly deformed. By plotting the present authors' figures for 70 : 30 brass, and taking 2 in. as the maximum gauge-length, the "extensibility" values recorded below in Table A were obtained. The results

TABLE A

70 : 30 Brass.		H.C. Copper.	
Reduction, Per Cent.	$(1 + \alpha.)$	Reduction, Per Cent.	$(1 + \alpha.)$
0	0·675	0	0·626
10	0·636	5	0·544
20	0·490	11	0·455
30	0·246	18	0·273
40	0·100	31	0·084
50	0·067	53	0·084
60	0·034	60	0·064

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which Cuthbertson and I obtained for copper are given alongside and show that the change of work-hardening capacity in the two metals is somewhat similar.

Dr. Cook (*in reply*): It ought to be made clear that the Bertella equation not only does not hold for conditions where the gauge-length is large relative to the cross-sectional area but it does not hold at all, for if percentage elongations and gauge-lengths are plotted logarithmically the resulting points cannot be connected by a straight line. This is because the equation is fundamentally unsound in not admitting of the existence of uniform elongation, although anyone who has had anything to do with the testing of the alloys referred to in the paper, whether in the form of flat test-pieces or otherwise, well knows that one of their outstanding characteristics is a large value for uniform elongation. The equation is only applicable to cold-worked materials where the amount of cold-work is such that the alloy no longer has any uniform elongation.

CORRESPONDENCE.

Mr. Reid L. Kenyon[*]: This is an excellent paper on the effect of shape and size of test-specimen on the tensile values. Although such data have been available on other metals, the corresponding results on copper alloys will be welcomed.

The results reported are in agreement in most respects with those obtained on various other metals, but there are a few exceptions that I wish to point out. The data presented in Fig. 3 indicate that above a thickness of 0·020 in., the percentage elongation is independent of the thickness of the test-specimen. With a constant gauge-length of 2 in. and a constant specimen width of 0·500 in. the slenderness ratio $L/\sqrt{A}$ changes with thickness. Templin,[†] Nichols, Taylerson, and Whetzel[‡], and Kenyon[§] have found that the percentage elongation decreases with increasing values of the slenderness ratio. The failure of the authors' results to follow this relationship raises a question as to the uniformity of the material of different thicknesses.

I have calculated the slenderness ratios corresponding to the elongation values plotted in Figs. 3 and 4. In Fig. A the circles represent the data from Fig. 4 which were obtained on material of the same thickness. Variation in slenderness ratio in this case is due to variation in specimen width. Although there is some irregularity in the location of the points, due no doubt to some extent to the difficulty in taking numerical values from Fig. 4, they follow the relationship indicated by the solid line. In other words, with uniform material, this 70 : 30 brass follows a relationship between slenderness ratio and percentage elongation similar to that found by other workers for aluminium and for iron and steel sheets. The crosses in Fig. A are for the data given in Fig. 3 and show an entire lack of relationship in this case. While some of the points lie reasonably near the line, there are more that do not, and I believe that this indicates lack of uniformity in the test material because the relation-

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[†] R. L. Templin, "Methods for Determining the Tensile Properties of Thin Sheet Metals," *Proc. Amer. Soc. Test. Mat.*, 1927, 27, (II), 235; 1926, 26, (II), 378.

[‡] J. T. Nichols, E. S. Taylerson, and J. S. Whetzel, "Tension Test-Specimens for Sheet Steel," *Proc. Amer. Soc. Test. Mat.*, 1927, 27, (II), 259.

[§] R. L. Kenyon, "Per Cent. Elongation in the Tensile Test as a Method of Measuring the Ductility of Thin Sheets," *Metals and Alloys*, 1932, 3, 220.

ship between elongation and slenderness ratio for a given material is independent of shape of cross-section as has been shown by Templin.*

The authors report that considerable variation in rate of strain had no effect on the percentage elongation. I found that mild steel sheets † exhibited a considerable decrease in the percentage elongation with increase in the rate of strain. In the latter case, the rates of strain were computed from the measurements of the actual specimens, not from nominal machine head speed.

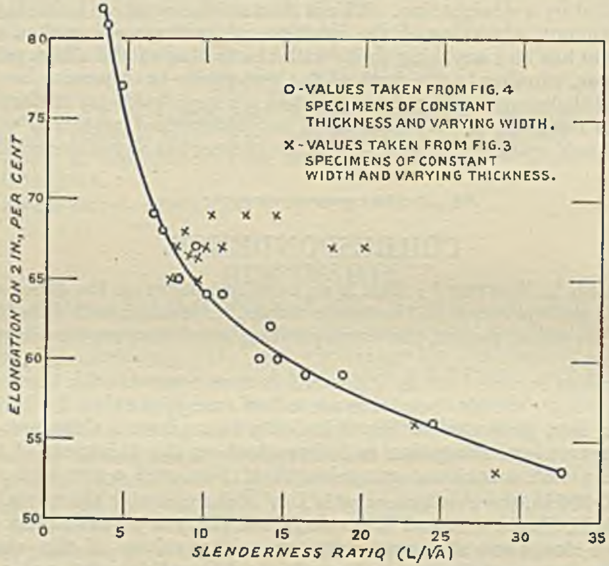

Fig. A.—Relationship Between Slenderness Ratio and Percentage Elongation. From data by Cook and Larke (this volume, p. 168).

The authors do not describe in detail their testing technique and one wonders how the rates of strain shown in Fig. 5 were determined. This leads to another question: Were the specimens of different length tested at different machine head speeds so that the rate of strain was always the same per in. of gauge-length? The testing machine stretches the entire parallel section and the head must move fast enough to stretch all of it (regardless of the measured gauge-length) at the desired rate of strain. This is merely a detail in the computation of the proper head speed (on a hydraulic machine where this is subject to close regulation) so that the desired rate of strain is obtained.

I have found the most convenient method of determining uniform elongation is from an autographic stress–strain curve. The technique has been described in detail in a previous paper.‡ The method of measuring the elongation of short subdivisions of the gauge-length proved to be inaccurate on the mild steel specimens described in my paper § referred to by the authors. The reduction at fracture apparently is not so highly localized in this material as in the copper alloys reported in this paper.

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* R. L. Templin, *loc. cit.* † R. L. Kenyon, *loc. cit.*

‡ R. L. Kenyon and R. S. Burns, "Autographic Stress–Strain Curves of Deep Drawing Sheets," *Trans. Amer. Soc. Steel Treat.*, **1933**, July.

§ R. L. Kenyon, *loc. cit.*

The authors' findings in regard to the effect of the location of the fracture on the elongation value agree with mine on mild steel sheets. It has been found on such material that tensile specimens with a 2·25 in. parallel length and 2 in. gauge-length, 0·500 in. wide, give reliable elongation values if the fracture is not less than 0·5 in. from either gauge-mark. There have been numerous cases, however, in which one of two duplicate specimens would break within less than 0·5 in. of the gauge-mark and still have an elongation value as high as or higher than the other specimen which may have broken almost exactly at the mid-length. It is my belief that the elongation value is often affected by variations in cross-sectional area that are too minute to be observed or measured by ordinary methods and that this may account for such inconsistencies. The elongation is a valuable measure of ductility, but must be interpreted with some consideration of the sources of error that may arise from the nature of the test-specimen apart from the properties of the material.

Mr. R. L. TEMPLIN: * Some years ago I carried out tensile tests using a specimen quite similar to that shown in Fig. 1 which required the use of flat smooth-face wedge grips with a dowel pin which would extend through the hole in the specimen end and then on into the adjacent wedge. While this type of grip or wedges gave appreciably better testing results than the older type of coarse-tooth wedges when testing thin sheet metals, yet I found that still more consistent results would be obtained if shackles were used of the type described in my paper † to which the authors have referred. This latter type of shackle also permits a marked reduction in the cost of preparation, as well as in the testing of specimens. I would appreciate the authors' comments on the relative merits of the two types of shackles referred to.

The AUTHORS (*in reply*): We are glad to note from Mr. Kenyon's very interesting remarks that the results reported in the paper are in general agreement with those obtained on other metals. Mr. Kenyon has raised the point in connection with our findings that the percentage elongation is independent of the thickness of the test-specimens within the range of thicknesses 0·020 to 0·125 in., but we cannot agree with his suggestion that it is due to lack of uniformity in the specimens tested. All the samples were cut from the same ingot and the annealing of the samples was carried out together, after they had been cut into test-pieces. The annealing was carried out under such conditions that oxidation which occurred was negligible. Moreover, metal taken from the same ingot was used in considering the effect of variations in width, and Mr. Kenyon agrees with the findings regarding the effect of this factor.

We do not contend that theoretically the elongation is independent of the thickness, when the gauge-length and width are maintained constant, but we do consider that within the range of thicknesses we examined the differences in elongation are very small. The measurements of elongation were carried out to an accuracy of 0·25 per cent., but even so, as will be seen from the curve in Fig. 3 of the paper, relating percentage elongation to thickness, that with the points obtained for thicknesses ranging from 0·20 to 0·125 in. there was no option but to draw a straight line parallel to the abscissa. The differences between the maximum and minimum elongation values obtained in this range are of the same order as the differences which Mr. Kenyon obtained in elongation measurements on test-pieces of similar form and size in mild steel. However, he obtained a slight, but progressively increasing, elongation

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† *Proc. Amer. Soc. Test. Mat.*, 1926, **26**, (II), 378.

with increasing thickness, but with our measurements we were unable to record elongation values with this progressive increase.

The rate of strain was in fact determined in accordance with the method described by Mr. Kenyon. The full length of the parallel portion was allowed for, and preliminary tests for the determination of the correct head speed were carried out prior to testing the samples from which records were taken.

We have not made use of the special type of shackle referred to by Mr. Templin, and therefore are not in a position to give an opinion regarding the relative merits of this type of shackle and the one which we used.

EXPERIMENTS IN WIRE-DRAWING. PART IV.—ANNEALING OF H.-C. COPPER WIRES OF VARYING HARDNESS–ELONGATION VALUES.*

By W. E. ALKINS,† M.Sc., Member, and W. CARTWRIGHT,† O.B.E., M.Sc., Member.

Synopsis.

The results of determinations of the elongation values of a series of wires of a very pure high-conductivity copper, drawn with widely varying amounts of reduction and annealed at varying temperatures for varying periods of time, are recorded in full and briefly discussed.

1. Introduction.

In a previous communication ‡ the authors gave an account of a series of annealing experiments carried out at varying temperatures and for varying periods of time on a number of samples of wire, approximately 0·1 in. in diameter, drawn to widely different hardnesses from a single heavy wire-bar of unusually pure high-conductivity copper. It was shown that, the greater the amount of the cold-work done on the wire, the lower is the temperature at which it begins to lose its work-hardness and the greater the rate of loss at any temperature, but the higher is the tensile strength of the "fully annealed" material. The breaking load of the wires was the only physical property for which data were given.

2. Scope of the Present Paper.

Since the publication of the above-mentioned work, a very general desire has been expressed to the authors by drawers of copper wire that the elongation test results should be made available. It is in an endeavour to comply with this wish that the present paper has been written. It is confined to a statement and very brief discussion of

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† Research Department, Thomas Bolton & Sons, Ltd., Oakamoor.

‡ *J. Inst. Metals*, 1933, 52, 221–239.

the elongation values corresponding with the breaking load data already published.

3. Material.

In view of the interest that has been shown in the chemical composition of the copper used, and of the obvious importance of the question, further attention has been given to the estimation of the impurities present. The authors wish to thank in this connection Mr. W. Sheppey, who has made a detailed chemical analysis, and Dr. F. J. Brislee, who has prepared and read spectrograms. Their work completely confirms the view that the material was in fact of an unusually high degree of purity; as such it was in entire agreement with the intentions of the authors, who wished to study first the annealing behaviour of the purest available—and not necessarily therefore of a typical commercial—high-conductivity copper. The composition can now be stated as follows :—

	Chemical.	Spectrographic.
Copper, per Cent.	99·953	...
Silver, ,, ...	0·0008	trace
Lead, ,, ...	less than 0·001	...
Iron, ,, ...	0·003	less than 0·005
Nickel, ,, ...	0·0005	...
Oxygen (by determination), per Cent. .	0·041	...
or		
Total, copper plus oxygen, . . .	99·994 per Cent.	
Total, impurities excluding oxygen .	0·006 ,,	

The preparation of the wires is fully described in the previous paper,* in which are also discussed the methods used for annealing and the range of annealing treatments given.† The percentage reductions given to wires Nos. 1–11 by cold-drawing (after intermediate annealing) to the uniform finished diameter of approximately No. 12 S.W.G. (0·104 in.) are repeated in Table IX of the present paper.

4. Method of Testing.

The elongation tests were made on a hand-operated Farrar machine of simple type, on a length of 10 in. between the grips. The wires were stretched as steadily as possible at an approximately constant speed and fractured, and the elongation value was read, at the instant of fracture, in terms of percentage elongation in 10 in. The results were read to the nearest 0·5 per cent.

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* *Loc. supra cit.*, p. 222, and Table I, p. 223.

† *Ibid.*, pp. 222–223.

In the case of wires having a considerable general elongation, this method of testing gives results which are rather lower than those obtained by stretching a test-piece more than 10 in. long between grips, on which a 10-in. gauge-length is marked off well clear of the grips. For wires possessing an elongation of 35 to 40 per cent., the difference is 1·5 to 2 per cent. With hard wires the difference is inappreciable.

5. RESULTS.

The mean elongation values of the whole of the eleven wires after the different annealing treatments are tabulated in Tables I–VIII,

TABLE I.—*Annealed at* 130° *C.*

No.	Mean Elongation per Cent. in 10 in.					
	Annealing Period, Hrs.					
	½.	1.	2.	6.	12.	24.
1	1	1	1	1·5	1	1
2	1	1	1	1	1	1
3	1	1	1	1	1	1
4	1	1	1	1	1	1
5	1	1	1	1	1	1
6	1	1	1	1	1	1
7	1	1	1	1	1·5	1
8	1	1	1	1	3	3
9	1	1	1·5	4	8	16·5
10	1	1	1	2·25	5·75	12·5
11	1	1	1·5	3·25	6·75	10·75

TABLE II.—*Annealed at* 155° *C.*

No.	Mean Elongation per Cent. in 10 in.					
	Annealing Period, Hrs.					
	½.	1.	2.	6.	12.	24.
1	1	1	1	1	1	1·5
2	1	1	1	1	1	1
3	1	1	1	1	1	2·25
4	1	1	1	1	1	2·75
5	1	1	1	1	1·75	6·25
6	1	1	1	1	6·25	7·25
7	1	1	3·5	8·5	18·5	17
8	1	2·5	3	13·5	22	27·75
9	1	6	13	25·25	30·5	34
10	1	2·25	10·5	20·75	28·5	33
11	1	6·5	11	21	26	28

of which all except the last relate to a single temperature; in Table VIII are collected the test results after ½-hr. annealings at temperatures of 330° C. and above. The present data can thus be readily and directly correlated with the data for breaking load given in Tables II–IX of the earlier paper.

TABLE III.—*Annealed at* 170° *C.*

No.	Mean Elongation per Cent. in 10 in.					
	Annealing Period, Hrs.					
	½.	1.	2.	6.	12.	24.
1	1	1	1	1	1	1
2	1	1	1	1	1	2
3	1	1	1	3·5	9	14
4	1	1	2	3·5	8	17·5
5	1	1	1	4	14·5	23·5
6	1·75	1	4	10·5	14	17·5
7	2	5·75	13	25	20·5	33
8	3	3	19·5	31	31	35
9	4	16	25·5	34	34·5	37
10	4·25	14·5	27	33·5	35	36·5
11	4·5	13·5	23	30·5	32	34

TABLE IV.—*Annealed at* 180° *C.*

No.	Mean Elongation per Cent. in 10 in.					
	Annealing Period, Hrs.					
	½.	1.	2.	6.	12.	24.
1	1	1	1	1	1	1·5
2	1	1	1	1·25	2·5	8
3	1	1·25	2	10	22	26
4	1	1·5	1·75	11·5	22·5	26
5	1	1·75	2·5	17·5	18·5	25
6	1	1·75	7·5	24·5	24·5	35
7	1	5·5	7	26	34·5	37·5
8	2·5	10·5	26	34	36·5	37
9	4·5	22·5	32	36	37	37
10	5·5	26	33·5	36	37	36·5
11	9·5	22	30	33·5	35	35

In the as-drawn condition all the wires had, within the limits of accuracy of the method of testing, the same elongation—1 per cent.—and the recurrence of this "hard-wire" elongation value makes it possible, by inspection of the Tables, easily to follow the commencement of annealing. At 130° C. (Table I), softening is apparent only in the case of the (four) most severely drawn wires after treatments of 6 hrs.'

duration and over—the value 1 per cent. persists throughout the Table except in the extreme right-hand lower corner. As the temperature of annealing increases, the area occupied by the figure 1 shrinks progressively towards the left-hand upper corner of the Table, *i.e.* the lightly drawn wires undergo annealing less readily than those which have been severely cold-worked. Whereas a significant increase of elongation is apparent with a number of the hardest drawn wires after 6 hrs. at 130°, after 1 hr. at 155°, and after ½ hr. at 170° C., the No. 1 wire (36 per cent. reduction) shows only the slightest softening after 24 hrs. at 205° C. and is by no means fully annealed even after 24 hrs. at 230° C.

TABLE V.—*Annealed at* 205° *C.*

No.	Mean Elongation per Cent. in 10 in.					
	Annealing Period, Hrs.					
	½.	1.	2.	6.	12.	24.
1	1	1	1	1·25	1·5	2
2	1	2	4	14·75	27·5	19·5
3	2	13	20·5	34·5	37	37·75
4	3	18	26	36	37·5	36·75
5	4	18	30	27·75	34·5	36
6	7·5	32	34·5	36·5	37·25	36·5
7	26	21	31	34	37	34·5
8	29	36·5	36·5	35	36	37
9	31	36	37	36	37	37
10	32·75	37·25	36·75	36·5	37	36
11	29	35	36	35·5	36·25	35

TABLE VI.—*Annealed at* 230° *C.*

No.	Mean Elongation per Cent. in 10 in.					
	Annealing Period, Hrs.					
	½.	1.	2.	6.	12.	24.
1	1·5	1·5	1·5	3·5	8	15
2	4	20·5	28	38	40·25	38
3	31	36·5	39	39	41·25	39·75
4	30·5	36·5	39·25	39	40·75	38·75
5	31	37	37	38	39·75	38·5
6	34·5	34	37·5	36·5	38·5	37·5
7	38	37·5	36·25	36	38	36·5
8	37·5	36·25	37·25	37·5	39·5	38
9	37·5	37·5	38·5	38	38	38
10	38·5	37	38	37·5	38·25	37·5
11	36·5	36	37	36·5	37	37

In marked contrast with the behaviour of the lightly worked wires several of the most heavily drawn wires are annealed down to elongation values of the order of 30 per cent. after 24 hrs. at 155° C.; they are annealed to values of 35 per cent. and over after 1 hr. at 205° C. and after ½ hr. at 230° C.—treatments which are without appreciable effect on No. 1 wire.

TABLE VII.—*Annealed at 280° C.*

No.	Mean Elongation per Cent. in 10 in.					
	Annealing Period, Hrs.					
	½.	1.	2.	6.	12.	24.
1	6·75	23	30·75	36·5	36·5	35·25
2	36·5	38·75	39	39·75	40·75	39·5
3	39	40·5	40·5	40·75	40·75	40·5
4	38·75	39·5	39·75	38·5	41	40
5	37	39	39·25	38	39	39·25
6	37·25	37·75	37·5	38·5	38	39·5
7	37	37·75	38·75	38	38·5	38·5
8	36·25	36·5	38·5	38·5	38·5	38·5
9	37·25	38·5	37·5	38·5	38·75	37·75
10	36·5	37·75	38	38	39	38
11	37	37·5	37	37·75	38·5	38

TABLE VIII.—*Annealed for ½ hour.*

No.	Mean Elongation per Cent. in 10 in.				
	Annealing Temperature, ° C.				
	330.	450.	650.	750.	850.
1	38·5	38	40	37·5	37·25
2	39	39·5	39·25	38·25	35·75
3	39	40	39·5	37·75	34·5
4	39	38	39·75	38	34·5
5	37·5	38	38·75	35	33·25
6	37·5	38·5	36·75	36·25	34
7	37	38	37·5	35·5	32·75
8	37·5	38	38·5	33	34·25
9	37	37·5	37	34	33·5
10	38	38	38·25	32·25	33·25
11	36·5	38·5	37·5	33	31·5

It is worthy of remark that, even at the low temperatures, wire No. 9 (94·8 per cent. reduction) appears to anneal to a greater extent, as judged in the light of elongation values, than wire No. 11 (96·7 per cent.); the behaviour of wire No. 10 (95·8 per cent.) is on the whole intermediate between that of No. 9 and that of No. 11.

The variation of percentage elongation with temperature is illustrated, in the case of ½-hr. annealings, in Fig. 1; in order to show all the wires in the same diagram, use has been made of the device of moving up the elongation zero through five units, from each wire to the next. The steeply-ascending left-hand portions of the curves bring out the much greater tendency shown by the hardest-drawn wires to become annealed at lower temperatures.

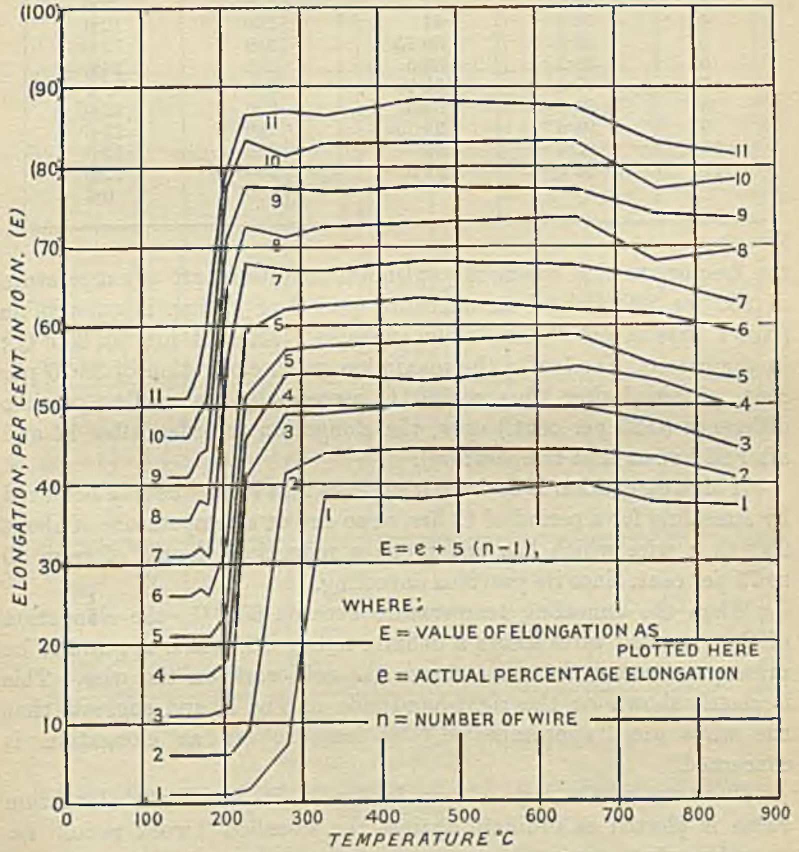

FIG. 1.—Relationship between Elongation and Temperature. Half-Hour Annealings.

It is, in general, true that in the case of each wire the greatest elongation is obtained by annealing at a moderate temperature for a fairly long time. In Table IX are collected particulars of the annealing treatments which resulted in the highest elongation for each wire, and

TABLE IX.—*Maximum Elongation Values.*

No.	Reduction of Area, per Cent.	Maximum Elongation, per Cent.	Temperature, ° C.	Time, Hrs.
1	35·9	40	650	0·5
2	59·0	40·75	280	12·0
3	69·6	41·25	230	12·0
4	76·6	41	280	12·0
5	83·5	39·75	230	12·0
6	88·3	39·5	280	24·0
7	91·3	38·75	280	2·0
8	93·4	39·5	230	12·0
9	94·8	38·75	280	12·0
10	95·8	39	280	12·0
11	96·7	38·5	{280 {450	12·0 0·5

the frequency with which the optimum conditions are a temperature of 230° or 280° C. and an annealing period of 12 hrs. is remarkable (No. 1 wire is not "completely annealed" after 24 hrs. at 280° C.; in the case of No. 7 wire the maximum mean elongation of 38·75 per cent., obtained after 2 hrs. at 280° C., exceeds by the smallest possible difference (0·25 per cent.) only, the elongation recorded after 12 and after 24 hrs. at that temperature).

If high elongation is desired, it appears that it may best be achieved by annealing for a period of 12 hrs. or so and at a temperature of about 250° C. a wire which has undergone a reduction of area of from 50 to 75 per cent. since its previous annealing.

When the annealing temperature exceeds 650° C., the elongation of the annealed wires shows a definite falling off, which appears to be more pronounced the more severe the cold-work on the wire. This is clearly shown on the right-hand side of Fig. 1, and suggests that the wires are "over-annealed," at least so far as elongation is concerned.

Diagrams of the type shown in Fig. 2, in which the elongation value is plotted as ordinate against the so-called "work ratio," *i.e.* $\frac{\text{annealing diameter}}{\text{finished diameter}}$, as abscissa, have again been found very useful in assisting towards a satisfactory conception of the whole of the annealing phenomena.

No attempt will be made here to correlate the elongation values set out in Tables I–VIII with the data for breaking load given in Tables II–IX of the previous paper. All the results are, however, now available for the purpose, and a number of interesting and significant features can be established if the data for the two properties are compared.

ACKNOWLEDGMENTS.

The authors wish once again to record their thanks to Messrs. Thomas Bolton & Sons, Ltd., and particularly to Mr. Thomas Bolton, for permission to publish these results. Similarly they desire to acknowledge again the assistance given by a number of colleagues at Oakamoor.

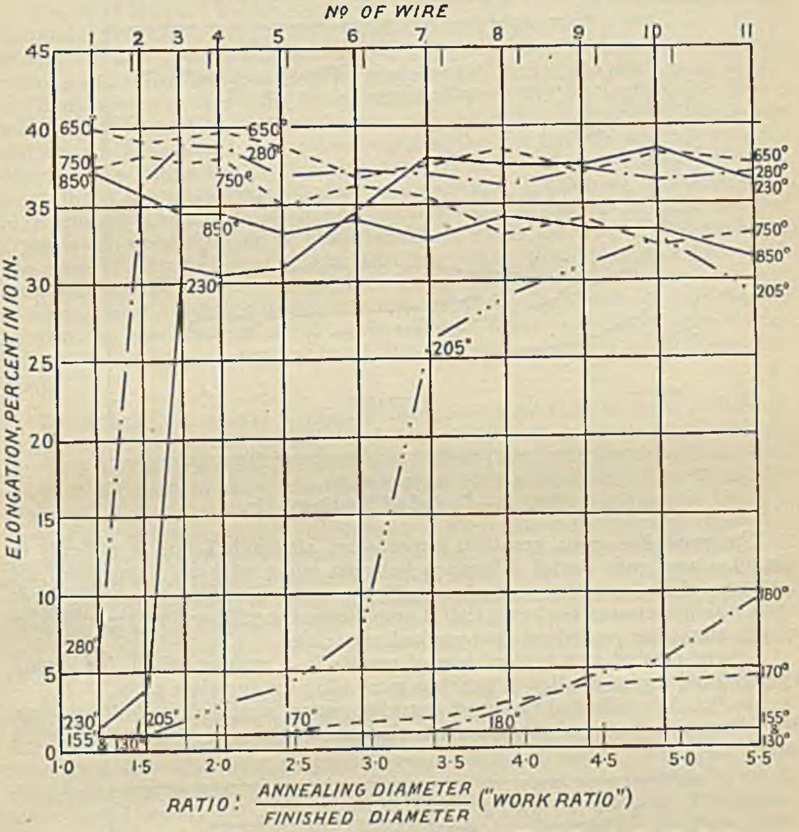

Fig. 2.—Relationship between Elongation and "Work Ratio." Half-Hour Annealings.

DISCUSSION.

Professor F. C. Thompson,* D.Met., M.Sc. (Member): This second section of the authors' work is particularly to be welcomed because, in conjunction with their earlier work, it represents probably the most thorough examination which has ever been made of the effects of annealing on wires drawn to different

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* Professor of Metallurgy, The University, Manchester.

extents. Dr. Alkins, in introducing the paper, said very optimistically that the figures would tell their own story. They may tell their own story to the authors, but anyone who has taken the trouble to attempt to analyze the results may be forgiven if he finds himself thinking, as I do, that the story is very far from told!

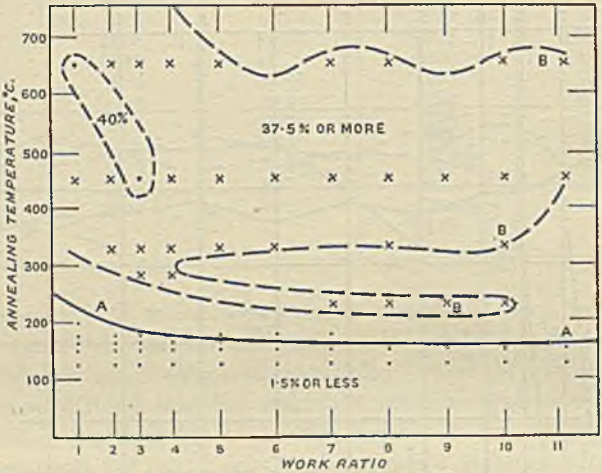

Fig. A.—Period of Heating ½ Hr.

The work has great practical importance, although I find it difficult to visualize any very useful difference between wires with an elongation, for instance, of 37·5 per cent. and of, say, 39 per cent. The biggest service, however, which the paper renders is that it emphasizes the extraordinary complexity of the annealing process of cold-worked materials.

I have plotted two typical sets of results in a manner which for a two-dimensional representation is perhaps more illuminating than most.

In Fig. A is collected the most complete series, annealed for half an hour, the elongation being plotted against what the authors have called the work ratio.

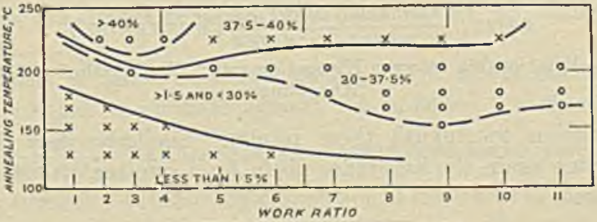

Fig. B.—Period of Heating 12 Hrs.

This diagram—and I believe that the authors' figures are sufficiently reliable to justify it—indicates the complexity of the changes which occur during the process of annealing. Anyone who is particularly interested in the annealing of wires may be strongly recommended to plot the authors' previous work on the tensile properties in a similar manner.

If the results are plotted for a 12-hr. period of annealing (Fig. B), a different type of curve, but one which is completely consistent, is obtained.

I feel, therefore, that the evidence is too strong to be doubted that in the first place the authors' results, unexpected as they may be, are reliable, and secondly that there is this weird complexity in the change in mechanical properties on annealing.

Dr. H. O'Neill,* M.Met. (Member): A year ago I ventured to criticize the method of preparation of the material from which these wires were drawn, and I should like to repeat my criticism simply in order to clear the ground for making reference to the interesting decrease in elongation and slight increase in breaking load when the annealing temperature exceeds 650° C. for heavily drawn wires. My suggestion is that X-ray analysis of the wires would probably show something about the statistical distribution of the crystallographic directions in which the crystals are situated in the annealed material. Re-crystallized copper wires still possess a preferred orientation, and with the high annealing temperatures it appears that this preferment is such that the crystals are re-orientating to some condition where there is, on the average, less ease of slip. I assume that the decreasing elongation and increased breaking load indicate that the mean directions of the crystals are arranged to offer greater resistance to deformation. If the authors have an opportunity to examine the annealed wires by the Debye–Scherrer method some useful information might be obtained regarding this particular and most interesting point.

Dr. Alkins (*in reply*): Professor Thompson says that he finds it difficult to agree that there can be any important difference between wires having say 37·5 and 39 per cent. elongation on 10 in. We think that a difference of 1·5 or 2 per cent. in the elongation of wires giving values between 30 and 40 per cent. connotes a real difference between such wires, though the importance of the difference is difficult to judge. From the point of view of works' inspection such a difference in elongation values may assume a very real importance. If in a specification the minimum is fixed at 30 per cent., coils of wire which give 31 per cent. at each end—and by the nature of the case only the ends can be tested—are sent out. If the customer happens to cut up the coils and takes tests from the centre, he frequently complains if he obtains values of 29 per cent.

Our method of plotting was the subject of some remarks by Professor Thompson. I would ask you to remember that our immediate object was to comply with the request to publish our elongation values, and we have not attempted any elaborate graphical presentation of them. We agree that the results can be plotted in many ways, and we think it is possible to reach some useful conclusion from most of the methods of plotting. Professor Thompson's conclusions from his method are interesting, and at the same time gratifying because he finds it possible to derive from this novel method of representation testimony to the accuracy of our results and to the reality of some of our findings.

Dr. O'Neill repeated his earlier criticism of our method of preparing our wires. We cannot yet visualize any more satisfactory method of preparation which is at the same time practicable, and Dr. O'Neill has not yet been able to make any constructive suggestion to meet his own criticism.

We are in complete agreement with his remarks on X-ray examination. In a paper presented at the present meeting,† Dr. O'Neill and Dr. Farnham describe what they have found with some of these wires of ours. Mr. Cartwright and I have no facilities for carrying out X-ray investigations, but we will gladly provide samples of our wires for examination by anyone who has the necessary facilities, as we did for Dr. O'Neill and his colleague.

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* Research Metallurgist, London, Midland, and Scottish Railway Company, Derby.

† This volume, p. 201.

CRYSTAL RE-ORIENTATION ON HEATING DRAWN COPPER WIRES.*

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

SYNOPSIS.

The behaviour of a silver-free copper wire reduced 59 per cent. by cold-drawing, has been compared after "low-temperature treatment" (L.T.T.) with that of two silver-bearing wires reduced 59 per cent. and 49 per cent., respectively. L.T.T. hardening occurs in the first, but not in the last of these. X-ray spectroscopy makes it evident that preferred orientation is less developed in these silver-bearing wires. The general effect of L.T.T. at 130° C. is to reduce the amount of [111] preferment, but to cause an increase of [100] preferment. This change-over probably causes "orientation hardening." In these silver-bearing wires, however, the change is only relatively small in extent, and this appears to explain the differences as regards L.T.T. hardening.

INTRODUCTORY.

THE present investigation arose out of some work on the effects of annealing copper wire recently undertaken by Alkins and Cartwright.[1] The behaviour of similarly drawn wires after low-temperature treatments varies with the silver content of the metal. Table I makes this evident, and the authors are indebted to Messrs. W. E. Alkins and W. Cartwright, of Messrs. Thomas Bolton & Sons, Ltd., for the information given therein, and for kindly placing specimens of their material at the authors' disposal.

The silver-free copper shows a tensile hardening of 2·6 per cent. after L.T.T. at 130° C. for 2 hrs., whereas silver-bearing wire 4S gives a corresponding increase of only 0·4 per cent. and No. 3S actually softens. The authors therefore examined these wires by X-ray spectroscopy to detect any observable differences in crystalline behaviour.

INDENTATION TESTS.

The existing evidence for L.T.T. hardening in wire No. 2 was an increase in tensile maximum load, but the authors have further con-

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* Manuscript received April 27, 1934. Presented at the Annual Autumn Meeting, Manchester, September 5, 1934.

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‡ Senior Lecturer, Department of Metallurgy, The University, Manchester.

TABLE I.—*Drawn Copper Wires, Nominal Diameter* 0·104 *in.* (*Alkins and Cartwright.*)

Wire Number.	No. 2.*	No. 3S.	No. 4S.
Reduction of Area by Drawing, per Cent.	59	49	59
Maximum Tensile Load, lb.			
As drawn	457	450	473
Heated 130° C. for 1 hr.	469	446	474
,, ,, ,, 2 hrs.	469	445·5	475
,, ,, ,, 6 ,,	466	445	477
Composition, per Cent.			
Copper	99·95	99·855	
Silver	nil	0·093	
Lead	nil	0·018	
Iron	0·003	0·001	
Oxygen	0·047	0·031	

* Original values reported in paper ref. (1).

firmed the effect by indentation tests. These were made by mounting the specimens in plastic wood, carefully sectioning them parallel to the direction of drawing by rubbing on emery cloth, and then making 1-mm. ball tests at different indenting loads. Great accuracy was not obtained, presumably owing to the hardness gradients which are known to exist across the section of such drawn wires. The results given in Table II must not therefore be held to disprove the observation of Pfeil [2] that L.T.T. hardening is in reality nothing more than an effect due to an increase of the Meyer *n* value. As they stand, the present figures indicate a definite hardening in wire No. 2 of at least 5 per cent.

TABLE II.—*L.T.T. Hardening of Wire No.* 2.

	As Drawn (59 per Cent. Reduction of Area) and Aged for 2 Years.	Ditto and Heated 130° C. for 2 Hrs. Aged for 3 Months.
Brinell Hardness No. ($H_{1/10/30}$)	93 kg./mm.^{2}	101 kg./mm.^{2}
Meyer Index *n*	2·03 (approx.)	2·03 (approx.)
Ultimate Ball No., kg./mm.^{2} ($P_u = 1{\cdot}273a_1$)	99	104

X-RAY TESTS ON UNETCHED WIRE.

Debye–Scherrer spectrograms using unfiltered Cu X-radiation were obtained from the different specimens. Intensity measurements were made with a Cambridge (Dobson) microphotometer through three of the reflection lines on the films, in an equatorial direction. This direction passes through the centre of intensity maxima on the (200) and (220) lines (see Fig. 1, Plate XV), and the results for the outside layer of wire No. 2 are given in Table III.

TABLE III.—*Photometric Survey of X-Ray Spectrograms of Unetched Wire No. 2.*

Photometric Curve.	As Drawn.			Annealed at 130° C. for 2 Hrs.		
	(111).	(200).	(220).	(111).	(200).	(220).
Height . . .	1,626	1,564	1,644	1,268	1,280	1,408
Width, cm. . .	0·067	0·073	0·085	0·036	0·043	0·054
Blackening . .	21,680	22,840	30,590*	10,040	11,810	16,540
Relative height .	1	0·961	1·011	1	1·010	1·110
,, width .	1	1·090	1·266	1	1·194	1·500
,, blackening	1	1·054	1·411*	1	1·176	1·648

* Film rather over-exposed, and this value is probably low.

The bottom line of Table III is the most significant, and indicates that the (200) reflection becomes relatively more intense (by 12 per cent.) as a result of the L.T.T. Incidentally, according to Schmid and Wassermann [3] and Wood,[4] the outer layer of a copper wire such as this is almost devoid of preferred orientation. By comparing the figures obtained by the present authors with the theoretical relative intensities given below for unworked copper, however, it will be seen that the (200) reflection is much stronger than normal. This indicates that an abnormal number of crystals have a [100] direction parallel to the axis of the wire.

The normal theoretical relative intensities calculated from scattering data and the appropriate absorption and temperature factors are as follow :

Relative Intensities for Unworked Copper.

Plane.	(111).	(200).	(220).
Cu wire : 0·104 in. diam. . . .	1	0·601	0·979
0·047 ,, . . .	1	0·583	0·949
0·024 ,, . . .	1	0·556	0·913
Intensity measurements from powder spectrogram of unannealed copper filings (corrected to 0·047 in. diam.) . . .	1	0·634	0·785

The blackening figures, corrected for difference in density and diameter, obtained from a casual powder spectrogram kindly loaned by Dr. A. J. Bradley, confirm the general order of the theoretical normal values given above for copper wire.

X-RAY TESTS ON ETCHED WIRES.

As wires such as these are generally more "preferred" towards the core, we etched away the outer layer in 25 per cent. nitric acid, and obtained spectrograms from the new surface. Wire No. 2 was also given further successive heatings in paraffin until recrystallized. The results of intensity measurements for this specimen are reported in Table IV, the "blackening" column on the right being the one which best indicates the changes.

TABLE IV.—*Photometric Survey of X-Ray Spectrograms from Wire No. 2, Etched to* 0·047 *in. Diameter.*

Treatment.	Plane.	Photometric Curve.			Ratios.		
		Height.	Width.	Blackening.	Height.	Width.	Blackening.
(1) As drawn	(111)	0·264	0·049	2,700	1	1	1
	(200)	0·456	0·055	5,015	1·730	1·120	1·858
	(220)	1·236	0·064	16,970	4·675	1·304	6·285
(2) Annealed at 130° C. for 2 hrs. (L.T.T. hardening)	(111)	0·315	0·048	3,400	1	1	1
	(200)	0·624	0·053	7,140	1·980	1·103	2·100
	(220)	1·200	0·065	16,320	3·805	1·355	4·800
(3) Ditto, plus 170° C. for 2 hrs.	(111)	0·442	0·056	5,390	1	1	1
	(200)	0·846	0·059	10,345	1·911	1·052	1·919
	(220)	1·502	0·075	23,020	3·360	1·339	4·265
(4) Treatment (3), plus 205° C. for 2 hrs.	(111)	0·382	0·055	4,715	1	1	1
	(200)	0·638	0·056	8,475	1·670	1·019	1·797
	(220)	1·120	0·078	18,290	2·930	1·419	3·879
(5) Treatment (4), plus 280° C. for 2 hrs. (recrystallized)	(111)	0·620	0·062	8,555	1	1	1
	(200)	0·666	0·070	9,515	1·172	1·128	1·112
	(220)	0·958	0·080	15,220	1·543	1·290	1·779

L.T.T. at 130° C. has caused a relative increase in intensity of the (200) reflection by 13 per cent., whilst the (220) reflection has decreased by 24 per cent. The recrystallized wire still shows preferment.

Wires 3S and 4S (containing silver) yielded the results given in Table V after similar etching.

It is obvious that there is less preferred orientation in wire 4S than in No. 2 which is silver-free. Although No. 3S has been drawn to about the same tenacity as No. 2, it is only very slightly "preferred" in this present layer. Fig. 1 (Plate XV) shows the difference after L.T.T. of the spectrograms of these two wires. Further etching of No. 3S gives

Table V.—*Wires 3S and 4S, Etched to* 0·047 *in. Diameter.*

	Photometric Curve.	As Drawn.			Annealed at 130° C. for 2 Hrs.		
		(111).	(200).	(220).	(111).	(200).	(220).
3S	Height . . .	720	480	912	842	564	980
	Width, cm. . .	0·050	0·053	0·063	0·050	0·055	0·063
	Blackening . .	7,565	5,420	1,142	8,910	6,655	13,280
	Relative height .	1	0·667	1·266	1	0·670	1·164
	,, width .	1	1·060	1·260	1	1·100	1·260
	,, blackening	1	0·716	1·509	1	0·747	1·491
4S	Height . . .	455	434	1,204	719	684	1,620
	Width, cm. . .	0·046	0·049	0·060	0·044	0·045	0·061
	Blackening . .	4,515	4,495	15,590	6,940	6,930	20,070
	Relative height .	1	0·954	2·646	1	0·951	2·253
	,, width .	1	1·065	1·364	1	1·023	1·386
	,, blackening	1	0·995	3·454	1	0·999	2·892

results in Table VI, indicating that the interior (and more severely displaced) metal is more highly preferred than the outside.

Table VI.—*Wire 3S, Etched to* 0·024 *in. Diameter.*

Photometric Curve.	As Drawn.			Annealed at 130° C. for 2 Hrs.		
	(111).	(200).	(220).	(111).	(200).	(220).
Height . . .	234	292	874	416	498	1,204
Width, cm. . .	0·078	0·078	0·080	0·063	0·070	0·080
Blackening . .	3,765	4,665	14,430	5,430	6,780	19,730
Relative height .	1	1·248	3,727	1	1·197	2·894
,, width .	1	1·000	1·026	1	1·111	1·270
,, blackening	1	1·239	3·833	1	1·248	3·634

The relative intensities for the various wires and layers are represented in Fig. 2. One difference between the silver-bearing and silver-free specimens is that as a result of L.T.T. the former show but a slight intensity increase for the (200) reflection. This is 0·4 per cent. for No. 4S, as compared with 13 per cent. for No. 2 (0·047 in. diameter).

Crystalline Reorganization on Heating.

Using the normal theoretical relative intensities as a blank, and considering that the equatorial position of the (111) line has no intensity maximum (and may be said to represent unpreferred metal), a calculation can be made of the relative distribution of the crystals between the unpreferred and the *two* preferred positions which copper wire is known to assume.[3] One of these positions is responsible for the maximum on the (200) line, and both contribute to that on the (220). The results of such a calculation are represented in Fig. 3. The lengths of the lines with arrow-heads indicate the extent of the change-over in preferred orientation as a result of L.T.T. The percentage distribution of the crystals between the two preferred positions is given in Table VII.

As stated in the synopsis, this change-over in distribution appears to be associated with the L.T.T. hardening, and probably by giving a smaller number of crystals which are in a position for easy slip. Furthermore, the intensity rise of the (200) line due to L.T.T. is 4 per cent. for No. 3S (0·047 in. layer), but only 0·4 per cent. for No. 4S (0·047 in. layer), and 0·7 per cent. for No. 3S (0·024 in. layer). Within limits, therefore, heavier drawing or displacement gives less change-over to the [100] preferred position after L.T.T. This would be consistent

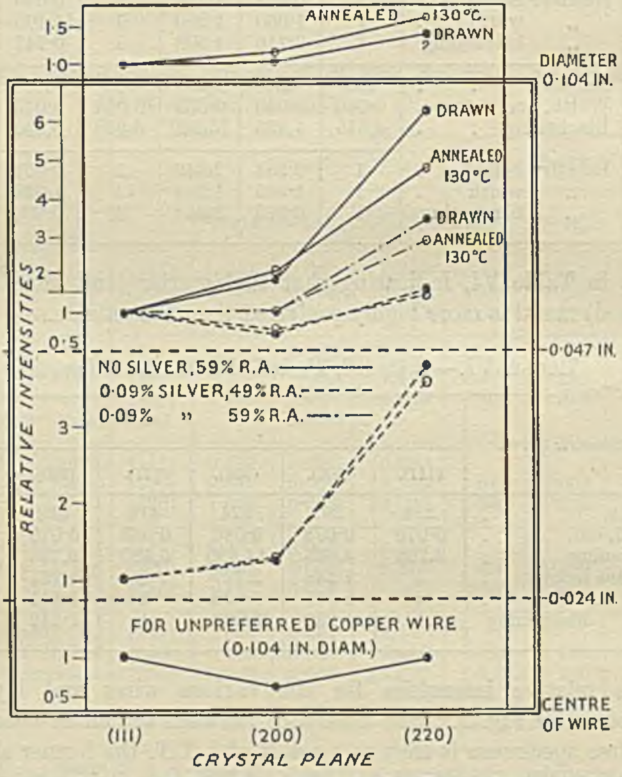

FIG. 2.—Diffraction Intensities for Copper Wire.

Table VII.—*Percentage Distribution of the "Preferred" Crystals Between the Two Positions.*

Specimen.			[100] Position.	[111] Position.
No. 2	(0·104 in.)	As drawn	100	0
		L.T.T. 130° C.	100	0
	(0·047 in.)	As drawn	39	61
		L.T.T. 130° C.	64	36
		,, 170° C.	64	36
		,, 205° C.	66	34
		,, 280° C.	100	0
No. 3*S*	(0·047 in.)	As drawn	39	61
		L.T.T. 130° C.	49	51
	(0·024 in.)	As drawn	38	62
		L.T.T. 130° C.	42	58
No. 4*S*	(0·047 in.)	As drawn	27	73
		L.T.T. 130° C.	35	65

with the finding of Alkins and Cartwright,[1] that heavily-drawn wires show practically no L.T.T. hardening.

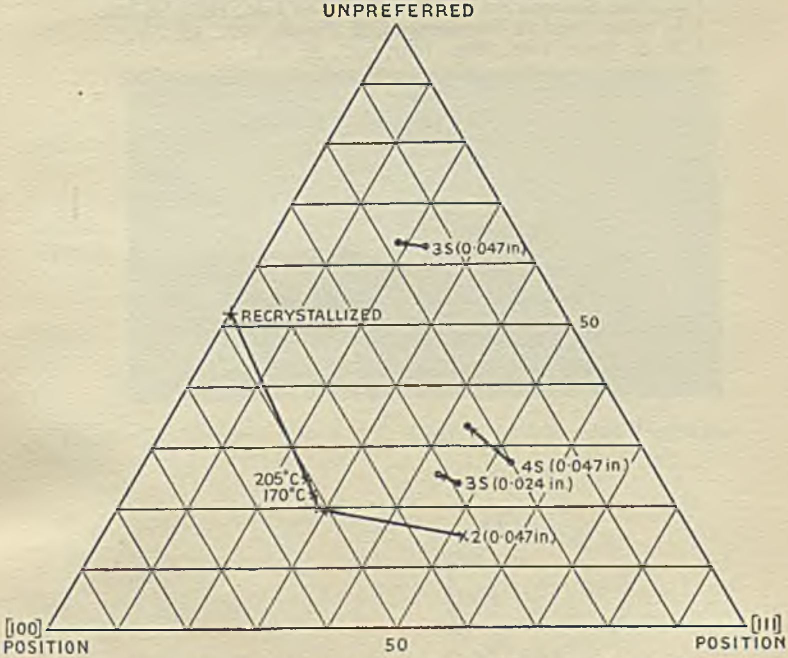

Fig. 3.—Percentage Distribution of Crystals. (The Arrow-Head shows the Condition reached after L.T.T. at 130° C.)

Removal of internal stress by heating should tend to cause a reduction in the width of a spectral line such as the (220). Conversely, the generation of colloidal-like new grains by heating should cause a broadening of the lines. The nett effect to be observed in our figures is a slight widening of the (220) line after heating the wires, the width values being measured at half the heights of the intensity peaks.

ACKNOWLEDGMENTS.

This work was carried out with the encouragement of Professor F. C. Thompson, D.Met., and with apparatus largely provided by financial grants from Messrs. Imperial Chemical Industries, Ltd. Professor W. L. Bragg, F.R.S., kindly gave the authors permission to use the microphotometer of his department, and they are indebted to Dr. A. J. Bradley and Dr. J. F. Keggin, for helpful discussions. One of the authors (G. S. F.) holds an Overseas Research Scholarship awarded by the Royal Commission for the Exhibition of 1851.

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[2] L. Pfeil, *Carnegie Schol. Mem. Iron Steel Inst.*, 1927, 16, 153.
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[4] W. A. Wood, *Phil. Mag.*, 1931, [vii], 11, 611.

PLATE XV.

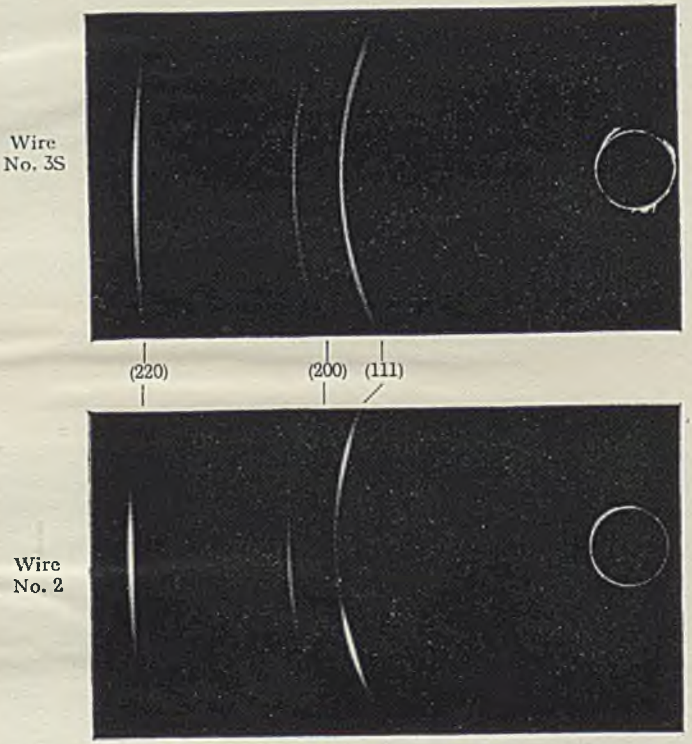

FIG. 1.—Spectrograms after L.T.T. at 130° C. for 2 Hrs. (0·047 in. diam.).

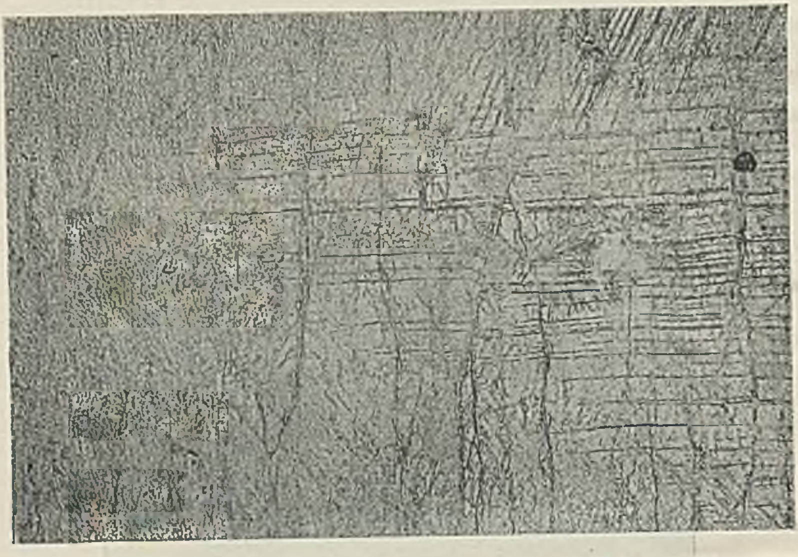

FIG. 1.—Surface of Specimen O Etched with NH_4OH H_2O_2. × 100. Rolling Direction Horizontal.

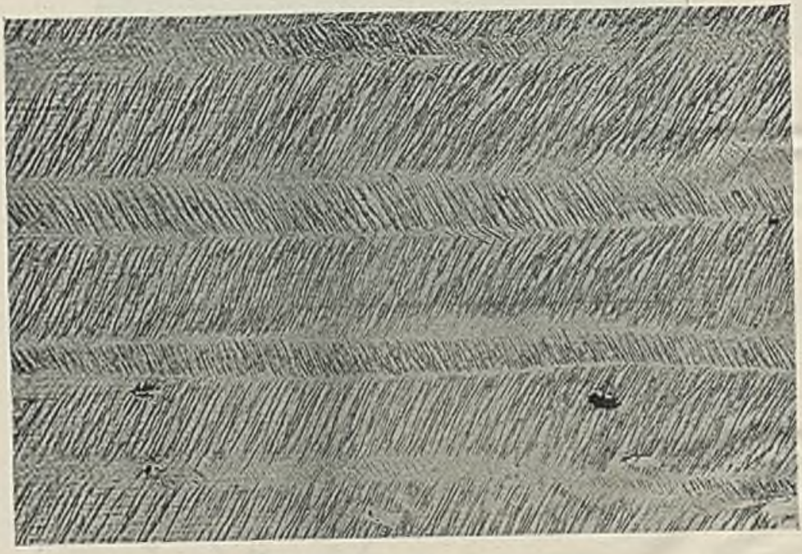

FIG. 4.—Surface of Specimen C Etched with NH_4OH H_2O_2. × 100. Rolling Direction Horizontal.

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THE DEFORMATION LINES IN ALPHA BRASS.*

By CARL H. SAMANS,† Ch.E., M.S., Ph.D., MEMBER.

SYNOPSIS.

A microscopic study of 70 : 30 brass single crystals of two different orientations which had been reduced 50 per cent. in thickness by cold-rolling revealed the presence of many of the so-called "lines of deformation." X-ray determinations, by the Davey–Wilson method, of the orientations in the rolling plane showed conclusively that the markings were mechanical twins parallel to octahedral planes.

INTRODUCTION.

DURING the course of a study of the effect of cold-rolling on the orientation of single crystals of 70 : 30 brass several specimens were secured which offered conclusive proof of the nature of the "lines of deformation" frequently observed in face-centred cubic metals. This note is a brief description of two of these specimens.

EXPERIMENTAL PROCEDURE.

Two sections approximately 1 in. long, $\frac{1}{2}$ in. wide, and $\frac{1}{8}$ in. thick were cut out of a single crystal made by a modification of Bridgman's‡ method of slow cooling from a melt. The first of these, specimen O, was oriented with an octahedral, (111), plane approximately in the rolling plane and a dodecahedral, $[\bar{1}01]$, direction in the rolling direction, whilst the second, specimen C, had a cube, (001), plane approximately in the rolling plane, and a cube, $[\bar{1}00]$, direction in the rolling direction.

These were reduced 50 per cent. in thickness by cold-rolling through a set of hand rolls 7 cm. in diameter. After rolling, the specimens were given a deep etch in nitric acid in order to remove the "flowed" layer on the surface, and were then mounted in solder for further examination. The polishing and etching treatments given in preparing the specimen

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* Manuscript received April 27, 1934. Presented at the Annual Autumn Meeting, Manchester, September 5, 1934.

† Chase Brass & Copper Co., Waterbury, Conn., U.S.A. This paper is a section of a dissertation to be presented to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

‡ P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1925, 60, 305.

for microscopic examination were made with great care, because it was known from previous work, notably that of Vogel,* that lines of deformation would be produced by polishing if care were not taken. The final stages of polishing and etching with a mixture of ammonium hydroxide and hydrogen peroxide were repeated several times as an additional safeguard.

The Davey–Wilson † method was used to determine the orientations of the specimens. In this method X-rays, reflected from the surface of an oscillating crystal, are recorded on two films, one of which is stationary, whilst the other oscillates with the specimen. Since reflection from a given plane, according to Bragg's law, can occur only for a definite angle of incidence, spots on the stationary film will be fairly sharp whether or not the reflecting plane is "bent" or otherwise distorted. Only the resolution of the K_a-doublet will be affected. On the other hand, distortion will cause the spots on the oscillating film to be spread over an area, and may even make them too indistinct to be measured unless the plane is close-packed. The poles of planes, then, the reflections of which are recorded on both films can be located exactly, whilst those of planes the reflections of which are on the stationary film alone can be fixed only as lying within fairly restricted limits on a definite stereographic small circle.

MICROGRAPHIC AND X-RAY STUDIES OF SPECIMEN O.

A microscopic examination of the surface of specimen O showed numerous "lines of deformation," of which those shown in Fig. 1 (Plate XVI) are typical. Four distinct sets of these markings are visible, making angles with the rolling direction of approximately 90°, + 63°, + 4°, and — 60°, clockwise angles from the rolling direction being considered positive, and counter-clockwise negative.

The X-ray determination of the surface orientation gave the orientation for the matrix which is plotted stereographically in Fig. 2. In these projections, poles located from spots on both films are designated by ⊙, those from spots on the stationary film only by ×, and those plotted to complete the projection by ⊡.

In addition to these spots, however, the stationary film had recorded nine others, almost mirror images of the first set, which could not be explained by the matrix orientation. In Fig. 3 these spots are plotted on a projection of the matrix orientation that has been twinned on the (111) plane. This orientation is seen to account for all nine extra spots, the stereographic small circles which are the *loci* of their

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* R. Vogel, *Z. anorg. Chem.*, 1921, 117, 271–280.
† T. A. Wilson, *Gen. Elect. Rev.*, 1928, 31, 612.

poles corresponding in every case with a similar pole on the projection.

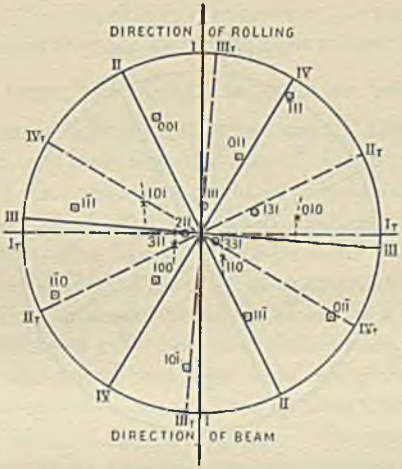

Fig. 2.—Comparison of Traces of the Lines of Deformation with the Matrix Orientation of Specimen O.

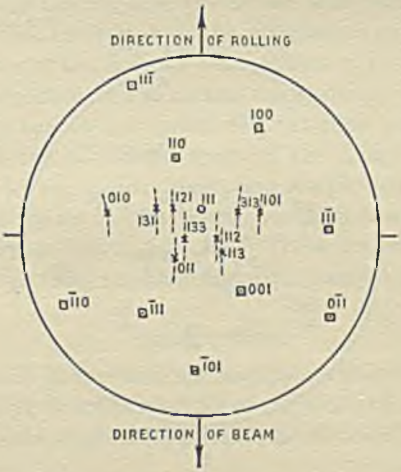

Fig. 3.—Orientation of Fig. 2 Twinned on (111), Showing Agreement of Extra Spots from Films of Specimen O.

The surface is thus shown to contain two orientations, one of which is derived from the other by twinning on the (111) plane. These orientations were redetermined several times, all of the films agreeing within a few degrees.

In Fig. 2 the traces of the lines of deformation are also plotted on the projection of the matrix orientation. The dashed lines represent

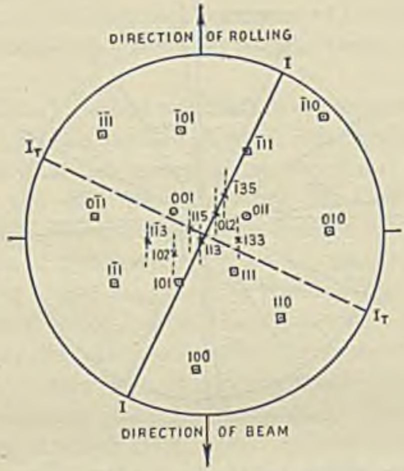

Fig. 5.—Comparison of Traces of the Lines of Deformation with the Matrix Orientation of Specimen C.

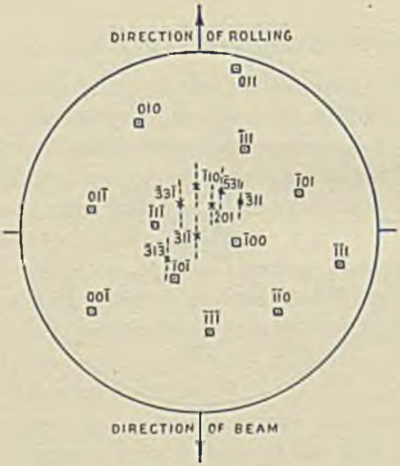

Fig. 6.—Orientation of Fig. 5 Twinned on ($\bar{1}11$), Showing Agreement of Extra Spots from Films of Specimen C.

the traces of the "lines of deformation" and the full lines the great circles normal to these traces which must be the *loci* of the planes causing them. There is a reasonable agreement between the traces and the poles of the octahedral planes. The irregular wavy markings approximately perpendicular to the rolling direction correspond with the traces of the (111) plane and must be, therefore, the material producing the twin reflections. The markings of this set of the four would be expected to reflect, as they are by far the most numerous and prominent.

MICROGRAPHIC AND X-RAY STUDIES OF SPECIMEN C.

In the undeformed specimen of orientation C there were four slip systems subjected to a high shearing stress. Consequently, the structure after a 50 per cent. reduction might have been expected to be quite complex. In about half of the surface a microscopic examination showed this expectation to be fulfilled. The other portion of the specimen, however, had deformed into lamellæ approximately parallel to the rolling direction. Some of these are shown in Fig. 4 (Plate XVI). It was originally thought that these were twin bands, but this idea was rejected when it was found that they were not parallel to octahedral planes. Attention was then directed to the lines that had been formed in the bands as a result of the deformation. The angles made with the rolling direction by these markings were approximately — 64° in the wide bands and + 59° in the narrow ones.

Whilst most of the X-ray films made from this specimen showed the orientations of both the lamellæ, the author was particularly fortunate to secure one which showed only the orientation of the wider bands. In Fig. 5 the trace of the lines of deformation in these bands has been plotted on the projection of the matrix orientation. It is seen that the pole of the $(\bar{1}11)$ plane lies very near the great circle perpendicular to the trace. In Fig. 6 the additional spots of the X-ray film which could not be explained by the major orientation are plotted on an orientation derived from that shown in Fig. 5 by twinning on the $(\bar{1}11)$ plane. The agreement is also excellent in this case. These lines of deformation are, then, the edges of thin mechanical twins parallel to the octahedral plane, $(\bar{1}11)$.

CONCLUSIONS.

On the basis of X-ray and microscopic evidence, the lines of deformation observed in cold-rolled single crystals of 70 : 30 brass have been shown to be the edges of thin mechanical twins parallel to octahedral planes.

ACKNOWLEDGMENTS.

The author wishes to offer sincere thanks to Dr. C. H. Mathewson of Yale University, and to Dr. D. K. Crampton of the Chase Brass & Copper Co., without whose assistance this work could not have been carried out. To Mr. H. L. Burghoff much credit is also due for making the single crystals and preparing the specimens for rolling.

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Microscopic and X-Ray Studies on Specimen C.

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Conclusions.

The evidence of X-ray and microscope confirms the lines of deformation observed in cold-rolled single crystals of 70:30 brass [illegible] to be [illegible] of thin mechanical twins parallel to octahedral planes.

Acknowledgments.

The author wishes to offer sincere thanks to Dr. C. H. Mathewson [illegible] Dr. [illegible] Committee of the [illegible] [illegible] and [illegible] preparing the specimens for [illegible]

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CRYSTAL DENSITIES OF INDUSTRIAL BRASSES FROM X-RAY DATA.[*]

By Professor E. A. OWEN,[†] M.A., D.Sc., Member, and LLEWELYN PICKUP,[‡] M.Sc. (Lond.), Ph.D. (Wales).

Synopsis.

Crystal density values have been obtained from X-ray data of copper-zinc alloys in thermal equilibrium, for compositions in the α-, $(\alpha + \beta)$, and β-regions. Whilst it is shown that the degree of porosity, cold-work, and grain-size have no effect on the results obtained, it is essential to take into account the heat-treatment given, when interpreting the values of alloys with duplex structures.

The relation between the composition of the pure α-phase and its density is not strictly linear, but both that of alloys in the pure β-region and that in the $(\alpha + \beta)$ region can be taken as linear to a high degree of accuracy. At the phase boundaries $(\alpha) - (\alpha + \beta)$ and $(\alpha + \beta) - (\beta)$ there are discontinuities in this relation.

Densities derived from X-ray data are considered to be nearer the true values than those obtained by any of the other methods hitherto employed, and hence, for copper-zinc alloys in true equilibrium the values obtained are the most reliable standards available for comparison purposes.

The usefulness of a density determination to ascertain the degree of unsoundness of a sample of alloy by comparison with a standard sample, has been pointed out by different metallurgists. One object of the investigations of Bamford [§] and of Bailey and Genders [||] was to determine the true densities of perfectly sound and homogeneous copper–zinc alloys of different compositions, to serve as standards of comparison. The main points raised in the discussions of these two papers were the question of the soundness of the samples used and the effect of cold-rolling on the density, the process of cold-rolling having been adopted by Bailey and Genders to close up any cavities present in the chill-cast alloy. It was reported that cold-rolling amounting to a 50 per cent. reduction was found to have no appreciable effect on the density, but it cannot be definitely concluded from this statement that perfectly sound material was thus produced.

To obtain the true crystal density of an alloy by means of the usual

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[§] Bamford, *J. Inst. Metals*, 1921, 26, 155.

[||] Bailey and Genders, *ibid.*, 1925, 33, 191.

method of weighing in air and in water there appear four aspects of varying importance to consider, namely: (1) freedom from porosity and impurities; (2) true thermal equilibrium; (3) effect of cold-work; and (4) effect of grain-size. In addition, if comparisons are to be made for ascertaining porosity, the casting conditions of the standard adopted and the sample to be compared must be the same, as a perfectly sound chill-cast sample, because of its unstable constitution, will not give the true crystal density corresponding with its composition. For example, Bailey and Genders found traces of the β-phase in a chill-cast alloy containing 71 per cent. copper, whereas this composition is well within the pure α-region of the thermal equilibrium diagram.

Values of the true crystal density can be derived from X-ray data, and these are independent of the grain-size, the presence of porosity, and the amount of distorted (amorphous) metal in the sample photographed. Therefore, of the four aspects already mentioned, only the true thermal equilibrium need be considered. It has been shown by the good agreement of the authors' determinations of the phase boundaries of the copper–zinc system with those of other workers that the X-ray data which have been published elsewhere * can be taken as applying to these alloys in their condition of true thermal equilibrium, and hence these can be used to obtain true values of crystal density. In the present paper, crystal densities derived from these data are given, as it is possible that these results will be of interest for comparison with, and a supplement to, the density investigations of Bamford and of Bailey and Genders. By such a comparison, some indications of the order of change in density due to cold-work and to grain-size may be found, two features about which little definite knowledge seems available. Further, apart from these simplifications of the problem, a higher degree of accuracy is available with the X-ray method than with the usual density method.

METHOD OF CALCULATION.

Pure copper and the α-phase in the copper–zinc system have a face-centred cubic structure having four atoms to the unit cube; then, if a is the parameter value (in A.) of the lattice of an alloy containing N atomic per cent. copper, the crystal density is given by the expression; †

$$\rho_a = 0{\cdot}06596\{Nm_{\mathrm{Cu}} + (100 - N)m_{\mathrm{Zn}}\}/a^3 \text{ grm. per c.c.}$$

where m_{Cu} and m_{Zn} are the atomic weights of copper and zinc atoms, respectively $(0 = 16)$.

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* Owen and Pickup, *Proc. Roy. Soc.*, 1932, [A], 137, 397.

† For the purpose of calculation, the atomic weight of hydrogen is taken to be 1·0078, $m_{\mathrm{Cu}} = 63{\cdot}57$, $m_{\mathrm{Zn}} = 65{\cdot}38$, oxygen = 16, and the mass of the hydrogen atom = $1{\cdot}662 \times 10^{-24}$ grm.

The β-phase of this system has a body-centred cubic structure having two atoms to the unit cube, so with the same notation the crystal density of this phase is given by the expression:

$$\rho_\beta = 0{\cdot}03298\{Nm_{\mathrm{Cu}} + (100 - N)m_{\mathrm{Zn}}\}/a^3 \text{ grm. per c.c.}$$

Utilizing the values of N and a from the authors' previous work,* these formulæ have been used to obtain the crystal densities of the α- and the β-phases. In these pure phase regions, since the lattice is unsaturated, the temperature from which the sample is quenched has no effect on the parameter value provided that the composition remains unaltered and does not enter an adjacent mixed region at any temperature.

Table I contains the calculated densities of the α-phase at different compositions in the pure region and at its saturated compositions on the α-(α + β) boundary at different temperatures.

TABLE I.

	Parameter, A.	Copper, per Cent.		Calculated Density 18° C., grm./c.c.
		By Weight.	Atomic (N).	
Pure α-region . . .	$3{\cdot}607_8$	100	100	8·938
,, ,, . . .	$3{\cdot}629_1$	89·3	89·6	8·799
,, ,, . . .	$3{\cdot}657_6$	76·4	76·9	8·626
,, ,, . . .	$3{\cdot}673_2$	70·3	70·9	8·531
,, ,, . . .	$3{\cdot}692_9$	62·8	63·5	8·413
Boundary of α-region at 350° C.	$3{\cdot}694_2$	62·5	63·15	8·404
,, ,, ,, 400° C.	$3{\cdot}695_7$	61·9	62·55	8·396
,, ,, ,, 500° C.	$3{\cdot}696_0$	61·8	62·45	8·394
,, ,, ,, 600° C.	$3{\cdot}694_3$	62·5	63·15	8·404
,, ,, ,, 700° C.	$3{\cdot}690_5$	63·9	64·5	8·426
,, ,, ,, 800° C.	$3{\cdot}686_4$	65·4	66·0	8·443

These results are shown graphically in Fig. 1, where it is seen that the relation between crystal density and composition in weight per cent. copper is not strictly linear.

Table II gives the calculated crystal densities of alloys of different compositions in the pure β-phase region.

These results are plotted in Fig. 1, where the relation between density and composition can be taken as almost linear.

In the mixed regions, where both phases are saturated, the parameter value of each phase, and therefore the density, is a function of the temperature, and is independent of the composition within the region. This change of parameter value with temperature is brought about by the change in the saturated solubility of the phases with temperature;

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* *Loc. cit.*

so that an alloy with a fixed composition within this region has a crystal density depending on the temperature from which it has been quenched. For example, at a temperature t° C., suppose the saturated compositions of the α- and the β-phases are at A and B per cent. copper, these are the α-(α + β) and (α + β)-β boundaries at t° C. Take an alloy containing p per cent. copper within this region, then the relative amounts of α- and β-phases present at the time of quenching are proportional to $(p - B)$ and $(A - p)$. If ρ_α and ρ_β are the crystal densities of the saturated α- and β-phases quenched from this temperature, then the density of an alloy of this composition quenched from t° C. is given by the formula:

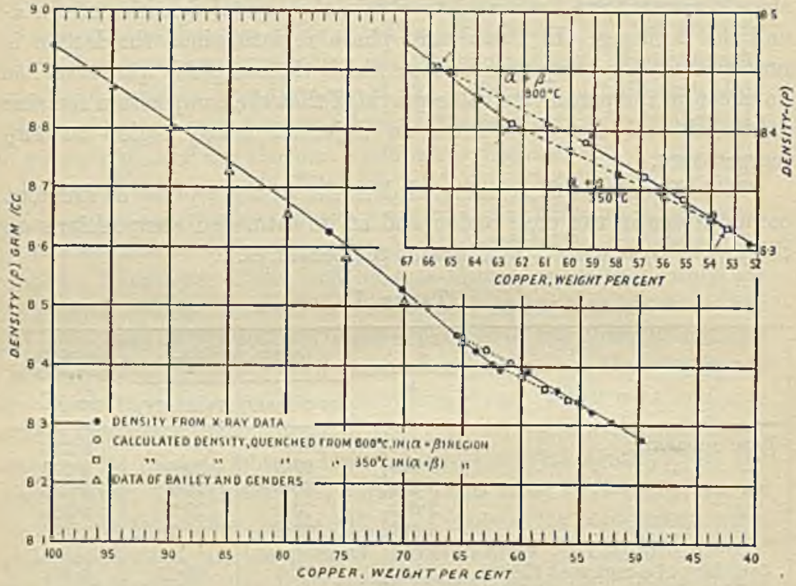

Fig. 1.

TABLE II.

Parameter (a), A.	Copper, per Cent.		Calculated Density 18° C., grm./c.c.
	By Weight.	Atomic (N).	
$2{\cdot}934_7$	59·4	60·1	8·389
$2{\cdot}938_8$	56·9	57·6	8·360
$2{\cdot}941_3$	55·2	55·9	8·343
$2{\cdot}943_8$	53·9	54·6	8·324
$2{\cdot}946_4$	52·3	53·0	8·306
$2{\cdot}950_5$	49·75	50·5	8·277

$$\rho_{\alpha\beta} = (A - B)/\left(\frac{p - B}{\rho_\alpha} + \frac{A - p}{\rho_\beta}\right) . \quad . \quad . \quad . \qquad \text{(i)}$$

In Table III, values of A and B, with corresponding values of ρ_α and ρ_β from Fig 1, are collected for use with the above formula, which may

TABLE III.

Temperature, t° C.	Boundary.*		$A - B$.	Density, grm./c.c.	
	$\alpha - (\alpha + \beta)$ (A).	$(\alpha + \beta) - \beta$ (B).		ρ_α (from Fig. 1).	ρ_β (from Fig. 1).
350	62·5	53·3	9·2	8·406	8·318
400	61·9	53·8	8·1	8·398	8·324
500	61·8	54·6	7·2	8·397	8·332
600	62·5	55·4	7·1	8·406	8·344
700	63·9	58·7	5·2	8·430	8·382
800	65·4	59·4	6·0	8·453	8·389

* See Owen and Pickup, *loc. cit.*

be written for calculation purposes in the more convenient form,

$$\frac{1}{\rho_{\alpha\beta}} = C - p \, . D \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(ii)}$$

where
$$C = \frac{A\rho_\alpha - B\rho_\beta}{\rho_\alpha\rho_\beta(A - B)} \quad \text{and } D = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha\rho_\beta(A - B)}$$

The values of the constants C and D in formula (ii) for different values of t° C. are given in Table IV.

TABLE IV.

Temperature, t° C.	C.	D.
350	0·12750	0·00013680
400	0·12718	0·00013069
500	0·12705	0·00012904
600	0·12673	0·00012400
700	0·12699	0·00013064
800	0·12814	0·00015042

In order to ascertain the change in density produced in an ($\alpha + \beta$) alloy of fixed composition when quenched from different temperatures, formula (ii) with Table IV have been used. The densities of alloys with compositions 60, 58, 56, and 54 per cent. copper, which remain in the mixed regions at the quenching temperature are contained in Table V.

The densities of the alloys containing 60, 58, and 56 per cent. copper have been plotted in Fig. 2 against the quenching temperature. The form of each curve is similar, showing a minimum density in the temperature range 400°–500° C. The last two alloys pass, at the higher temperatures, into the pure β-region, where the density is constant. Fig. 2

TABLE V.

Quenching Temperature, t° C.	Crystal Densities of Alloys in ($\alpha + \beta$) Region.			
	Copper, per Cent. by Weight.			
	60.	58.	56.	54.
350	8·382	8·363	8·344$_5$	8·326
400	8·379	8·361	8·343	8·325
500	8·381$_5$	8·363	8·346	...
600	8·385	8·368	8·350	...
700	8·393	...	...	...
800	8·396	...	...	...

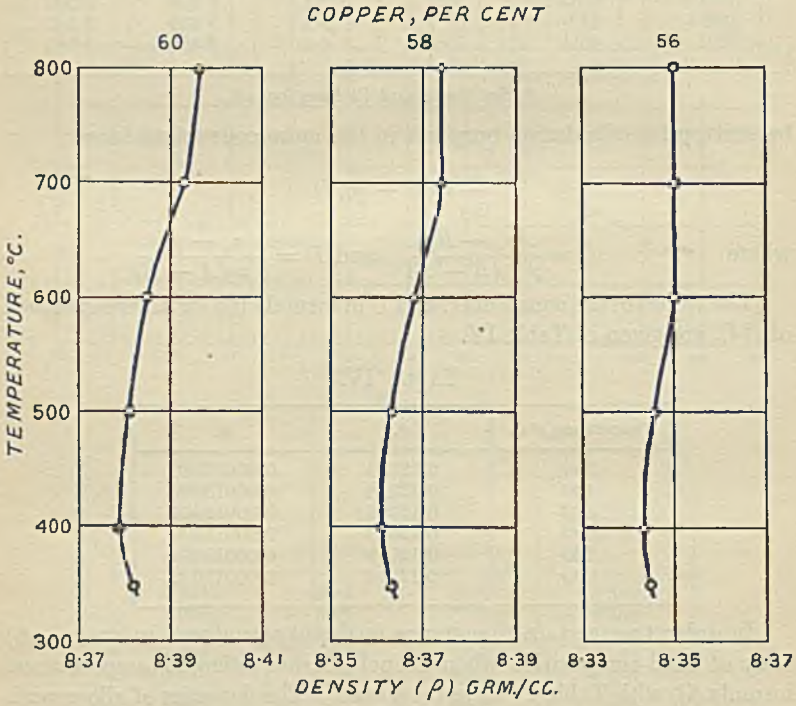

FIG. 2.

shows clearly that alloys with compositions in a mixed region can have density values which depend on the temperature from which they have been quenched. If an alloy is allowed to cool from an annealing temperature, the density value may vary considerably, depending on the rate of cooling. Such considerations as these lead the authors to emphasize that the precise heat-treatment of a sample with a composition in the mixed region should accompany the determined value of its density. As already mentioned, this precaution is not of such importance for alloys in the pure regions, provided that the heat-treatment is sufficient to bring about the true thermal equilibrium. As a consequence of these observations, since lump samples often require considerable periods of annealing to produce, throughout their entire mass, the state of true thermal equilibrium, density values on such samples obtained by the usual method must be interpreted with caution. In a paper * on copper–cadmium alloys, the authors have investigated the effects of different annealing heat-treatments in producing the true stable equilibrium, and have concluded that this state can be most expeditiously attained when the alloy is in the form of powder or fine filings; therefore, the values of the crystal densities of alloys in the $(\alpha + \beta)$ region, calculated by means of formula (ii) and Table IV, are probably nearer the true values than those obtained with lump samples by the direct method. In Fig. 1, the density of alloys in the $(\alpha + \beta)$ region and the neighbouring α- and β-pure regions, which have been quenched from 350° C. and from 800° C., are plotted against the composition in weight per cent. copper.

Fig. 1 shows the relation between the density and composition from 100 to 50 per cent. copper. In the range of composition between 67 and 55 per cent. copper, there is a variable range of densities depending on the heat-treatment. Similar phenomena are shown in the completed curve of Bailey and Genders, and their explanation is fundamentally that given in the present work.

According to Fig. 2, when an alloy consisting entirely of β-phase above a certain temperature, breaks up into α- and β-phases on cooling, there is a decrease in the density. This observation confirms that of Bailey and Genders. They also state that "a pure β alloy (52 per cent. copper) showed no appreciable change in density, whether quenched in water from 700° C. or slowly cooled to 300° C. at a rate of 10° C. per minute." From the authors' observations, no change in density is to be expected in any pure phase at whatever rate the sample is quenched or cooled, provided that the lattice structure remains unaltered.

The data given by Bailey and Genders, from which they deduce the production of porosity by a constitutional change $(\beta \longrightarrow \alpha)$ during the annealing treatment at 500° C. to produce equilibrium, are interesting. Referring, however, to their data on alloy 65·2 per cent. copper, the annealing at 500° C. after quenching and rolling gives a low density value, which can also be explained by the presence of cavities, which have only been diminished in volume, and not eliminated by the cold-

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* Owen and Pickup, *Proc. Roy. Soc.*, 1933, [A], 139, 526.

working. There appears to be some support to this conclusion from a comparison of the densities at different compositions, obtained by these authors, and those calculated from the present X-ray data, the X-ray densities being slightly higher in alloys in which the constitutional change ($\beta \longrightarrow \alpha$) cannot take place (see Fig. 1).

The densities obtained from X-ray data for alloys in equilibrium in the pure α-region are shown in Table VI, and are the densities which the authors consider should be used for standards of comparison. In the case of alloys with compositions in the ($\alpha + \beta$) region the heat-treatment given must be carefully specified, as the densities of alloys in mixed regions are found to depend on the heat-treatment to which the alloys are subjected.

TABLE VI.

Copper, per Cent.	Density from X-Ray Data, grm./c.c. at 18° C.
100	8·938
95	8·876
90	8·812
85	8·747
80	8·677
75	8·604
70	8·528
65	8·448

After comparing the present authors' density values with those of Bailey and Genders, it is concluded that the effects of cold-work and of grain-size on the density must be small, in comparison with the effect due to unsoundness.

CONCLUSION.

To obtain accurate values of the density of perfectly sound alloys by the usual method of weighing in air and in water, involves considerable experimental difficulties, the greatest of which appears to be the elimination of any unsoundness or porosity which may be present.

The values obtained from X-ray data are the crystal densities, and are probably nearer to the true densities than those obtained by other methods, in which difficulties arise due to porosity, cold-work, grain-size, and also heat-treatment in the case of alloys with duplex structures.

The densities of alloys consisting of a single phase are not affected by heat-treatment when in true equilibrium, whilst alloys consisting of a duplex structure can give a range of values depending on the heat-treatment which they have received.

The effects of cold-work and of grain-size on the density are small, but at present few quantitative data are available.

DISCUSSION.

Dr. R. Genders,* M.B.E. (Member): Some years ago, Mr. G. L. Bailey and I were interested in the estimation of the degree of unsoundness in brass specimens by determination of the density by the ordinary method of weighing in air and water. We found that in some cases we obtained densities higher than the values (for sound material of the same composition) interpolated from the data available at that time. Consequently we undertook the redetermination of the density of the copper–zinc alloys, and the results, covering the whole range of composition of the industrial brasses, were published in 1925.†

At that time we realized that X-ray measurements could be utilized for the calculation of crystal densities, and we were obliged to refer somewhat critically to the relatively low accuracy of the method as then practised. Since that time, however, X-ray technique has been developed and highly accurate results obtained over a wide range of metallic alloys. The present authors have accordingly utilized X-ray data published some time ago in connection with their survey of the constitution of the copper–zinc alloys and have calculated a set of values parallel to those which Mr. Bailey and I put forward in 1925.

Considering that the specimens were made from different materials, were analyzed possibly by different methods, and were generally independent in all respects, the agreement is very close, and may be regarded as confirming both sets of data. It is clear that the X-ray method is capable of giving accurate determinations of crystal density.

The authors confirm also the effect of heat-treatment on the density of duplex brass alloys, and the absence of such effect in the pure phase alloys. They conclude further that the effect of such factors as grain-size and cold-work on density must be very small.

In discussing this paper I should like to emphasize its value not only in its present connection but also as a demonstration that there is now available a second method of determining accurately the maximum density of alloys which is free from some of the difficulties associated with the ordinary method of weighing in air and water. Although it has those advantages, and is independent of the soundness of the material, the X-ray method is nevertheless not more accurate, I consider, than properly conducted weighing experiments, especially in the case of alloys such as the brasses, which contain an element volatile at high temperature. This factor tends to complicate the heat-treatment of alloys which, for X-ray purposes, must be heat-treated in the form of powders, and may affect the reliability of the results obtained.

The density of pure copper given by the authors is 8·938; the previous value, obtained by Mr. Bailey and myself on slightly cold-worked copper, was 8·933. From time to time various higher values have been put forward in published work, and it is reassuring that these have not been confirmed. The true value for pure copper may now be regarded as 8·935 ± 0·002.

At the commencement of the paper the authors make a statement, possibly slightly misleading, regarding the effect of cold-rolling cast brass specimens to a 50 per cent. reduction in thickness. With regard to that point, Mr. Bailey and I were able to prove quite conclusively that a sample of brass rolled to 50 per cent. reduction in thickness suffers no appreciable change in density due to the effect of cold-work on the crystal lattice—such as one might expect, for instance, from the production of amorphous material—while at the same time that reduction can be relied upon to close up completely any unsoundness present, and give a density which is not increased by further working.

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* Research Department, Woolwich.

† *J. Inst. Metals*, 1925, 33, 191.

In our paper Mr. Bailey and I pointed out some curious effects obtained by heat-treatment of the $\alpha + \beta$ alloys. This matter appears to have been only partially considered by the authors. The production of unsoundness by phase change was involved, and in this respect the method of X-ray measurement has its limitations.

Professor D. Hanson,* D.Sc. (Vice-President): This paper is of interest to metallurgists because it reveals the extraordinary accuracy with which modern X-ray technique can be applied to some of our own problems in connection with the investigation of the constitution of metallic alloys. I have no doubt that the X-ray methods have now reached a point at which they can add very considerably to the accuracy of the methods which we have had to use in the past. Those methods require, however, very great care, not only in the actual X-ray technique itself but in the preparation of the samples which are used, because the whole of the accuracy can be lost if appropriate material is not employed.

That brings me to a consideration of one small item in this paper, where the authors refer to the method of using filings with a view to arriving at a quicker equilibrium on annealing. They are inclined, I think, to attribute the quickening to the smallness of the particles, but I do not think that is correct; it is probably due to the fact that in preparing those filings each little particle is cold-worked, and we now know that cold-worked material attains equilibrium much more quickly than material which is not cold-worked. In fact, in metallographic investigations it is quite common to cold-work specimens before annealing in order to hasten the attainment of equilibrium. There is a danger in this method of using filings, however, because if there is heterogeneity on a large scale it may be that neighbouring filings will differ appreciably in composition, and then there is no possibility of diffusion giving equalization of composition, so that errors may be introduced in this way which would vitiate the accuracy and value of the results.

The other point to which I should like to refer arises from a comment made by Dr. Genders, who referred to this so-called new method of measuring density and said that the agreement of these results with his own work proved the accuracy of the X-ray method. That is not, I think, a fair comparison to make. This new method of measuring density is not to be compared in any way with the method of measuring densities by weighing in air and water. The X-ray method really determines the spacing of the atoms, and from the known weights of the atoms the densities can be calculated. It takes no account of irregularities in the atomic structure or of the presence of non-metallic inclusions or of holes, and it is a method which measures something entirely different from the method of measuring in air and water. That ought to be borne clearly in mind. X-rays give the density of the "perfect" crystal of the metal and take no account of small amounts of other things, so that the average density of the sample might be very different from that revealed by X-rays, even though there were no holes or anything like that in it. That should also, I think, be brought to the attention of the practical man. A friend of mine said that he had been told of this new X-ray method for measuring densities and wondered whether he could use it on his castings and if it would prove a rapid and useful method of measuring densities in practice. It is not anything of the sort, of course; it does not measure densities in such a way as to reveal internal unsoundness and so on, and that point should be emphasized.

Mr. G. L. Bailey,† M.Sc. (Member): This paper is largely devoted to a

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* Professor of Metallurgy, The University, Birmingham.

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

comparison of the authors' results with the density values which Dr. Genders and I put forward some years ago,* and it is on one point in this comparison that I should like to make a few remarks. We had observed that the change in structure from β to α on annealing a chill-cast α + β brass is accompanied by a reduction in density, and we now have confirmation of that change by the present authors utilizing the latest improvements in X-ray technique. We found, however, that this reduction in density was the result of a change in the actual density of the crystals together with an added fall in density due to the production of unsoundness. The present authors state that this additional fall can be explained by the presence of cavities which had only been diminished in volume and not eliminated by cold-working.

I find it very difficult to accept that solution and to agree that it provides an explanation of the phenomena we observed. For instance, quenching such a brass after annealing restores that material to its original density; that is to say, quenching not only reverses the density change due to the change in structure but also that due to the production of unsoundness.

Further, the method of preparation of the various compositions of brass we examined was the same through the whole range pure α, α + β, to β, and only in the α + β was there any reduction in density on annealing. Had the original castings contained gas cavities, then 50 per cent. cold-work would be expected to close them only partially, and the subsequent annealing might produce a reduction in density due to the expansion of those gases; but that did not operate in the higher copper–brasses nor would it explain the reversibility of the change on re-quenching.

Our views on this matter were clearly expressed in two sentences † which I may perhaps be permitted to quote:—"It would appear that on annealing a cast and rolled alloy containing β, the fall in density consequent to the change from β to α is accompanied by an added fall which can be largely neutralized by compression and may therefore be assumed to be due to the formation of cavities. At the same time, the fact that quenching the annealed alloy can reverse the whole of the fall suggests that the unsoundness is produced as a consequence of the constitutional change during annealing, and does not consist of cavities such as exist in a casting."

I have emphasized this point to indicate that we were fully aware of the possible presence of unsoundness in our castings in spite of all precautions, and when we observed this decrease in density on annealing its possible connection with such unsoundness was our first consideration. We were able to satisfy ourselves, however, that a complete explanation of the phenomenon could not be obtained on these lines and nothing that the present authors have said seems to me to alter the position.

CORRESPONDENCE.

The Authors (*in reply*): A comparison of the relative accuracy of the X-ray method with that of the method of weighing in air and in water for the determination of density, made by Dr. Genders, is not possible, as indicated by Professor Hanson. While the former may be called an "ultra microscopic" method, the latter is a "macroscopic" method. The X-ray data are based on the measurement of a fundamental physical constant, namely, the lattice parameter of the crystal unit. It was for this reason that they were put forward in the present paper as being the most suitable standards for comparison purposes; they concern perfectly sound material. The reduction in density when

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* *J. Inst. Metals*, 1925, 33, 191.

† *Ibid.*, p. 198.

an alloy changes from β into $\alpha + \beta$, shown by our work, has been noted by Dr. Genders and Mr. Bailey, but such a change does not necessarily mean that unsoundness had resulted in the sample. In Fig. 2 the data showing this decrease in density were calculated from the density of the saturated α and β phases, and the results applied to perfectly sound material. There does not appear to be any specific reason why during this change the total volume of a sample should, to produce cavities, become still greater than that required to accommodate the change as suggested by Dr. Genders and Mr. Bailey. The X-ray data cannot throw any light on the production of such cavities.

We are indebted to Professor Hanson for his remarks, especially those which point out the fallacy in comparing the two methods of determining density. For the data to be of value the filings have to be homogeneous, and for the precautions taken and the experimental work done on this point, we would refer Professor Hanson to our previous papers,* from one of which the present results have been calculated. The ingots were always annealed in lump form to produce homogeneity before filings were taken. When the material is in the form of filings there is no doubt that the effect of cold-work and not the smallness of the particles is the main factor in attaining equilibrium. We regret that the paper may have conveyed to Professor Hanson a wrong impression on this point. The question of possible volatilization was overcome by annealing the filings in small sealed evacuated glass containers for short periods (a few minutes were sufficient at 500° C.). The actual sample irradiated was afterwards chemically analyzed.

Although Mr. Bailey maintains that he and Dr. Genders found no evidence of unsoundness in their samples in the pure α region, the X-ray densities are definitely slightly higher than the densities they found. With regard to the second sentence quoted by Mr. Bailey from his and Dr. Genders' paper, we would add that a higher density after re-quenching is consistent with the presence of cavities, if the contraction on quick cooling is sufficient to close them up. We maintain, therefore, that it cannot be definitely concluded that perfectly sound material had been produced. Apart from this difference the agreement between the data of Genders and Bailey and the X-ray data (using two quite different methods) is very close. By using the X-ray data as standards of comparison, the amount of porosity in a sample of brass which has a known composition and is free from impurities can be obtained with accuracy when its bulk density is measured by weighing in air and in water.

Dr. A. L. **Norbury** † (Member): The authors appear to have obtained very accurate results by their method which, as they rightly claim, has certain advantages over the ordinary method of weighing in air and in water. In 1923 I published results ‡ giving the densities of zinc–copper α solid solutions in the 0–16 per cent. zinc range. I believed that by hammering them to about 60 per cent. reduction in thickness I had obtained sound metal and accurate density results. These results for copper α solid solution alloys containing zinc and other elements are reproduced in Fig. A. They were calculated to a slightly different basis from the authors' since allowance had been made for the air displaced. This, however, only had the effect of adding about 0·001 to my density results. The chief point I wish to make is that the results lie on a curve of the form shown in Fig. A and not of that shown by the authors in Fig. 1. The authors only examined one composition in the 0–15 per cent. zinc region in question, and this point lies almost exactly on the curve shown in Fig. A. It would consequently be interesting if they could examine further alloys in this region by their method, to settle the matter.

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* *Proc. Roy. Soc.*, 1932, **137**, 397; 1933, **139**, 526.

† Senior Metallurgist, British Cast Iron Research Association, Birmingham.

‡ *Trans. Faraday Soc.*, 1924, **19**, 586.

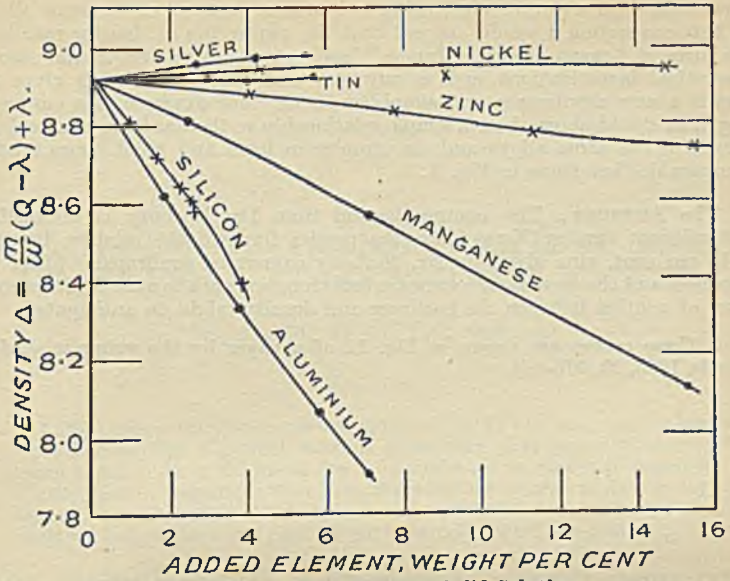

FIG. A.—Densities of Copper α-Solid Solutions.

I have also calculated the results shown in Fig. A as "mean atomic volumes" as shown in Fig. B in the following manner :—

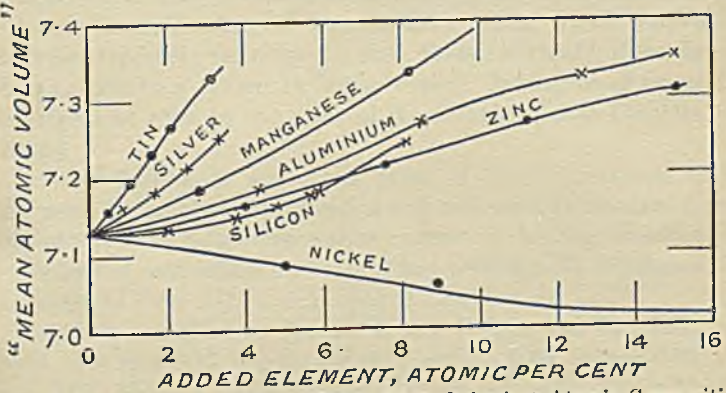

FIG. B.—"Mean Atomic Volume" Values Plotted Against Atomic Composition, Copper α-Solid Solutions.

In a binary alloy of metals *A* and *B*, mean atomic weight = atomic weight *A* × per cent. *A* in alloy + atomic weight *B* × per cent. *B* in alloy.

$$\text{" Mean atomic volume "} = \frac{\text{mean atomic weight}}{\text{density of alloy}}$$

It will be seen that the curves in Fig. B all have the same form which lends support to the form of the zinc–copper curve shown in Fig. *A*. The curves also bear a simple relationship to hardness curves * on the same alloys. In this connection I would suggest that the expression of density results in the form of "mean atomic volumes" has certain advantages in the case of theoretical investigations such as my own and the authors'. It gives the results a new significance and simplifies them. For example, the curves in Fig. B as stated above, bear a simple relationship to the hardness–composition curves of the same alloys and are simpler in form and much more readily comparable than those in Fig. A.

The AUTHORS: The communication from Dr. Norbury is interesting, but without further X-ray data the precise form of the relation between 0–15 per cent. zinc given by Dr. Norbury cannot be confirmed. Since the hardness and the crystal structure are both functions of the atomic forces some form of relation between the hardness and density might be anticipated.

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* These curves are shown in Fig. 12 of a paper by the writer in *J. Inst. Metals*, 1923, 29, 407–444.

THE MAGNETIC TRANSFORMATION POINT OF HEAVILY COLD-WORKED NICKEL.*

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By H. QUINNEY,† M.A., Member.

Synopsis.

The Curie point of commercial nickel of 99·62 per cent. purity has been found to be 330° C., which is much lower than that generally accepted for pure nickel. After the metal has been subjected to torsional overstrain the Curie point on heating is raised considerably but returns to its original value on cooling. No such effect is observed with mild steel since the strain is relieved before the metal reaches the relatively high Curie point.

Many physical properties of ferromagnetic materials change rather abruptly at temperatures near the so-called Curie point. Lacking a precise experimentally useful definition of the Curie point, we may perhaps be in uniformity with general usage by employing the expression to denote a small range of temperatures within which the various properties, especially the magnetic ones, change abruptly, these changes not being due to a change in lattice type.‡ It may be of interest in this respect to refer to the work of N. Michejew,‖ Ray Chaduri, and S. Satô.§

In what follows an account is given of the temperatures of the Curie point for highly-strained nickel and mild steel as obtained from a study of: (1) the temperature–time curves on heating and cooling; (2) changes in magnetism on heating and cooling; (3) expansion and contraction of these metals on heating and cooling.

The nickel supplied by Messrs. Henry Wiggin and Co., Ltd., was alloyed with iron 0·15, magnesium 0·12, carbon 0·05, copper 0·04, and silicon 0·02; giving a nickel content of 99·62 per cent. The mild steel had the following composition: carbon 0·15, silicon 0·2, manganese

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* Manuscript received December 27, 1934. Presented at the Annual Autumn Meeting, Manchester, September 5, 1934.

† University Engineering Laboratory, Cambridge.

‡ Bredig suggests, however, a possible change of lattice type between 357° and 363° C. for pure nickel.

‖ N. Michejew, *Physikal. Z. Sowjetunion*, 1933, 3, 393.

§ S. Satô, "On the Thermal Measurement of the Latent Energy in Cold-Worked Metals and Alloys," *Sci. Rep. Tôhoku Imp. Univ.*, 1931, 20, 140–177.

0·63, sulphur 0·043, phosphorus 0·027, nickel 0·08, and chromium 0·041 per cent.

The advantage of torsional overstrain as a means of giving a heavy degree of cold-working to metals has been made use of by the author in a long series of tests which has been made during the last few years.*

With ductile metals subjected to tension, the amount of cold-working which can be introduced is limited by the fact that a local weakening occurs, with the familiar necking and consequent fracture.

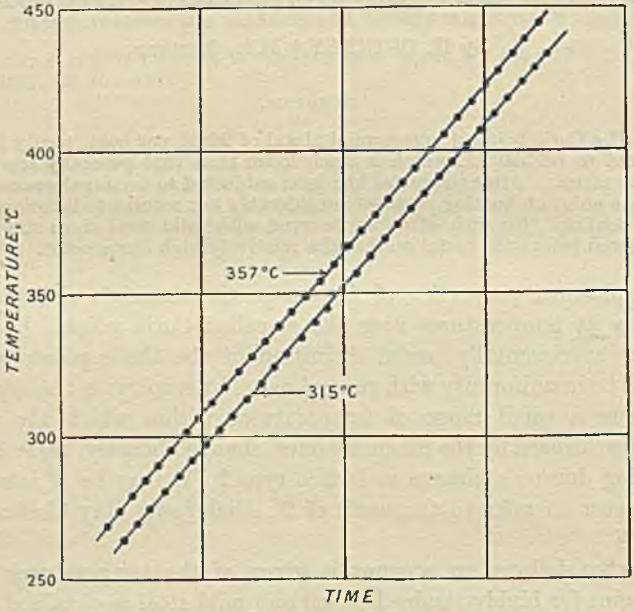

Fig. 1.—Nickel.

In torsion no neck is formed, and plastic deformation occurs throughout the whole length, with the result that the amount of cold-working which can be introduced before rupture is enormously increased. This is particularly marked in nickel as normally supplied by the manufacturer (Messrs. Henry Wiggin and Co., Ltd.). In two equal specimens of the same material it was found possible to do nearly 100 times as much work in torsion as was possible in tension.*

The difference, however, is much less in the case of mild steel.

When these torsion tests were first undertaken it was observed that in most cases there was an appreciable lengthening along the axis after the elastic limit was passed. The author,* accordingly, constructed the

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* Taylor and Quinney, *Proc. Roy. Soc.*, 1934, [A], 143, 310.

machines, on which such tests are made, to allow of axial expansion of the specimen and the consequent avoidance of any axial compression. Ductile specimens, tested in this way in pure torsion, preserve their original cylindrical form up to the point of rupture, and a specimen can be prepared for heat-treatment from the twisted bar, without the necessity of machining the surface other than facing two ends of the cylinder, and drilling the hole required to accommodate the thermocouple.

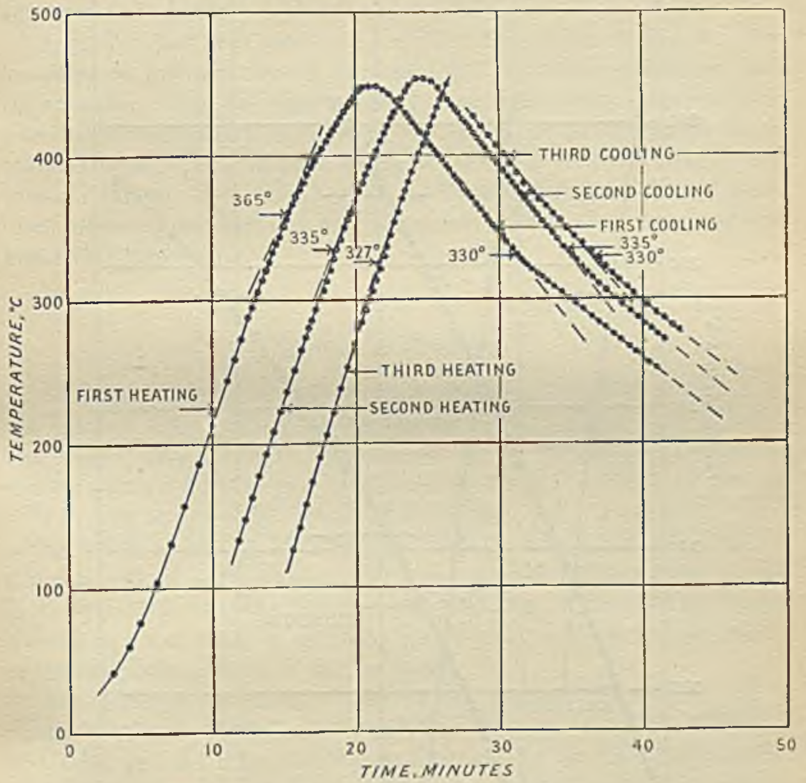


Fig. 2.—Nickel.

Two types of torsion specimens were used. In one, the part of the specimen to be twisted was initially $3\frac{1}{2}$ in. long, and its diameter was $\frac{5}{8}$ in., in the other the part to be twisted was 4 in. long and $\frac{3}{16}$ in. in diameter.

Temperature–Time Curves.

Considering first the temperature–time curves, Fig. 1 shows part of the temperature–time curve for a $\frac{5}{8}$-in. diameter specimen of nickel, heavily overstrained in torsion, tested in a vacuum up to a temperature of about 600° C., heat being supplied at an approximately uniform rate, and then reheated a second time through the Curie temperature. It will be seen that the Curie temperature is approximately 357° C. in the first case and about 315° C. in the second case, and that a fairly well-defined discontinuity of slope occurs at these temperatures.

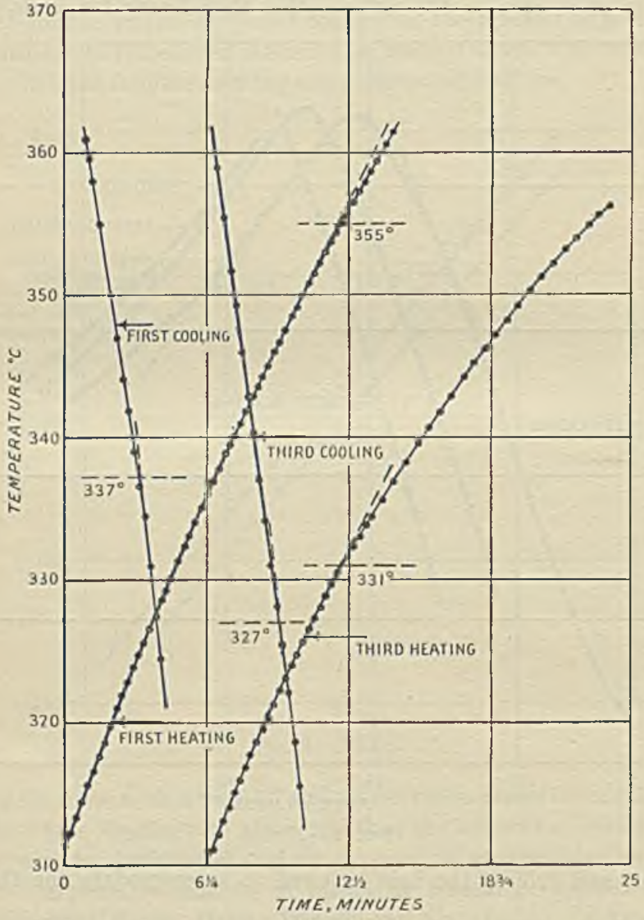


Fig. 3.—Nickel.

Fig. 2, shows the temperature–time curves obtained for a $\frac{3}{16}$-in. diameter nickel bar, twisted 25 complete turns before heating in an open furnace. (Between 30 and 40 turns are possible before fracture develops.) Again the Curie point on first heating is about 365° C. The temperature did not exceed 450° C. before cooling took place, and the Curie temperature on cooling is seen to be in the region of 330° C. On second heating the Curie point is reduced to about 335° C. and reappears at about this same temperature on cooling. The specimen was then heated to about 900° C. and the Curie points on heating and cooling appeared to be in the neighbourhood of 330° C.

A further test was made on a similar bar shown in Fig. 3. The temperature was not allowed to exceed 366° C. before cooling, so that the annealing effect was reduced so far as possible. The curve indicates a temperature of 355° C. on heating and 337° C. on cooling for the Curie temperatures. The specimen was next heated to 1000° C. and allowed to cool. It was then tested again for Curie points and the temperatures indicated are 331° and 327° C. approximately, these temperatures being very uncertain.

MAGNETIC CHANGES.

In determining the changes in magnetic properties with temperature the bar and yoke method, first invented by John Hopkinson in 1885, was used. The specimen, surrounded by a non-inductively-wound electric furnace, formed part of a magnetic circuit to which a constant M.M.F. was supplied by means of a primary coil. A secondary coil connected to a suitable ballistic galvanometer was also included in the magnetic circuit. The change of flux produced by reversing the current in the primary coil, was measured by the fling of the galvanometer. No attempt was made to estimate the true intensity of magnetization or the magnetizing force in the specimen.

Fig. 4 shows the relation between the temperature recorded by a rhodio–platinum thermocouple, suitably inserted into the strained specimen, and the magnetization as observed by the ballistic galvanometer fling, when the specimen is first heated steadily up to a temperature of about 800° C. The magnetization steadily increases with temperature to approximately twice its original value, until the point *A* is reached, then falls abruptly at a temperature of 341° C., and the specimen appears to have become non-magnetic at point *B* about 360°–370° C.

The first heating is continued up to a temperature of about 800° C., *i.e.* considerably in excess of the Curie point, and the restoration of magnetization when the specimen again cools through the Curie temperature about 320° C. shows a considerable increase, being approximately three times as great as on commencement of first heating with

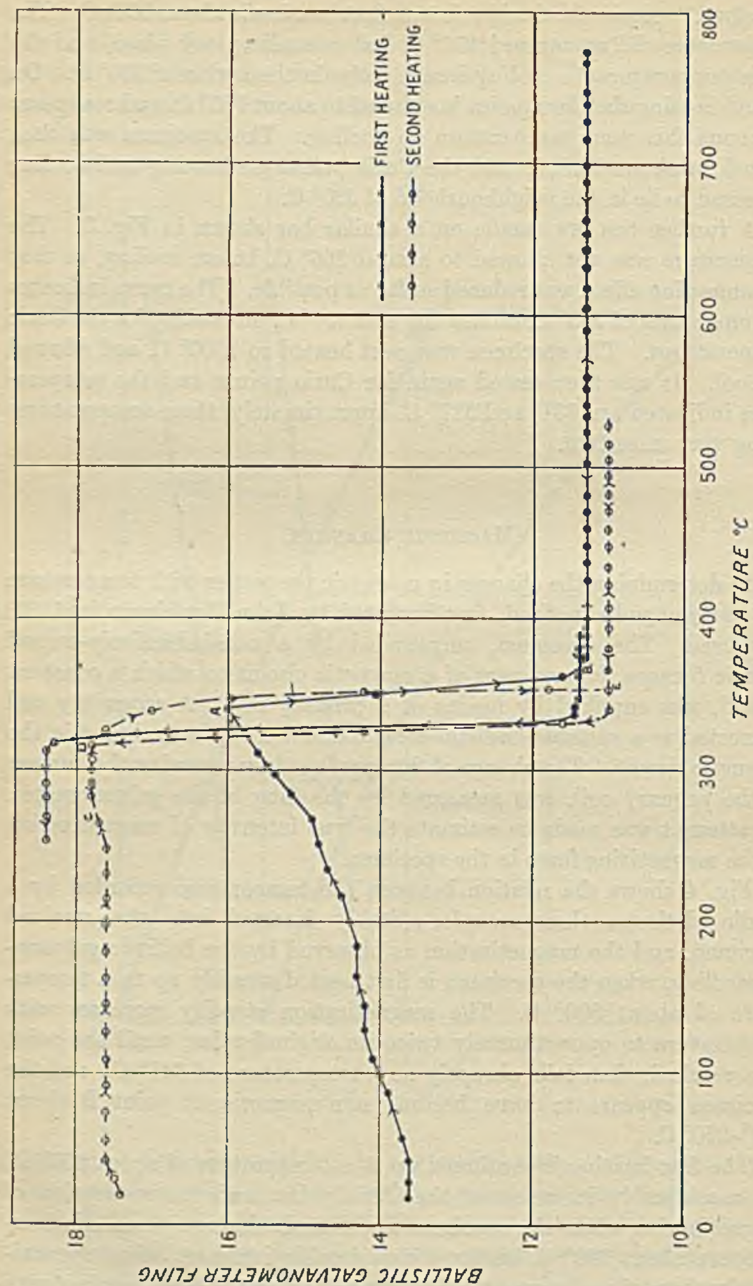

FIRST HEATING
SECOND HEATING
A
B
D
E
E
TEMPERATURE °C
0
100
200
300
400
500
600
700
800
BALLISTIC GALVANOMETER FLING
10
12
14
16
18

Fig. 4.—Nickel.

the specimen in the strained unheated condition. The heating and slow cooling of the originally overstrained nickel from a temperature of 800° C. undoubtedly removed almost completely the effects of overstrain.

The second heating curve shows that the magnetization remains practically constant except for the "hump" between the points *C* and *D*, which appears for low values of magnetizing force, for iron as well as nickel, at a temperature about 50° C. before reaching the Curie temperature.

The decrease in magnetization on second heating commences at *D*, 317° C., proceeding less abruptly than on first heating, and the specimen appears to have become non-magnetic at *E*, 350° C. The Curie temperature interpreted from the curve obtained for second heating, in the same way as was done for first heating, would appear to be 330° C. The temperature for second heating was not taken above 530° C. and the curve obtained by cooling lies almost over that obtained after cooling when first heated.

Although approximately the same M.M.F. was applied in the first and second heatings, the flux produced when the specimen is non-magnetic is less in the second heating than on the first heating. This is probably due to small changes in the air gaps in the two cases, which are unavoidable.

A considerable lag is shown between the Curie temperature determined in this manner on heating and cooling nickel, amounting to rather more than 20° C.

Fig. 5 shows the corresponding results obtained from a specimen of similarly overstrained commercial mild steel. As in the case of nickel, there is a general tendency for the magnetization to increase as the temperature approaches the Curie point. This increase in mild steel is, however, very much less than in the case of nickel, for the particular magnetizing force employed, although for other magnetizing forces the differences might not be so pronounced. The magnetizing force was the same as that used for nickel. It is proposed to carry out a series of tests using other values of *H*. The Curie temperature is, however, much higher, and the consequent recovery from overstrain due to heating to the Curie temperature is more complete than is the case for nickel.

The first and second heating curves shown in Fig. 5 do not indicate any appreciable difference between the Curie temperature obtained for strained, and unstrained mild steel. Moreover, the lag between the heating and cooling values of the Curie temperature is very considerably less than for nickel, being only about 5° C., as against 20° C. for nickel.

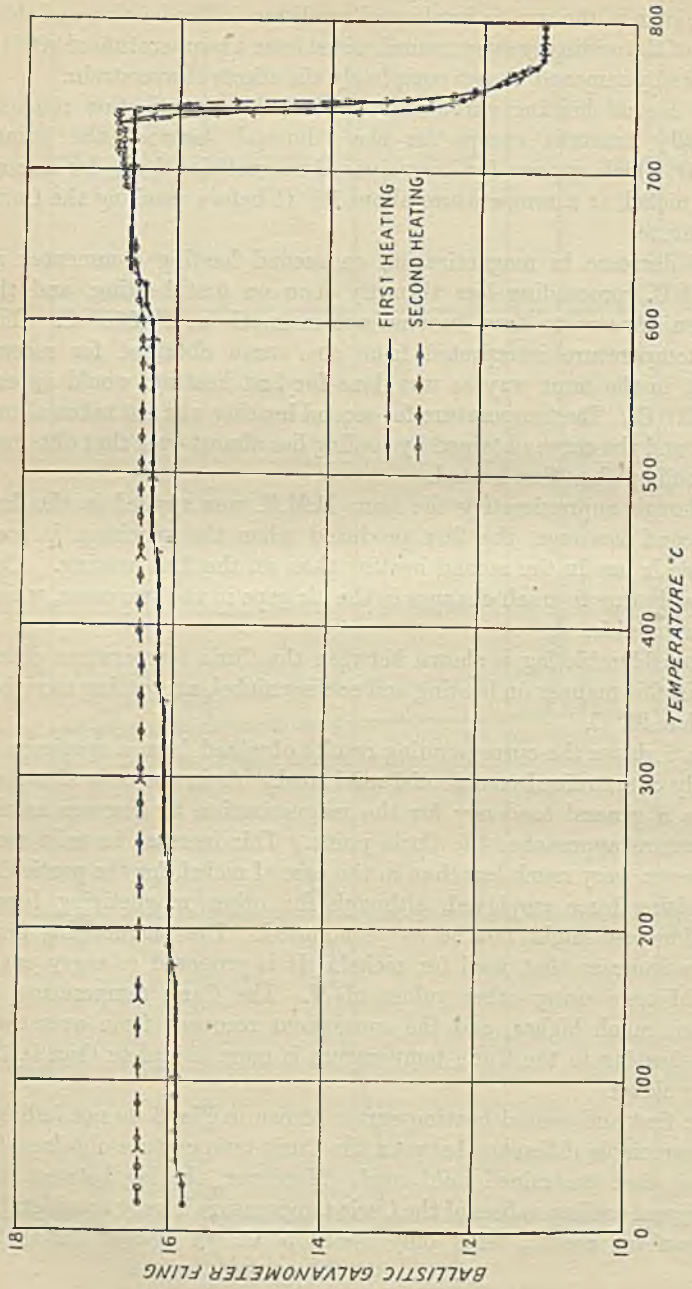
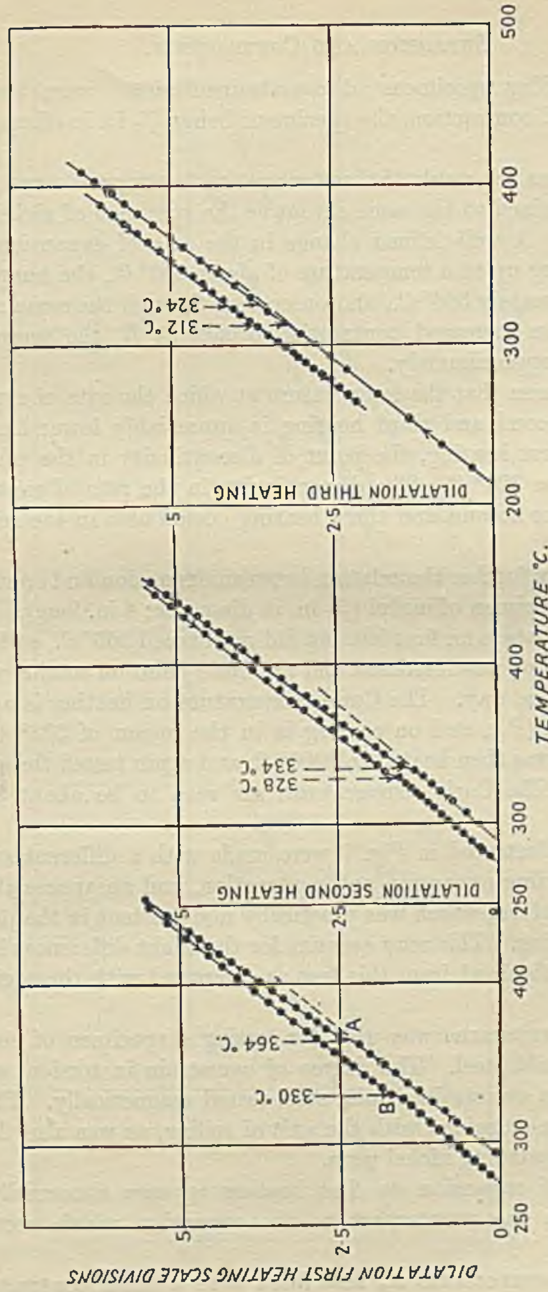


Fig. 5.—Mild Steel.



DILATATION THIRD HEATING
324 °C.
312 °C.
DILATATION SECOND HEATING
334 °C.
328 °C.
DILATATION FIRST HEATING SCALE DIVISIONS
364 °C.
330 °C.
A
B
5
2·5
0
500
400
300
200
250
TEMPERATURE °C.

FIG. 6.—Nickel.

EXPANSION AND CONTRACTION.

Corresponding specimens of overstrained nickel were tested for expansion and contraction, the specimens being $\frac{3}{16}$ in. in diameter and 4 in. long.

Fig. 6 shows the result of three successive heatings of a specimen of nickel overstrained to the same extent as the specimen of nickel tested magnetically. A well-defined change in the rate of expansion occurs at A on heating up to a temperature of about 460° C., the temperature being approximately 364° C., and on cooling through the same range of temperature an increased contraction occurs at B, the temperature being 330° C. approximately.

It will be seen that the temperature at which the rate of expansion changes on second and third heating is appreciably lower than that obtained on first heating, the point of discontinuity in the third case being as low as 324° C. The discontinuity in the rate of contraction on cooling after second and third heating occurs also in the region of 320° C.

Fig. 7 shows further the relation between expansion and contraction for a heated specimen of nickel ($\frac{3}{16}$ in. in diameter; 4 in. long). In this case the temperature on first heating did not exceed 365° C., so that the effect of annealing was restricted and the Curie point on cooling was not influenced in this way. The Curie temperature on heating is approximately 358° C. (P_1), and on cooling is in the region of 335° C. (P_2). The specimen was then heated to 1000° C. and again tested through the Curie range. The Curie temperatures are seen to be about 330° C. (P_3 and P_4).

The tests illustrated in Fig. 7 were made with a different arrangement for recording expansion and contraction, and an appreciable end thrust was involved, which was practically non-existent in the previous method of testing. This may account for the slight differences in form of the curves obtained from this test as compared with those given in Fig. 6.

The same apparatus was used for testing a specimen of similarly overstrained mild steel. The degree of overstrain in torsion was the same as for the overstrained mild steel tested magnetically. The axis of the specimen coincided with the axis of rolling, as was also the case with the corresponding nickel tests.

The rate of expansion on first heating appears abnormally low, which may be the counterpart to the expansion which occurs on twisting.

The Curie temperature A_2 associated with a small contraction at

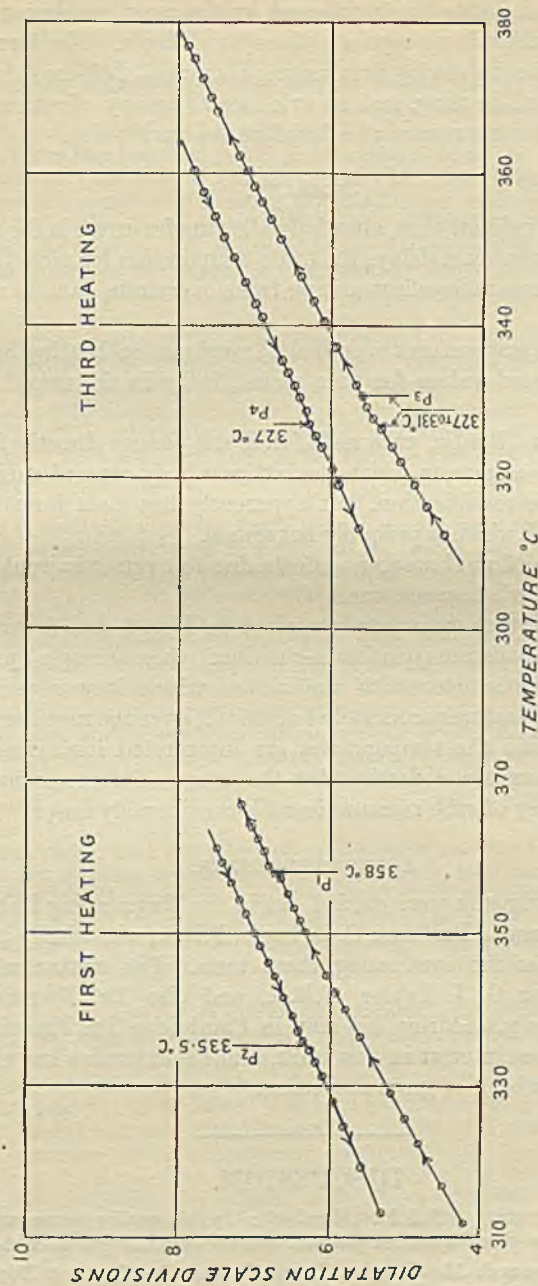

THIRD HEATING
FIRST HEATING
327°C
P4
327 to 331°C
P3
358°C
P1
P2
335.5°C
10
8
6
4
DILATATION SCALE DIVISIONS
310
330
350
370
300
320
340
360
380
TEMPERATURE °C

Fig. 7.—Nickel.

about 740° C., is immediately followed by the considerable contraction A_3, and it is difficult to separate these two effects. The form of the curve on contracting during first heating is markedly different from that shown on second heating, and no evidence as to any effect on the expansion due to overstrain can be found at the Curie point.

SUMMARY.

The results indicate that, after fully allowing for errors in the methods of recording, overstrain delays the Curie temperature for nickel on heating, but no measurable effect arising from overstrain can be observed on cooling.

The Curie temperatures recorded throughout on heating are lower than the accepted values for pure nickel, being in the neighbourhood of 330° C.

According to Bredig, pure nickel does not change directly from the ferro-magnetic α state, in which the lattice is body-centred cubic to the β paramagnetic modification, but apparently has an α form between 357° and 362° C. which is probably hexagonal.

In the case of mild steel, no effects due to overstrain could be observed at the Curie temperature.

The temperature measurements given in Figs. 2 and 6 were taken with a gold-palladium/platinum-rhodium thermocouple using an ionization potentiometer with the aid of which it was possible to determine temperatures accurately to 0·25° C., over the range employed. In all other cases the temperatures are interpreted from observation of the galvanometer deflection for the range of temperatures used and the accuracy of such measurements is considerably lower.

ACKNOWLEDGMENTS.

These experiments were carried out in the Engineering Laboratory at Cambridge under Professor C. E. Inglis, F.R.S., who kindly provided all the facilities for conducting these tests. The author wishes to thank Professor G. I. Taylor, F.R.S., and also Dr. Francis Bitter for valuable help. During his stay in Cambridge Dr. Francis Bitter has taken a keen interest in this work, and his extensive knowledge of the subject has been of great assistance.

DISCUSSION.

DR. L. B. PFEIL,* A.R.S.M. (Member): In his earlier paper with Professor Taylor the present author pointed out the advantages of cold-working

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* Senior Research Metallurgist, Research and Development Department, The Mond Nickel Company, Ltd., London.

metals by torsion, showing that, by this method, more severe cold-working could be obtained than by straining in tension. There is, however, the objection to this method of cold-drawing that the working is more severe at the surface than at the centre, so that results such as Mr. Quinney has obtained are to be looked upon as a mean between those which would be obtained with severely cold-worked metal and those obtained with annealed metal. From the practical point of view there would be more interest in the results of tests carried out on nickel which had been cold-drawn, by which process severe cold-working can readily be produced. It would be useful if the author could include the results of Brinell hardness determinations over the cross-section of one of his specimens so that some impression might be gained of the degree of cold-drawing which should be applied to nickel in order to produce a metal having properties similar to those recorded in the paper.

The author speaks of "a fairly well-defined discontinuity of slope" in the time–temperature curves shown in Fig. 1, but this discontinuity is not easy to see, and might well have escaped attention had it not been known that nickel underwent a magnetic change near the temperatures indicated.

Figs. 2 and 3, which also show time–temperature curves, are rather unconvincing. With a neutral body in the furnace a smooth time–temperature curve should be obtained, while, with a specimen subject to a transition, approximately the same curve should be followed until the transition temperature is reached, when the curve should depart from that of the neutral body but subsequently tend to return to it. From the author's curves in Figs. 2 and 3 it might be supposed that after the transition the specimens continued to evolve or to absorb heat. It seems probable that, had the author plotted his results in the form of inverse rate or as derived difference curves, thermal changes would have been more clearly demonstrated.

The magnetic changes shown in Fig. 4 are interesting from an academic point of view, and industrial use might be made of a material which increased in intensity of magnetization with increasing temperature. Materials which decrease in magnetization with increasing temperature are well known, but in an application such as magnetic shunts it might prove more easy to produce a duplex shunt made up from both types of metal, rather than to attempt to adjust the composition of an alloy until it had the exact characteristics which are required.

It would seem that the effect of cold-work in raising the Curie point in nickel is not directly due to the hardening, since in some of the author's experiments the temperature was not raised sufficiently high to cause recrystallization and softening of the nickel, yet the effect of the cold-work was neutralized so far as the magnetic change was concerned. It would appear that lattice distortion was responsible for the raising of the change point which he has observed.

I find that the absence of information regarding the exact magnetic conditions of Mr. Quinney's experiments reduces the usefulness of the paper, especially since it has been shown that the change in magnetic properties of nickel with increasing temperature depends on the intensity of magnetization. Rowland * in 1874 showed that with low magnetizing fields the permeability of nickel increases with temperature, whilst with intense magnetizing fields it decreases with temperature. Investigations by Hopkinson † in 1888 showed the same effect. It seems to me, therefore, that under different magnetizing conditions the author might have obtained in cold-worked nickel results quite different from those shown in Fig. 4.

I hope that Mr. Quinney will be able to continue this work, including in

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* Rowland, *Phil. Mag.*, 1874, [iv], 48, 321–340.

† Hopkinson, *Proc. Roy. Soc.*, 1888, 44, 317.

the investigation the effect of intensity of magnetization and also the effect of raising the temperature (but only to a moderate degree, such as 300° C.), and then cooling again, with a view to finding out whether the same curve would be followed repeatedly. It would be of value also to know whether long heating at 200°–300° C. would change the shape of the curve.

Dr. C. J. SMITHELLS * (Member): I have read this paper with interest, because we have done a certain amount of research on some of the properties of nickel. After reading the paper, I am not absolutely clear as to its exact object, but I take it that the object is rather an academic investigation; and, if that is the case, I think that it would have been better if the material chosen had been a definite material. The material taken in this case is a commercial nickel of an analysis very much inferior to the average manufactured by the firm which supplied this particular batch. It contains 0·12 per cent. of magnesium, 0·15 per cent. of iron, and rather high carbon. I was a little surprised to see no mention of manganese. Manganese is not invariably present but is very commonly present in commercial nickel, and its effect on many of the properties is very marked. I should like to know whether the fact that it is not mentioned means that there was none or that it was not tested for.

In 1932, Mr. Bansley and I † read a paper before this Institute on some of the mechanical properties of a series of samples of nickel, one of which was as pure as we could make it (over 99·9 per cent.), and the others had deliberate additions of most of the common impurities. In Fig. 16 of that paper we gave some curves showing the effect of temperature on the tensile strength which, according to the present author's definition of the Curie point, indicated the Curie point for those samples of nickel. These curves, which show the tensile strength at various temperatures up to 1000° C., bring out the marked effect of these relatively small quantities of impurities on the Curie point.

In the case of the 99·91 per cent. nickel, the kink in the curve corresponding to the Curie point is very nearly absent, and is at a fairly high temperature, nearly 400° C. The addition of 0·07 per cent. of magnesium only to the original nickel results in a very large increase in the discontinuity, and alters the temperature at which it begins. Another curve shows the effect of 2·33 per cent. of iron, and another of 0·34 per cent. of manganese, which moves the beginning of the deflection down to just a little over 200° C.

The point which I wish to make is that if the author wishes to determine the effect of one thing only, namely over-strain, it would be better to start with a really pure material. From the curves which I have shown, it seems to me doubtful whether this discontinuity would occur at all in really pure nickel. By making the nickel purer that discontinuity is changed, and therefore the impurities certainly have some bearing on the cause of the Curie point. The author states, in the summary at the end of his paper, that the Curie temperatures he records are lower than the accepted values for pure nickel, which I think must be attributed to the rather high percentage of impurities present in his nickel and which do, as is known, reduce the temperature at which the Curie point occurs.

With regard to the actual results, I agree with Dr. Pfeil in finding great difficulty in putting the kink at the same position as the author puts it. If we look at the points and forget that the lines are drawn in, I think that we should all put the kink at different places. With the curves in Figs. 1 and 2 it is extremely difficult to say where the kinks occur, and a differential plotting

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* Research Laboratories, General Electric Co., Ltd., Wembley.

† *J. Inst. Metals*, 1932, 49, 287.

or inverse rate curve would show how difficult it is to arrive at any conclusion from those points.

The author says that the rate of heating was *approximately* constant. The whole meaning of these curves, of course, depends on an absolutely uniform rate of heating, and a heating curve taken with no specimen, or with a specimen of copper which has no discontinuity, would have given us a little more confidence in the curves.

Fig. 4 is interesting, if I understand it correctly, because in that case there is no doubt about where the curve should run, but the first and second heating both show the Curie point or range occurring at about the same temperature, although the second heating is material which has been up to 800° C. and has certainly relieved the internal stresses and possibly caused some recrystallization. So, taking that curve alone, I conclude that overstrain has no effect at all on the temperature at which this Curie point occurs; but I do not think that conclusion can be right, because the expansion curves do show definitely that there is some change.

I think that the correct conclusion is probably that the effect of overstrain is one of lattice distortion, and it is not necessary to have recrystallization to get rid of it. The presence of impurities would, I think, have a very marked effect on lattice distortion resulting from cold-work, and if these results could be confirmed and duplicated on a sample of really pure nickel they would be of very great value.

Mr. W. R. BARCLAY,* O.B.E. (Vice-President): I am anxious to emphasize what Dr. Smithells has said. I have on one or two previous occasions pointed out how exceedingly difficult it is for those of us who are concerned with the electrical and magnetic properties of materials required in industry to benefit to the degree we should from such papers as this, because they deal with material which would not in the ordinary way be sent out for such special requirements. I do not know anything about the history of this material, but I should not like it to be supposed that the composition quoted in this paper is representative of nickel intended for electrical or magnetic purposes, and I wish to underline the remarks which Dr. Smithells has made, because not only in regard to magnetic properties but also electrical properties I have had difficulty at times in meeting the requirements of friends who specified definite values for properties such as, for example, the "temperature coefficient of electrical resistance."

I can assure the author and any other workers in this field that it is of vital importance not only to get the purest material but to know something also of its history; the degree of cold-working and the treatment during cold-working have a very considerable bearing on these properties. A somewhat analogous point, illustrating the importance of these latter factors, is the well-known behaviour of alloys such as Manganin, where repeated cold-working and repeated annealings totally upset the valuable feature of Manganin in possessing an almost zero temperature coefficient of resistance.

I hope that if the author proceeds with his investigations he will obtain nickel which is almost magnesium-free, or which, at least, contains very much less than the amount quoted in the paper.

The PRESIDENT: The author will reply to the discussion in writing.

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

CORRESPONDENCE.

The Author (*in reply*): I thank Dr. Pfeil for his remarks, although I am not in agreement with some of his observations. It so happened that in the earlier paper on "cold-working," by Professor G. I. Taylor and myself, to which he refers, continued compression tests were also made in which the work done was considerably in excess of that required to saturate the metal with internal energy. For most of these experiments in torsion and compression, it was possible and necessary to estimate the cold-working done, which is not so when the metal is cold-drawn through a series of dies, nor is it true that the cold-working is by any means uniform for cold-drawn metals.

An estimate of the variation in hardness along a radius, by means of Brinell hardness determination over a section, is of interest, and will show what variation of hardness exists, and the corresponding stress distribution is not difficult to estimate. With reference to Dr. Pfeil's comments on Fig. 1, I do not agree that there can be any doubt as to the existence of the two Curie points at 357° and 315° C., nor is this an isolated test. A number of similar curves of which Fig. 1 is representative have been obtained, and an examination of these, on the original large-scale graphs, leaves no room whatever for doubt as to their existence. The kink is certainly not large but is clearly associated with a change of specific heat.

With reference to Figs. 2 and 3, in connection with which the tests were made in an open furnace, the results are less satisfactory, but consistent results were obtained. Referring to Dr. Pfeil's remarks on the magnetization curves, the importance of performing tests for different values of the magnetizing force was not overlooked, and a hope was expressed that this would be possible in the future. The further suggested series of repetition tests, in which the temperature is not allowed to exceed, say, 300° C., is one which I propose to make, and the effect of maintaining the metal at that temperature I will also investigate, although I should be surprised to find that the increasing intensity of magnetization of overstrained nickel when heated to, say 300° C., is of a reversible character.

Dr. Smithells in his highly valued remarks enquires the object of these experiments, which I would like to repeat here as follows:

An attempt to discover whether the dilatation of polycrystalline rods of iron and nickel of the type used behave in the manner outlined:

A. Thus in iron a small region of a crystal grain in the absence of external fields will be magnetized parallel to a cube face, and will be expanded, due to magnetostriction, in the direction of magnetization. This expansion will diminish as the temperature increases and will disappear abruptly (anomalous contraction) near the Curie temperature. A small region in a nickel crystal, on the other hand, will be magnetized, in the absence of an external field, parallel to a cube diagonal, and will be contracted, due to magnetostriction, in the direction of magnetization. This contraction will diminish as the temperature increases, and will disappear abruptly (anomalous expansion) near the Curie temperature. The actual behaviour of a polycrystalline rod will depend on the following:—

1. The orientation of the crystal grains with respect to the axis of the rod;
2. The orientation of the magnetization of the little region within the crystal grain, which, in turn, depends on the presence of internal strains, as well as external fields.

B. To determine further how these changes are related to the temperature–time kinks, and the magnetic change points of the same metal.

I entirely agree with Dr. Smithells that with this object in view it would, in certain respects, have been better to have used a nickel of high purity. Before attempting these experiments, Dr. Francis Bitter and I made enquiries regarding the supply of bars of nickel which could be easily machined, and with the exception of a few small pellets of approximately chemically-pure nickel, which were unsuitable for our experiments, only commercial nickel was obtainable, and moreover the question of machining had to be considered.

The bars used, for which I gave a typical analysis, have since been separately analyzed by Messrs. Henry Wiggin, and the analysis given is as follows :

	Per Cent.
Carbon	0·062
Silicon	0·027
Copper	0·08
Iron	0·18
Magnesium	0·08
Manganese	0·30
Sulphur	0·012
Cobalt	0
Nickel	99·016 (balance)

Although the impurities present are even greater than those quoted in the paper, the magnesium content is nevertheless only half that stated, and is of the same order as that present in the nickel bars prepared in connection with Dr. Smithells' work in collaboration with Mr. Ransley. The influence on the Curie temperature, due to the magnesium content alone, is no doubt that found by them in their investigation on the tensile properties of this metal. The manganese content, to which no reference was made in the analysis given, is unfortunately as high as 0·3 per cent., which as Dr. Smithells shows, has the opposite effect.

In view of the profound influence of these impurities, I have come to feel that my original impression that the industrial metallurgist might be more interested in the behaviour of commercially-pure metals than those approximately chemically-pure may have been wrong. I might instance, however, the case of approximately chemically-pure gold with which I have lately experimented. I am informed by Messrs. Johnson, Matthey & Co., that the repetition of such metal is extremely difficult and correspondingly costly, but that an ordinary assay gold can be repeated with considerable accuracy.

Dr. Smithells surely overstates the case when he refers to the necessity for absolute uniformity in rate of heating. Problems involving uniform heat-flow at all times present insuperable difficulties, and such difficulties were experienced in the experiments described. Unusual precautions were taken, however, and an idealized rate of heat supply was calculable to a considerable degree of accuracy; the statement that the rate of heat supply was approximately constant is meant to direct attention to this fact.

Further, with reference to Mr. Barclay's observations on the importance of using pure nickel for these experiments, I hope to procure, in the manner suggested, nickel bars of such composition as is likely to be of interest in magnetic and electrical problems, and if possible to compare their properties with an approximately chemically-pure nickel.

A REFLECTIVITY METHOD FOR MEASURING THE TARNISHING OF HIGHLY-POLISHED METALS.*

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By L. KENWORTHY,† M.Sc., A.R.C.S., Member, and
J. M. WALDRAM,‡ B.Sc., A.C.G.I.

Synopsis.

This paper describes an apparatus and method for carrying out the quantitative assessment of tarnish on highly-polished metals, by reflectivity measurements. The method involves the separate determinations of the specular and diffuse components of reflection, and the use of an empirical formula combining these two properties. The application and validity of the method are illustrated by the results of periodical measurements, and observations made on specimens of pure tin and 2 tin alloys exposed to indoor and outdoor atmospheres.

In the course of research on the atmospheric corrosion and tarnishing of metals and alloys, it was found necessary to measure, by means of the change of reflectivity, the tarnishing and dulling of highly-polished metals when exposed to the atmosphere. The object of this paper is to describe the apparatus and method employed for this purpose.

In devising a method, the wide utilization of highly-polished metalwork was borne in mind, and a considerable amount of preliminary work was carried out to ensure that the quantitative assessment made should be a proper indication of the appearance; but although it is often desirable that materials used in decoration should possess and exhibit a high degree of polish, a high reflection factor, *per se*, is not a criterion. For instance, a clean silvered glass mirror represents the most suitable surface, having both a high polish and a high reflection factor; but a white blotting-paper surface, having a high reflection factor, but no polish, is less suitable than a surface of polished black slate as used for switchboards, which has a very low reflection factor, but a high polish. A glazed white porcelain surface, having a high

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reflection factor and some polish, is probably less suitable than the slate surface in that it does not exhibit its polish, which is masked by diffuse reflection. When a polished surface is used in decoration it forms images by specular reflection of objects in the vicinity, and if

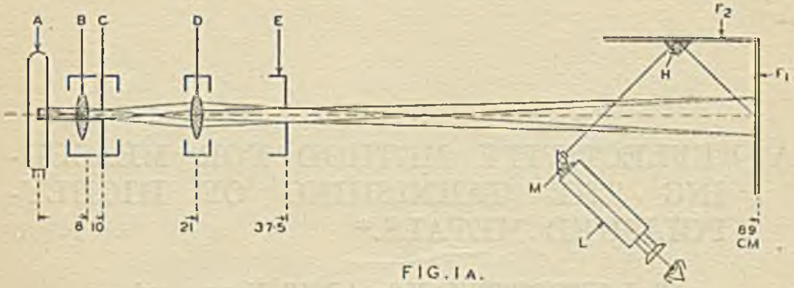


FIG. 1A.

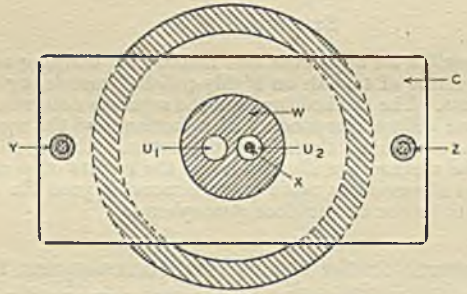
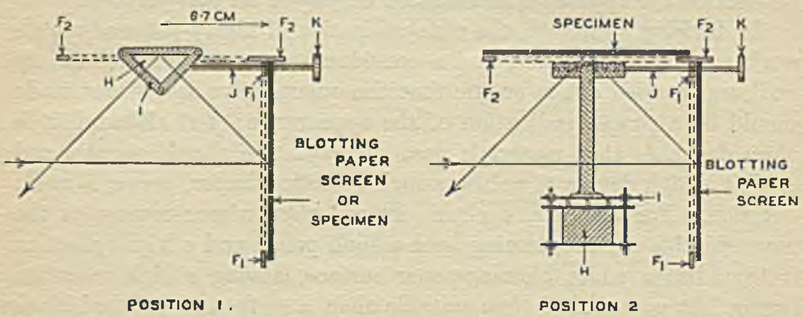


FIG. 1B.



POSITION 1.

POSITION 2

FIG 1C

Fig. 1 A–C.—Apparatus for Measurement of Reflectivity. (See key on page opposite.)

the appearance is to be satisfactory the image formed should be crisp, the proper degree of contrast being retained between the different parts. Dark parts of the image must appear really dark. In the case of a tarnished surface there is an appearance of fog all over the image. The marring of the appearance is due not so much to the fact

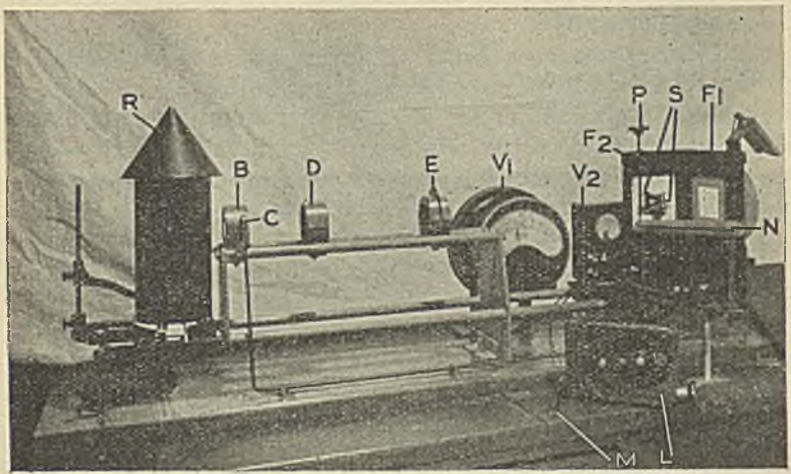


Fig. 2.—Photograph of Apparatus. The photometer is shown removed from its mounting, in order that essential parts of the apparatus shall not be obscured in the photograph.

KEY TO FIGS. 1 and 2.

A—Lamp; 110 volt, 100 watt coiled-coil Kodascope type.
B—Condenser lens, approximately 19 cm. focus.
C—Brass slide. See Fig. 1B.
D—Projection lens, approximately 9 cm. focus.
E—Screen.
F_1, F_2—Specimen guides.
H—Right-angled silvered prism.
I—Prism platform and adjustments.
J—Spindle.
K—Knob, operating prism.
L—Photometer.
M—Prism elbow.
N—Photometer mounting.
P—Knob operating prism screens.
R—Lamp-house.
S—Prism screens.
U_1, U_2—Apertures in slide.
V_1—Voltmeter across projection lamp.
V_2—Voltmeter across photometer lamp.
W—Cover glass.
X—Ball bearing, $\frac{3}{32}$ in. diameter, stuck to glass.
Y, Z—Limit stops for slide.

that the bright parts are not bright enough, but that the dark parts are not dark enough. If such a surface, or a dusty mirror, is partly cleaned, the general effect is that the clean parts appear darker than the uncleaned parts.

Evidently, therefore, a tarnished mirror reflects in two modes at the same time and its behaviour depends on (1) its specular reflection properties, defining the degree of polish and ability to form bright images, and (2) its diffuse reflection properties, defining the amount of fog which has been formed to mar the bright image. If these two properties are measured it is then possible to assess some arbitrary function which is a fair "figure of merit."

Vernon in his earlier work * was, so far as we are aware, the first to apply reflectivity methods to the study of atmospheric tarnishing. In this work, however, he was concerned only with the measurement of specular reflectivity, and a review of the literature showed that there was no published method or standard apparatus which would fulfil satisfactorily the requirements of the present investigation.

METHOD.

Preliminary experiments indicated that simple methods, such as those involving the use of an optical wedge or a disappearing-filament optical pyrometer, as alternatives to a photometer and optical bench, were insufficiently sensitive or accurate for the purpose. The use of the sphere reflectometer, which is another obvious method for measuring these properties, was tried and found to be unsuitable for several practical reasons; moreover, it was considered that a method involving direct observation of the specimen was to be preferred as more closely resembling practical conditions.

After several trials, the scheme indicated in Fig. 1A was adopted. The method is, briefly, as follows: the specular reflection factor is measured as the ratio of the observed brightness of an illuminated white object, after reflection at the surface under test, to its brightness after reflection at a prism whose reflection factor has been determined. A correction for brightness due to diffuse light is made. The diffuse reflection is measured as a specific reflectivity, *i.e.* the ratio of the brightness of the surface under test, to that of a matt white surface, under standard conditions of illumination and direction of view. In Fig. 1A, F_1 is a standard white surface, illuminated by an optical pro-

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* "First Report to the Atmospheric Corrosion Research Committee of the British Non-Ferrous Metals Research Association," *Trans. Faraday Soc.*, 1924, 19, 851.

jection system and viewed by a photometer L *via* a prism H. For the determination of the specular reflection factor, H can be replaced by the specimen at F_2 (Fig. 1c, position 2) and a second determination of brightness made. A correction must be made for any diffuse reflection which will contribute to this brightness; a spot of light with a dark centre is therefore projected on to F_1 and the brightness of the dark centre measured. This gives the contribution due to diffuse reflection, which can be subtracted. For the determination of diffuse reflectivity, H is replaced and the white surface and the specimen viewed in turn when placed at F_1. It will be seen that the specimen is illuminated normally and viewed at 45°.

APPARATUS.

The apparatus used is illustrated in Figs. 1A, 1B, and 1C, and in the photograph Fig. 2. The source of light A (Fig. 1A) was a 110-v. 100-watt coiled-coil Kodascope projection lamp, run at 70 v., from the d.c. mains. Constant voltage was maintained by a barretter (1-amp. 40–100-v. type) and variable resistance in series. The optical system was that of a lantern projector, B being the condenser, C the slide, and D the projection lens. An image of the lamp filament was formed at E, and a screen was placed there with an aperture exactly fitting the image so as to cut off all stray light. B, C, D, and E were mounted in brass tubes and were carried on a parallel rod optical bench. The construction of the slide C, which permitted the projection of either a clear circular spot or a similar spot with a dark centre, will be clear from Fig. 1B, and the mounting of the prism H, and the means for taking it out of the optical system for the measurement of specular reflection factor, is shown in Fig. 1C. Two additional screens S shown only in the photograph, Fig. 2, operated by the knob P, were arranged over the two faces of the prism, having apertures only just large enough to fill the field of the photometer; they were replaced in position when the prism was removed. These screens are particularly important. The specimens and the white comparison surface were carried in brass slides running in guides in the vertical plates F_1 and F_2, in which windows $3\frac{1}{2}$ in. square were cut, through which the specimen was observed. Mechanical stops were arranged to bring under observation either the centre of the specimen or a spot on the centre line midway between the centre and the edge. The photometer was a Holophane Lumeter, provided with a field lens of 5-in. focus and a right-angled prism, which enabled the photometer to be placed in a position far more convenient for taking observations. The field lens formed an image of the exit pupil of the photometer at F_1.

It was found necessary to have all parts rigidly fixed, and the design of the mounting will be sufficiently clear from the photograph.

MEASUREMENT OF SPECULAR REFLECTION FACTOR.

A white blotting-paper screen was placed at F_1. The lumeter was set up so as to view the centre of the projection spot at 45° from the normal by reflection at either the prism or a specimen placed at F_2. The reflection factor of the prism was found once for all by comparing a reading of the brightness of the spot seen through the prism with a reading with the lumeter moved to view the spot directly at 45°. The following readings were then taken :

(*a*) The clear spot was projected in the centre of the blotting-paper screen and a reading was taken *via* the prism;

(*b*) The reading (*a*) was then repeated on the black spot with the clear surround, in order to determine the amount of light due to diffuse reflection from the prism, and this value was subtracted from the value of (*a*). The readings of (*a*) and (*b*) should theoretically be constant and (*b*) should be very small. Checks on these values were made periodically;

(*c*) and (*d*). These were readings similar to (*a*) and (*b*) taken *via* the specimen.

The specular reflection factor is then given by the following expression :

$$R_S = \frac{c-d}{a-b}\rho_1$$

where ρ_1 = reflection factor of the prism.

MEASUREMENT OF DIFFUSE REFLECTIVITY.

One more reading (*e*) was necessary for the determination of the diffuse reflectivity. For this, the blotting-paper screen was replaced by the specimen at F_1. The slide was moved so that the clear spot without the black centre was projected. A reading was then taken *via* the prism. The diffuse reflectivity is given by the expression :

$$R_D = \frac{e\rho_2}{a-b} \text{ where } \rho_2 = \text{the reflectivity of the blotting paper.}$$

The effect of buffing marks could be avoided, when determining this component, by measuring the specimens with the lengths of the marks horizontal, and thus in the plane of the normal to the specimen and the photometer.

The arrangement and procedure above described were adopted after trials with several other methods. A few of the difficulties encountered may be indicated briefly. It was necessary when measuring specular reflection to use the surface under test as a reflector between the photometer and the bright spot, not between the bright spot and the illuminating system, to avoid errors due to departure from flatness. Owing to the nature of the diffuse reflection, it was necessary to choose a direction of view well removed from the angle of specular reflection, otherwise small changes in direction of view considerably affected the result. All the lenses and glass surfaces had to be very carefully cleaned, in order to avoid diffusion of light by dust, which can cause a serious error. It is specially important to set the screens on the prism faces so as to prevent light from the bright surround from entering the photometer when viewing the dark spot. It was also found that, in making correction for diffused light, the dark spot must be in the centre of the bright spot. A measurement made adjacent to the bright spot gave a lower value. Finally, the projection system must be so set as to give a very even illumination of the spot. If the condenser is arranged to collect too much flux from the lamp, the illumination will be increased at the expense of evenness.

CALCULATION OF "FIGURE OF MERIT."

A figure of merit incorporating the specular and diffuse reflectivity was computed by the use of the following empirical expression:

$$M = \sqrt{\frac{R_S(R_S + R_D)}{R_D + 1}} \times 10$$

It will be seen that with this expression when the diffuse component is zero, the value of the "figure of merit" is simply the specular reflection factor, multiplied by 10.

In order to illustrate the application of the method, the results of exposure tests on samples of pure tin, commercial tin, and Britannia metal are given. These tests were designed not only with the object of determining the rate of tarnishing, but also to investigate the effect of cleaning on the subsequent rate of tarnishing. For this purpose, four plates of each material were exposed, two plates being untouched throughout the exposure and the other two cleaned at intervals. In addition, two extra plates of Britannia metal were exposed, and these were brushed at frequent intervals to determine the effect of dust.

The specimens, which were 4 in. square and of 12 S.W.G. thickness, were buffed by a firm of metal platers and polishers. Before being exposed, they were swabbed thoroughly in acetone to remove most of the grease, and were then given a final degreasing treatment with trichlorethylene vapour. The initial reflectivity measurements were then made and the plates exposed in a vertical position in an indoor atmosphere. Measurements on all the plates were made after 3, 6, 11, 16, 21, and 26 weeks' exposure, and after each of these, two specimens of each material were cleaned and measured again before being re-exposed. The extra two specimens of Britannia metal were given no cleaning treatment, but were lightly brushed daily with a camel-hair brush (except at week-ends) in order to remove dust.

Graphs connecting "figure of merit" and time of exposure for the three materials are shown in Figs. 3–5. In these graphs, the specimens which were subjected to continuous exposure are represented by smooth curves and those which were cleaned periodically by stepped curves, the vertical portions of which indicate cleaning.

The methods employed for cleaning, which were (1) swabbing with distilled water or (2) swabbing with soap and water, are indicated by the numbers shown above each vertical portion of the curves, and the treatments to which these refer are given below the graphs.

In discussing briefly the results obtained, attention is directed to the fact that the rapid initial drop in "figure of merit" shown by the continuously exposed specimens was caused to a large extent by deposition of dust. This is well illustrated in Fig. 5. The smooth dotted curve shows the relationship between "figure of merit" and time of exposure for the plates which were brushed, and therefore represents loss of "figure of merit" due entirely to tarnishing. As this tarnish was not detected visually until after about 9 weeks' exposure, the method is shown to be sufficiently sensitive to record slight changes which cannot be detected by direct visual observation.

In the case of the specimens which were periodically cleaned,* swabbing with distilled water for the first two cleanings, *i.e.* after 3 and 6 weeks' exposure, was sufficient for all the materials to restore a large proportion of the original "figure of merit." For the subsequent cleanings, however, soap and water were used, as water alone did not prove sufficiently effective. The small amount of tarnish that developed between these cleanings was apparently completely removed by this treatment, the only change in appearance at the end of 26 weeks being a slight scratching caused by cleaning, to which the small drop in "figure of merit" is largely, if not entirely, due.

In conclusion, it may be mentioned that the observations and

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* It should be noted that in the case of pure tin, the specimens used for the cleaning tests were not exposed with the same degree of polish as the specimens which were exposed continuously.

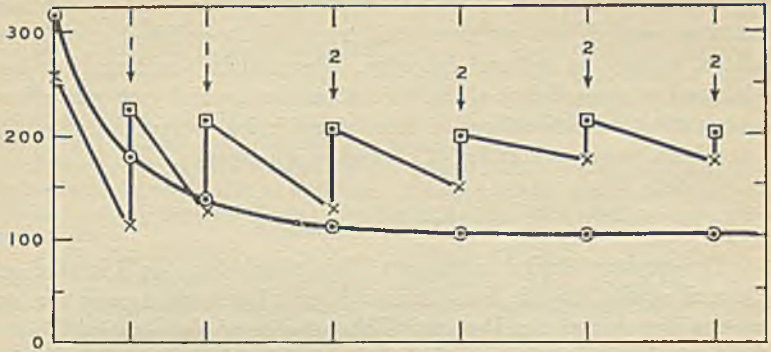

FIG. 3. PURE TIN.

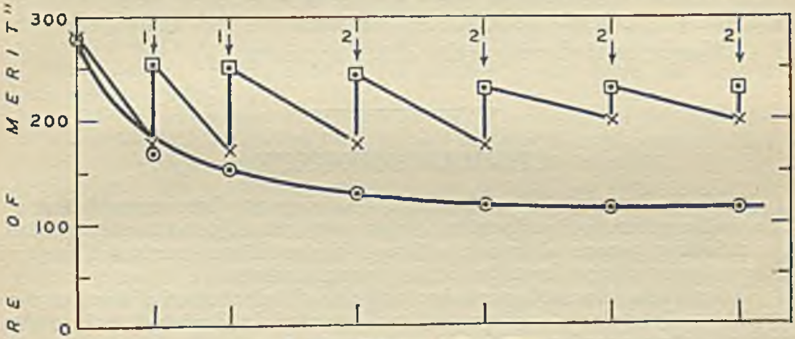

FIG. 4. ORDINARY TIN.

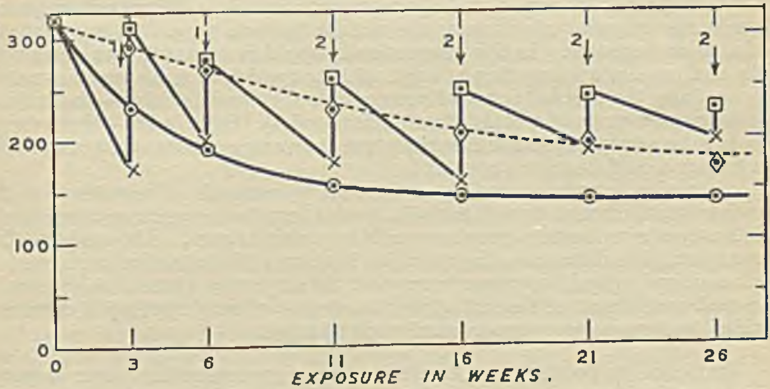

FIG. 5. BRITANNIA METAL.

FIGS. 3–5.—Cleaning Treatments: 1, Wash with Water; 2, Wash with Soap and Water.

measurements which have been described are representative of a large number carried out on many different highly-polished metals and alloys, as used in art and industry. From these, evidence has been obtained of the validity of the present method, which not only affords a quantitative estimation of loss of reflection properties, but also provides a serviceable index of change in appearance.

ACKNOWLEDGMENTS.

The authors desire to express their thanks to the Director and Council of the British Non-Ferrous Metals Research Association and to the Director of the Research Laboratories of the General Electric Co., Ltd., Wembley, for permission to publish this paper. In addition, one of us (L. K.) wishes to thank Professor R. S. Hutton, M.A., D.Sc., and Dr. O. F. Hudson, A.R.C.S., for much valued advice, and Mr. F. G. Morris for the construction of the apparatus.

CORRESPONDENCE.

MR. L. W. DERRY,* B.Sc. (Member): I have recently been engaged in work of a similar nature to that described in this paper, namely, the measurement of the reflecting powers of metals, although the work was conducted from a different point of view from that of the present authors.

I congratulate the authors on the simplicity of their method of assessing the tarnishing of metals and on the undoubted commercial value which their results possess, but would offer the following observations.

In the first place, I would emphasize, for the sake of casual readers, that a single reading at 45° cannot be fully representative of the diffuse reflection as a whole, the intensity of which, as the authors indicate on p. 253, is essentially of a polar character. In this connection it would be interesting to know why the authors chose the particular angle of 45° at which to make measurements. Even from the special point of view which they had in mind—that of the artistic appearance of metals when illuminated by bright lights—there would seem to be reason why the diffuse reflection at an angle closer to that of specular reflection would be more important.

I am also very interested in, and would welcome the observations of the authors on, the figure of merit formula, since I have had experience of the great difficulty of representing complex results by a single figure. The authors offer no explanation of the reasoning on which the form of their particular expression is based, and indeed, it appears to me that the expression given does not award to each component of the reflection that degree of weight which it deserves, whilst its form appears unnecessarily complicated.

Professor A. PORTEVIN † (Member): This very interesting paper engaged our attention in a very special way, not only on account of its quality and importance, but also because we have been studying the reflective power of metals for many years with a view to characterizing the polish, colour and

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tarnish. After experimenting with the use of the disappearing filament pyrometer for photometric measurements, we have employed the photoelectric cell, since it appeared, that is, since 1925, when M. René Toussaint devised his photocolorimeter. In collaboration with him, we have established a method, and perfected a device, utilizing this apparatus and permitting the measurement of these divers characteristics, especially the tarnishing of polished metals. M. René Toussaint has published a *résumé* of this work.*

Before giving a brief account of our method, and a few examples of determinations, we would like to direct the attention of the authors to some errors which, our experience indicates, are likely to arise with their arrangement of apparatus :

(a) *Errors which are or ought to be negligible.*—If the beam of light is quite parallel, and above all well stopped down on all sides, and if there are no parasitic reflections in the whole of the apparatus, there should be no light corresponding with the centre of the dark spot, and the terms b and d, which the authors recommend to be calculated, should always be strictly zero. If they have a definite value, it is to be feared that the measurements are not exact. Simultaneously with R_S, what amounts to a diffused parasitic light may be perceived, which obviously is not the same with the prism as with the specimen, and which will vary with the illuminated part of the heterogeneous diffuser F (blotting paper). But in practice is it possible to stop down the beam with sufficient exactness ?

(b) *Errors which must not be neglected.*—It is necessary for the apparatus to be particularly strong and well constructed, in order that the angle 45° may be guaranteed with the standard prism, as well as with the specimen. It must be remembered that a variation of one degree or even less when dealing with polished metals may result in a considerable variation in the measurement. This is shown, for example, for 80 : 20 brass in Fig. A. On a specimen with a micrographic polish, R varies, on an average, by more than one unit for each minute of angle, whereas on a sand-blasted surface the variation is practically nil between 45° and 40°. Evidently the flatness of the specimen can only be guaranteed to within half a degree. It is always advisable to investigate the maximum of the luminosity by tests. Now, although this can be done easily by following the movement of a needle of an ammeter, it is much less easy to do with a luminous-disc photometer such as that used by the authors.

The measurements suppose that the source of light remains absolutely constant throughout the readings made with the prism and with the specimen (measurement of R_S), as well as with the blotting paper and the specimen (measurement of R_D). Now, in all cases, it is necessary to equalize the discs by eye, and, since this takes a certain amount of time, it is quite evident that the light will fluctuate with the current supplied by the accumulators.

We know by experience that for measurements on polished metals it is always necessary to compare the specimen with a standard, and rapid working is *essential*, even with one cell, in order to eliminate errors caused by fluctuations in the light.

Finally, we must direct attention to errors due to the eye and the personal equation of the observer. Thus the " figure of merit " adopted by the authors, which is entirely an empirical and conventional figure, does not appear to us to correspond with any definite characteristic of the metal. In our opinion, what we call the *total reflective power* can be considered for any surface whatever, as the sum of the *brilliance* or *polish* properly speaking, and of the *clarity of the colour* of the surface or diffused *light.* This total reflective power is measured in a plane normal to the surface, passing through the incident ray at an angle equal to the angle of incidence.

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* *Rev. Aluminium*, 1934, (61), 2409 ("The Photoelectric Cell and Its Use in the Measurement of the Brilliance and Colour of Metals ").

Whilst the brilliance, which is at its maximum at the preferred angle of reflection, varies rapidly as this angle is changed, and all the more rapidly the more highly polished the surface, the clarity of the colour does not vary whatever the azimuth of diffusion. It is of course understood that *if the source of light and the absorption remain constant,* the sum of the quantity of reflected light (angle of reflection) and the quantity of diffused light (all angles) is itself constant, so that any gain in brilliance or polish is acquired at the expense of the clarity of the colour, or, conversely, any loss in brilliance increases the clarity of the colour. All too often the close dependence of these two variables is forgotten, and the fact that the degree of light and shade, or average tone, of a colour depends not only on the actual absorption by the pigment, but also on the degree of polish on the surface. When metals tarnish (by corrosion, oxidation, sulphuration, &c.) the polish or brilliance diminishes, and, as a result of the formation of new substances (oxides, sulphides, &c.), the colour changes, and hence three variables appear during the course of tarnishing:

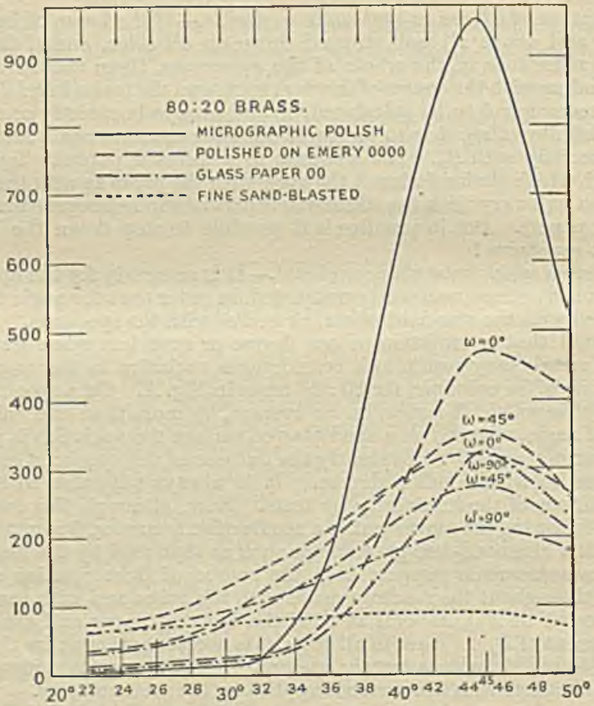

Fig. A.

(1) The modification of the brilliance and hence of the clarity of the colour.

(2) Variations in the absorptive power: (*a*) in the degree of light and shade or average tone; (*b*) in the relative absorption as a function of the wavelength producing tarnish colours.

The apparatus which we have used for several years is the Toussaint photocolorimeter, equipped with a special standard for the study of specimens with non-parallel faces, so that they can be examined under all angles of diffusion and reflection.

The parallel beam of light, which is conveniently stopped down, is horizontal, and passes through the axis of rotation of the stand, the photo-electric cell being placed above the specimen in a vertical line through the point of incidence.

If a reading is made at an angle of 45° the value of the total reflective power (R_{45}) is obtained; then $R_{45} = X + x$, where X = brilliance or polish, and x = the clarity of the colour.

At 22° in diffused light and remote from the angle of reflection (the cell not having been moved) a measurement is made of

$$x \frac{\cos 22^\circ}{\cos 45^\circ} = x \times 1{\cdot}3 = x'$$

(because of the difference of the angles under which the cell "sees" the specimen illuminated at 45° and 22°)

$$\text{from which } R_{22} = \frac{x'}{1{\cdot}3}.$$

Then, with the aid of the reading at 45°

$$X = R_{45} - R_{22}$$

that is to say, the value of the brilliance or polish, independent of the colour or diffused light.

As these readings are essentially relative (owing to the variation of the source of light, of the voltage of the cell, &c.), it is always necessary to compare the measurements with those of a standard (mirror, &c.) or, preferably, to take into consideration what we call the degree of polish; $\frac{R_{45} - R_{22}}{R_{45}}$, this degree of polish varying from 0 when $R_{45} = R_{22}$ (sand-blasting or complete roughening) to 1 when R_{22} is nil (perfect polish).

The tarnishing or loss of brilliance is equivalent to the *difference* of the degrees of polish before and after the exposure of the metal to the corrosive medium.

In our opinion, the advantages of our method are as follows:

(1) The "degree of polish" which replaces the "figure of merit" is not a conventional term but will express in a simple manner the value of the brilliance or polish.

(2) The brilliance or polish is measured *independently of the colour*, whereas in the expression "figure of merit" the parasitic factor R_D, which always varies considerably during tarnishing, does not disappear and is thus a source of error.

(3) The measurements are simple and rapid, and the apparatus needs no adjustment.

(4) Owing to the photoelectric cell, the measurements are independent of the eye of the observer, and may be made in filtered light, thus more surely eliminating errors arising from variations in the colour of the light, due to voltage variations.

Comparing the above with the work of the authors, it may be said that:

Their "specular reflection factor R_S" corresponds with our R_{45}.

Their "diffuse reflectivity R_D" is practically the same as our R_{22}.

It appears that the extreme values of our "degree of polish" (0 and 1) are simpler than those of the "figure of merit, M," which varies from $10R_S$ to $10/\sqrt{2}$.

With regard to atmospheric tarnishing, we will confine ourselves to directing attention to the *variation of the colour* of industrial metals: with a sand-blasted surface, in a diffuse light, at the end of three months we obtained the variations shown in Fig. B giving the differential curves. The slope of these curves is the same for all the metals we have tested : the orange-red tends to predominate over the violet-blue ; or, in other words, the colour becomes redder; this may likewise be proved in the case of most of the tints developed by exposure to air.

On the other hand, the mean ordinate, representing the variation of the average tone or degree of light and shade, is negative; this indicates that the colour becomes darker because of the changes which occur on exposure to air.

Thus, on the whole, the colour of industrial metals darkens and reddens through exposure to air; this change is less pronounced with aluminium, tin, and silver, than with magnesium, cadmium, lead, and bismuth; the reddening tendency is especially noticeable in bismuth, silver, and tin.

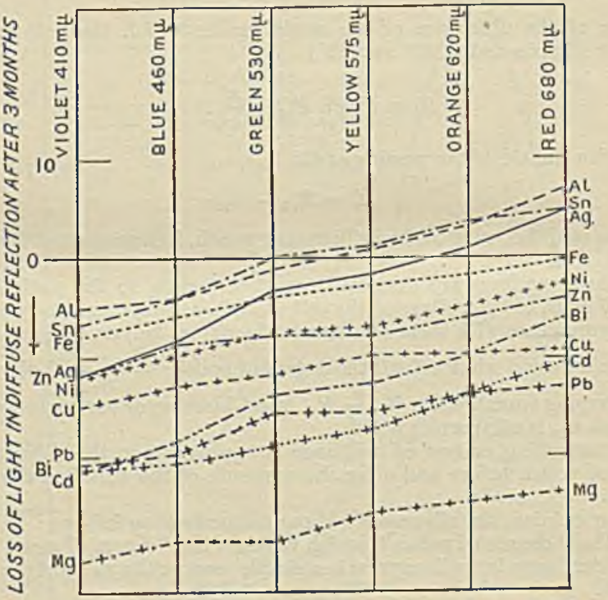

Fig. B.—Change of Colour of Industrial Metals in Air. Sand-Blasted Surfaces, White Standard—Barium Sulphate.

We have made similar observations on the colour of industrial copper alloys, bronze, and brass. No surprise should therefore be felt at the often contradictory statements as to the colour of metals and alloys which appear in chemical treatises.

With rise in temperature, oxidation increases and temper colours develop. These we have similarly studied, and have found that they may be used to recognize certain alloys; but a discussion of this aspect would lead us too far from our main subject.

Generally speaking, these colour changes are exactly defined by the "differential curves" such as those in Fig. B. They may be simply characterized by the variation from the average tone (or degree of light and shade) and by the relative deviation of the dominant complementary colours.

Thus, the examination of the tarnishing of metals is nothing more than a special case of the general study of the chemical change or corrosion of metals, when the loss of brilliance or polish (R_{45}) method is employed, as we have previously shown * There again it is impossible to confine oneself to one single determination at the angle of 45°, on account of inevitable inequalities in the surface of polished specimens, which cannot easily be prepared optically flat. It is necessary to vary the angle of incidence in the neighbourhood of 45° to find the value of the maximum intensity of reflection. Fig. C gives examples of this, showing that the maximum intensity of reflection is attained when the angle formed by the plane of the 3 points of incidence of the surface of the metal with the beam of light, is sometimes 45° and sometimes 46°.

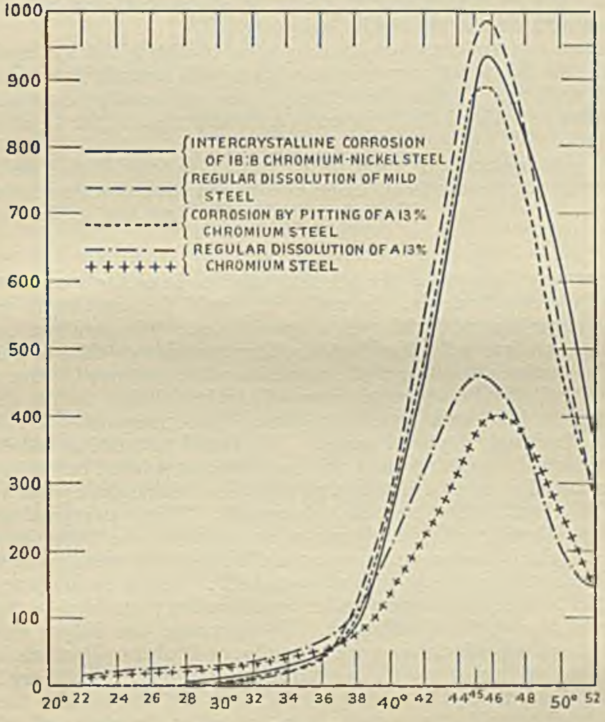

Fig. C.

Furthermore, in the optical study of corrosion it is impossible to hope to characterize the *type of corrosion* (simple dissolution with or without corrosion figures, corrosion by pitting, formation of a more or less coloured film, intergranular corrosion, &c.) by a single determination: it is at least necessary to draw a part of the curve round about the maximum, and even then, in certain cases, this does not appear to be sufficient to distinguish the different types when the corrosion is very slight. For this reason in Fig. C there are shown together the curves of five specimens of steel, which, after polishing micrographically, have been attacked in such a way as to produce different types of corrosion, but to such a feeble extent that they could not be recognized exactly by the usual weight methods, *i.e.* the loss in weight is of the order of magnitude of the experimental error.

* See especially A. Portevin, *Rév. Mét.*, 1929 26 640.

The three curves which are close together and have a very acute maximum correspond with:

(1) *Intercrystalline corrosion* of a non-rusting 18 : 8 chromium–nickel steel (quenched in water from 1100° C. and tempered for 3 hrs. at 650° C.) after attack for 48 hrs. in a boiling acid solution of copper sulphate;

(2) *Simple dissolution* of a mild steel by 2 per cent. alcoholic picric acid;

(3) *Corrosion by pitting* of a non-rusting steel with 13 per cent. chromium and 0·33 per cent. carbon after attack for 6 minutes in a non-agitated 15 per cent. solution of picric acid. (It should be noted that in this acid type of corrosion the pits are determined by the inclusions present in the steel, which is not the case with corrosion in saline solutions.)

These three types of corrosion are impossible to distinguish by the shapes of the curves; the two other curves in this figure with a much flatter maximum correspond with the *regular dissolution* of the non-rusting chromium steel (3 above) after agitation in 0·01 per cent. hydrochloric acid for 14 and 31 hrs., respectively.

In other circumstances or with other metals it is possible to determine the type of corrosion by the shape of the curves showing the reflection as a function of the angle of incidence. We hope to go further into this subject at a later date.

The AUTHORS (*in reply*): We are interested to have the comments of Mr. Derry and Professor Portevin. In reply, we would first emphasize the exact aim of our experiments, which was a special one. We were not concerned to know the absolute reflection factor, either specular or diffuse, nor with a study of the particular nature of the corrosion which occurred. Our aim was to assess, quantitatively, the appearance of highly polished metals and alloys intended for artistic and decorative use. This necessarily involved an empirical method and "figure of merit." We found that diffuse reflection had a great effect on the appearance of the metal for, as pointed out in the paper, it produces the effect of a haze or fog, as a result of which dark parts of images formed by the metal surface are not dark enough. This haze is produced when the tarnish is illuminated, but viewed at an angle remote from the angle of reflection. For this reason measurements of reflectivity were made with the specimen illuminated normally and viewed at 45°. This is an arbitrary choice, but is related to the phenomenon under consideration more closely than is the reflectivity at the angle of reflection. Furthermore, the diffuse reflectivity near the angle of reflection varies very rapidly, as Professor Portevin remarks, and measurements in that region were therefore avoided. Mr. Derry has very properly pointed out that a reading at 45° does not characterize the diffuse reflection distribution, but we were not interested in the shape of this distribution curve. In the region of 45°, with normal incidence, the diffuse reflectivity varies slowly with the angle of reflection and is therefore a fairly stable quantity.

The relative weight to be given to the diffuse and specular reflectivities is in any event arbitrary. The formula gives large weight to the diffuse reflectivity for the reasons given; the specular component is far less important. The unity term in the denominator was introduced to control the weight given to the diffuse component. In support of the values computed by the formula, we may say that some thousands of determinations revealed no inconsistencies between the "figures of merit" and the relative appearance of specimens. It should be noted that the minimum value of our "figure of merit" is 0 and not as Professor Portevin erroneously states $10/\sqrt{2}$. Professor Portevin's definition of the "degree of polish" is another empirical expression and amounts in our terminology to $\frac{R_s}{R_s + R_d}$. This form gives little weight to a slight diffuse component, and moreover gives the same "figure of merit," for example, to a piece of black glass and a piece of silvered glass. For our purposes this form is therefore unsuitable.

Professor Portevin's criticisms are based on a misconception of our method. Our measurement *b* is a measurement of stray light and of diffuse reflection of the prism, and is in practice very small—about 0·5 per cent. of the value of *a*, but the value of *d* is only zero when there is no diffuse reflection; it is a measure of the diffuse contribution at the angle of specular reflection and is therefore subtracted from the measurement *c*. Professor Portevin may perhaps have been misled by a mistake in our paper, for which we apologize; the word "prism" in line 3 of paragraph (*b*), p. 252, being incorrectly printed as "specimen" in the advance copies.

In order to stop down the beam of light, in our optical system, focussed images of U_1 and U_2 were formed at F_1, so that the edges of the spots were very sharply defined. No variation in brightness could be detected over the whole area of the illuminated part of the blotting-paper screen.

Voltage fluctuations on our circuit were small and were corrected when they occurred, and the method of taking observations was designed to eliminate them, as in all photometric procedure.

Professor Portevin has apparently failed to appreciate a fundamental difference between his method and ours. In our method a large uniformly bright disc is viewed by a *brightness* photometer after reflection at the specimen. In this arrangement, departure from flatness of the specimen or small angular errors of setting up do not affect the reading; they merely result in the photometer viewing another part of the disc of the same brightness as the centre. We are in a little difficulty in following Professor Portevin's method owing to his use of ambiguous and non-technical terms, but it seems to us to be faulty in principle in several ways, and does not really separate the diffuse and specular components of reflected light. This is evident from his Fig. A; for the true characteristic of any surface exhibiting specular reflection must show a discontinuity at the angle of specular reflection. It is unusual to measure reflection characteristics by rotating the specimen and keeping the directions of illumination and view unchanged, for the angles of incidence and reflection then both change simultaneously.

We do not propose to discuss Professor Portevin's further interesting results, as they are directed to a different end from our own work.

THE SPECTROGRAPHIC ANALYSIS OF SOME ALLOYS OF ALUMINIUM.* 681

By ERNEST H. S. van SOMEREN,† B.Sc., Member.

Synopsis.

The paper describes the technique of analyzing aluminium alloys by means of their spark spectra in the ultra-violet, using the method of internal standards.

Tables are given for the estimation of copper, zinc, iron, silicon, manganese, magnesium, nickel, tin, and cadmium; and also for the detection of lead, antimony, chromium, titanium, and bismuth.

A list of the aluminium alloys in commercial production would include considerably more than one hundred names, but analysis of samples shows a great deal of duplication in various countries, and the number of essentially different alloys in common use is probably between 40 and 80. An attempt is made in this paper to enable users of a spectrograph to find the approximate composition of any unknown aluminium alloy. With such data, supplemented if necessary by the usual physical tests and metallographic examination, either the alloy can be identified or a similar material prepared.

Previous publications on the spectrographic analysis of aluminium are infrequent; the chief contribution is that of A. Schleicher and J. Clermont,‡ who dealt with titanium, iron, and silicon in their first paper, copper in the second, and zinc in the third. Their method was to photograph the spark spectra, and obtain comparison lines by photographing copper spectra on the same plate with such an exposure as to obtain equality of intensity between specified copper and aluminium lines. The author, with the equipment at his disposal, was not able to reproduce the conditions they laid down, and has consequently not adopted a similar method.

Owing to the instability of the arc between aluminium electrodes,

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‡ *Z. anal. Chem.*, 1931, 86, 191; 1932, 90, 1, 321.

the spark is preferable to the arc for the routine testing of aluminium alloys. With the exception of the alkali metals, no impurity in aluminium is known to be important when present in such a small quantity that it cannot be detected by the spark method. Minute quantities of lithium, sodium, and calcium can best be detected by the arc method, and its application to sodium has been developed in the U.S.A. by A. W. Petrey,* who uses a small piece of aluminium arced between graphite rods. For this purpose a spectrograph covering the visible range only would be more suitable than one for the ultra-violet the dispersion of which in the visible spectrum is small. A quartz spectrograph will always allow the detection of calcium, and can be used for sodium and lithium if panchromatic plates are used.

The data in this paper are based on the spectra of 12 commercial alloys, and about 50 synthetic alloys prepared for this work only. The latter were all made from one strip of commercial Norwegian aluminium (99·6% aluminium) which was selected from material in works production after spectrographic examination of a number of samples. From this metal, with commercial cupro–manganese, commercial magnesium, electrolytic zinc, brass strip, and some soft-iron strip, a few "temper alloys" were made, and these were analyzed.

From these alloys and aluminium strip the other alloys were prepared; melts of from 250 to 750 grm. of material were melted in a small gas-fired furnace, using a little charcoal, but no flux, and were cast in flat cakes in a thick iron mould. As many of the alloys as possible were cold-rolled to strip about 3 mm. thick. Spectrographic testing of the material as cast, and after rolling, produced no evidence of inhomogeneity, except in one or two cases; these samples were discarded.

Five alloy samples were cast and analyzed by the Perry Barr Metal Company.

A small quantity of aluminium containing only 0·1 per cent. each of iron and silicon was obtained from Norway, and was used to prepare two alloys containing abnormally low quantities of these impurities.

The composition of the synthetic samples was checked by chemical analysis for about a third of the material used, so that the tables are based partly on analytical results and partly on synthetic figures.

Electrodes of cross-section about 3 × 8 mm. were cut from each sample, and the ends filed to a blunt wedge.

The instrument used was a Hilger medium quartz spectrograph (Model E3) giving a spectrum 150 mm. long from 2200 to 4500 A. (All wave-lengths are in International Angstrom units, usually quoted to the nearest integer.)

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* *Indust. and Eng. Chem.* (*Analyt. Edn.*), 1932, 4, 265.

A Hilger spark equipment was used, consisting of auto-transformer and transformer, the input being 1·2 amp. at 220 v., 50 p.p.s. A 4-mm. spark gap was used between two electrodes of each sample, situated 200 mm. from the slit, and aligned slightly off the optic axis of the instrument, so that the light passed through less than half the thickness of the prism. A condenser of capacity 0·014 microfarad was in parallel with the spark, and a self-inductance of 0·2 millihenry in series with it. The condition of the spark is best specified by comparison between certain aluminium lines; Al II 2369 should be slightly weaker than Al I 2378, and Al II 2317 should be slightly weaker than Al I 2319. The second line-pair is given because in some alloys containing copper the strong copper line 2370 makes comparisons with the adjacent aluminium line difficult.

The spark was always run for 5 seconds before starting the exposure, during which time its position was checked by a magnified image thrown on a screen by a lens; then an exposure of 20 seconds was given. Ilford thin film half-tone plates were used because they are remarkably uniform in sensitiveness over the range 2000–4000; they were developed with metolhydroquinone developer. These plates can be developed, fixed, washed, and dried in half-an-hour. Exposure and development were so adjusted that the group of lines at 2312–2322 was visible, but 2315 was very faint.

The slit-width used was about 0·04 mm., being such that the pair of aluminium lines 3064, 3066 appeared just separate. This wide slit made comparison of relative intensities easier; with a narrow slit some comparisons with diffuse lines are impossible. The plates were examined over opal glass with a lens giving a magnification of about 6 diameters.

The aluminium spectrum is not rich in lines, the characteristic pairs of lines are mostly too strong for comparison with impurity lines, but there are two important groups of faint lines, the wave-lengths of which are tabulated below, stating the strongest and faintest line in each group.

2312·4, 12·8	not resolved	3050·1
2313·5		3054·7
2315·0	faintest	3057·2 strongest
2317·5		3059·0 faintest
2319·1		3064·3
2321·6	strongest	3066·2

Although there is some doubt as to the allocation of some of these lines between the arc and spark series of aluminium (Al I and Al II), some of them have been used as internal standards for analysis, owing to the absence of other lines of suitable intensity.

It would be desirable to follow the example of certain German investigators and use for quantitative analysis only pairs of aluminium and impurity lines which are homologous, *i.e.* lines the relative intensity of which is independent of variations in the condition of the spark. For convenience in the examination of the spectra an arbitrary limit of 20 mm. was taken as the maximum distance between lines to be compared. Spectra of many of the samples were photographed with deliberately varied electrical conditions, various dimensions of sample, various times of running of the spark before exposure, and homologous lines were selected when possible; these are marked H in the tables. To avoid large gaps in the tables other pairs of lines have been included. The spark between aluminium electrodes produces more uniform spectra than that between lead or tin electrodes, and this departure from the ideal is justified in practice by its results.

Care has been taken to avoid using lines which coincide with lines due to common alloying constituents in aluminium; where this is inevitable a note is added to the tables.

Table I gives only the percentages of minor constituent at which the pairs of lines referred to are equal; weight percentages are used throughout. An attempt to expand the Table by including the concentrations at which the impurity line is less than, and greater than, the aluminium line would lead, in the author's opinion, to an illusion of greater accuracy than is warrantable. When interpolating from these tables it should be noted that generally if an impurity line is equal to an aluminium line at x per cent. of the impurity it will be definitely less at 0·8 x per cent., and equally definitely greater at 1·4 x per cent. (1·3 x per cent. if both lines are very faint). This unsymmetrical nature of the change in relative intensity has been observed by the author when making large numbers of observations on samples of fairly similar composition, and should be borne in mind when interpolating from the Table. It is supported by the fact that the general shape of curves connecting the relative intensity of a pair of lines with the concentration of an impurity (as measured with a microphotometer or wedge sector) is concave towards the concentration axis.

The percentages for equality quoted in the Table do not always correspond with the analysis of an individual sample, but each is the result of a number of observations on the spectra of a few appropriate samples, each photographed at least four times. This method of formulating tables introduces a possible error, which must be added to the uncertainty resulting from occasional reliance on synthetic figures for the composition of samples. The total uncertainty can be best expressed by stating the result of a spectrographic analysis in the form: the concentration of the impurity M lies between m per cent. and $2\,m$ per cent. In routine analysis of aluminium samples by this method accuracy will be increased by experience, and should, after a few months, be comparable with that of ordinary chemical analysis as practised in an industrial laboratory except for concentrations of more than 2 per cent. of alloying constituents.

Although the proportion of alloying constituents in many aluminium alloys is sufficient to make the aluminium lines in the spectrum fainter than in that of ordinary aluminium (with the same exposure), the lines due to the lesser impurities are also apparently fainter; consequently no appreciable modifications in the Tables appear to be necessary from this cause. This source of error has, however, not been completely explored, and is likely to be significant in some aluminium-zinc casting alloys.

The same aluminium lines are used for comparison with lines of different impurities, and Table I shows certain regularities in the percentages at which equality occurs. This regularity might be made use of in extending the Table to other percentages of impurities—for cadmium, for example. Unfortunately, a change in the author's occupation prevents him from checking the accuracy obtainable in this way.

Certain lines mentioned in Table I are sometimes masked by lines due to other metals, and then may not be used for intensity comparisons. These are set out in the first column of Table II; in the second column follows the symbol for the metal which interferes; and the last two columns specify a line due to that metal, and an aluminium line. If the line in column III is stronger than the line in column IV, then the line mentioned in column I must not be used. Usually comparison may be made by the help of an adjacent aluminium spectrum so exposed that its fainter lines are equal to the same lines in the spectrum of the sample. This is certain to be necessary in the analysis of aluminium containing nickel, where the comparisons marked N in Table I can never be made directly in the same spectrum, on account of other nickel lines.

In Table III are set out the lower limits for the detection of various elements in aluminium under the conditions laid down on p. 267. Two lines are given for each element, in order of sensitiveness. For antimony the only possible confirmatory lines are masked by iron and silicon; for bismuth no second line is likely to occur, and a narrower slit than usual must be used on account of the line Al 3066. For the detection

TABLE I.

		Aluminium Lines.														
		2204.	2315.	2317.	2319.	2322.	2372.	2378.	2460.	2568.	2652.	2660.	2928.	3050.	3055.	3057.
Copper All H	2200	2·8														
	2243		0·1	0·3	0·4	1·2										
	2247		0·05	0·15	0·2	0·5										
	2294		0·5	1·2	1·5	4·5										
	2400			7	9											
	3274													0·1	0·07	
Zinc	2558									5		0·5				
	3076														15	
	3283													H 5		H10
Iron All H	2344			0·22	0·3	0·8										
	2395			0·08	0·13	0·36										
	2663											2·0				
	2740											0·16				
	2743											0·6				
	3020													1±		2
Silicon	2435						H 10±		1·0							
	2507								0·45		H 2·8					
	2516								0·12		H 0·8					
	2519										H 10±					
	2881											0·12		H 0·6	H 0·45	
Manganese	2452								H 1±							
	2594											H 0·02				
	2656											H 1·2				
	2673											H 0·7				
	2890															H 5
	2933													H 0·6		H 1·2
	2939												0·08	H 0·4	H 0·25	
	2949												0·05		H 0·15	H 0·7

Magnesium	2777										H 9	0·6				
	2780										H 3	0·2				
	2803											H 0·002±				
	2852										H 0·2					
	2937													0·5	0·3	0·9
	3097													H 6	H 3·5	H 9
Nickel	2316		H 0·05		0·15	0·4 N										
	2438								H 1·0							
	2473								H 3±							
	3100													H 2 N	H 1·2	
Tin	2355							H 2·7								
	2706											0·5				
	2840											0·15				
	3175														H 0·6	
Cadmium	2265			0·1												
	2307		1±													
	3262													1·2		

N. See p. 269.

TABLE II.

I.	II.	III.	IV.
Al 2928	Mg	2937	2928
Al 2669	Cr	2677	2652
Al 2322	Cd	2313	2313·5
Al 2322	Ni	2316	2319
Al 3050	Ni	3100	3055
Si 2881	Cd	2981	2928
Zn 3076	Ti	3087	3055

of tin, lead, bismuth, and antimony the arc method is at least ten times more sensitive than the spark.

TABLE III.

Element.	Lower Limit Per Cent.	Lines Used.	
Copper	less than 0·01	3247	3274
Zinc	0·1	3345	3303
Iron	less than 0·02	2382	2740
Silicon	less than 0·02	2516	2881
Manganese	0·004	2594	2606
Magnesium	less than 0·002	2803	2852
Nickel	0·025	2316	3414
Tin	0·1	2840	2863
Cadmium	0·01	2265	2288
Lead	0·1	2833	3684
Antimony	0·2	2311·5	
Chromium	0·1	2836	2843
Titanium	0·03	3350	3361
Calcium	less than 0·01	3934	3968
Bismuth	0·1	3068	

Note to Table III.—Pb 2833 equals Al 2669 at 0·4 per cent.; Sb 2311 equals Al 2315 at 0·3 per cent.

ACKNOWLEDGMENTS.

The thanks of the author are due to the management of the Nordiske Kabel- og Traadfabrikker A.S., Copenhagen, for permission to publish this paper, the result of experimental work carried out in the laboratory of their rolling mill.

Thanks are also rendered to Ingeniør Henning Hansen, who analyzed most of the standard samples, to the Superintendent of Research of I.C.I. Metals, Ltd., Birmingham, for two analyses, and to the chief chemist of the Perry Barr Metal Co. (Birmingham) for the provision of five analyzed samples.

CORRESPONDENCE.

MR. M. MILBOURN,* B.Sc. (Member): This is a most interesting contribution to spectrographic literature, in that it deals with impurities in aluminium, which has a small number of lines available for intensity com-

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* Research Physicist, I.C.I. Metals, Ltd., Witton, Birmingham.

parison, by the simple "internal standard" method. The range of impurities studied and the number of homologous pairs are both remarkable.

The point which Mr. van Someren mentions concerning his inability to reproduce the conditions laid down by Schleicher and Clermont is of considerable importance. This is not an isolated case, and the lack of reproducibility is a real stumbling-block in the way of progress. Careful specification of all relevant conditions is certainly necessary, and in this connection it may be mentioned that Mr. van Someren's standardization line comparisons given in the first paragraph on p. 267 are rather indefinite.

The practical consideration that each investigator has his own standardized conditions of apparatus and technique means that results obtained by one may not be obtained by another. If reproducibility be desired, then some scheme of unification may be necessary.

Mr. D. M. Smith,[*] A.R.C.S., B.Sc., D.I.C. (Member): In connection with Mr. van Someren's observations on the weakening of the aluminium lines when alloying constituents are present in some quantity, the following notes may be of interest. I have tried to make the spark spectra of aluminium–silicon alloys (containing some 12 per cent. silicon) comparable with those of standard aluminium samples by suitably increasing the time of exposure. Whilst this appears to have some compensating effect, the aluminium oxide bands show more strongly in the alloy spectra when the aluminium lines are approximately of the same strength in both spectra. There is certainly need for further investigation of this subject, however, as some recent comparisons of chemical and spectrographic analyses of aluminium–silicon alloys have shown the spectrographic figures to be consistently lower than the chemical figures. It appears that the presence of the silicon causes a decrease in the intensity of the impurity lines as compared with the aluminium lines. A similar effect has also been observed in the case of alloys containing some 10 per cent. zinc, as pointed out by Mr. van Someren.

These observations do not detract in any way from the value of Mr. van Someren's paper. The method described, whilst not competing with chemical analysis in the accuracy of estimating the alloying constituents, provides a rapid means of identifying commercially important alloys of aluminium.

M. H. Triché: [†] The method employed by Mr. van Someren is extremely rapid, because the approximate composition of an alloy can be determined by a simple comparison of the impurity lines with those of the aluminium.

The author has filled an important gap in clearing up the problem of analysis of the aluminium alloys. In many cases the results found by his method will suffice; even in cases where each impurity is to be estimated with more accuracy the author's results enable this to be done more quickly, particularly in any method where the estimation of one metal is carried out with the help of an auxiliary metal. For instance, if an alloy is to be analyzed as a solution, another metal is added to the solution in such quantity that a pair of selected lines of the two metals have equal intensities. The quantity of metal to be added is more easily determined if the upper and lower limits of concentration of the metal being estimated are known.

The author's results will also be of use in the application of the method I have recently suggested: a spark (or arc) is passed between an electrode of the alloy to be analyzed and a solution or alloy containing an auxiliary metal; a line of the latter (tin, for example) is then compared with a line of the impurity (such as silicon) to be determined in the alloy. Equality of intensity of these two will be obtained more rapidly if the quantity of the

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[*] Investigator, British Non-Ferrous Metals Research Association, London.

[†] Laboratoire de Chimie Minérale, Faculté des Sciences de Paris.

impurity has been approximately found by the method described by Mr. van Someren. The two methods do not overlap, but supplement each other.

Naturally, one must, as suggested in this paper, study the influence of the nature of the alloy on the results obtained. In this connection I have shown* that for solutions equality of intensity of a line of an impurity (Mg) with that of an auxiliary metal (Cr) is not independent of the nature of the solution, and that the extent of this disturbance varies with the apparatus used to produce the spark.

To sum up, Mr. van Someren's results provide a method of obtaining rapid final results, or provisional figures which can be refined by other more accurate, and lengthy, methods.

The AUTHOR: In reply to Mr. Milbourn's comment on specification of spark conditions, I regret the vagueness of the term "slightly weaker than" on p. 267 to express the relative strength of certain aluminium lines. Subsequent measurements made by means of a stepped wedge of platinum on quartz show that a ratio of about 5 to 7 for the two lines was obtained, in terms of relative exposure. This means that the relative intensity of the two lines is that of two images of the same spectral line exposed (on the same sort of plate) with exposure times in the ratio of 5 to 7.

A more easily checked standardization of the spark conditions may be made by using a sample of aluminium containing some copper, and examining the three copper lines of wave-length about 2226, 2228, 2230. The middle one is a spark line, and its density should lie between that of the two others, resembling 2226 rather more than 2230.

In reply to Mr. Smith, I am interested to have confirmation of the curious effects of impurities on the general level of intensity of the aluminium spectrum. Besides the effect referred to, where about 10 per cent. of minor constituent weakens the aluminium spectrum, the converse effect also occurs; a sample of 99·9 per cent. aluminium requires about twice as long exposure as a 99·4 per cent. aluminium in order to get the same density of the aluminium lines. This is not altogether unique, it has also been observed that in comparing spectra from arcs with constant current that from a copper with 0·5 per cent. of tin or arsenic is denser than that from pure copper.

* Triché, *Bull. Soc. Chim. France*, 1934, (v), 1, 495–505.

THE SPECTROGRAPHIC DETECTION AND ESTIMATION OF MINUTE QUANTITIES OF IMPURITIES IN COPPER.*

By M. MILBOURN,† B.Sc., Member.

Synopsis.

An accurate and convenient method is described for the detection and estimation of small quantities of bismuth, arsenic, lead, iron, nickel, silver, antimony, and tin in copper. Details of technique, sensitivity, and line intensity comparisons are given.

Introduction.

The problem which gave rise to this work was the necessity for making spectrographic analyses on small samples of copper, weighing less than 0·5 grm. The usual arc method using copper rods was impossible, and the spark method was unsuitable on account of lack of sensitiveness; it was decided therefore to try a globule method of arcing such as has been described for tin and lead by Smith,[1] Brownsdon and van Someren,[2] and Hitchen;[3] and for copper by Hill and Luckey.[4] Breckpot[5] has also described somewhat similar work in which synthetic samples, consisting of copper oxide with small additions of other oxides, were tested in a graphite arc.

Working on small samples of copper, van Someren made the interesting observation that increased sensitivity to a number of impurity elements occurred when they were examined by the globule method of arcing. The present paper deals with the technique and line intensity comparisons to be used when applying this method to the detection and estimation of minute quantities of impurities in copper.

Technique.

The method used is essentially the same as that described elsewhere.[1, 2, 3, 4] An arc 4 mm. long and carrying 5 amp. is passed between a pure copper rod, made the positive electrode, and a small

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† Research Physicist, I.C.I. Metals, Ltd., Witton, Birmingham.

portion (0·2–0·5 grm.) of the sample to be examined, supported in a shallow cup in the end of a graphite rod (Hilger's H.S. graphite). The piece of sample used is pickled, washed, and dried on filter paper. The voltage across such an arc is generally about 40 v. and does not vary by more than ± 1 v. for any one sample.

If the sample adheres to the copper rod, or if the arc tends to pass to the graphite, then the electrodes should be manipulated until a suitable, steady arc is obtained. The cup in the end of the graphite rod should be of about 1·5 cm. radius, that is, just sufficiently deep to keep the molten globule in place.

The copper rod used contains the following small amounts of impurities, as estimated from tests in which a small portion of it was made the globule: Lead, slight trace (Pb 2833·1 A. just visible); iron, about 0·001 per cent.; nickel, about 0·0005 per cent.; silver, about 0·002 per cent.; antimony, about 0·001 per cent.; bismuth, arsenic, and tin, not detected.

Using other samples as globules and the above copper rod as anode, spectra are obtained in which lines due to such elements as lead, iron, or silver may be absent; hence these small amounts of impurities are not affecting the spectrum.

Similarly the graphite rod acts merely as a convenient conductor and an easily cleaned support for the globule, and does not enter into the arc. Cyanogen bands and lines due to impurities in the graphite, such as vanadium, titanium, and silicon, do, however, appear when a graphite rod is used as anode instead of the copper rod. For this reason, the copper rod is preferred.

Hilger's medium quartz spectrograph (E.315) has been used throughout the work, with the arc 20 cm. from the slit, and no condensing lens between them. An exposure of 15 seconds was given using Ilford Process Panchromatic plates. This exposure is about half that necessary for a solid electrode arc. The slit width of 0·015 mm. was fixed to give the required resolution.

It has been found that weight of sample, provided that it is between the limits stated, has no appreciable influence on the results.

Exposures made at intervals in the continuous arcing of various globules for 2 to 3 minutes showed that lines due to impurities do not decrease in intensity during the first minute's arcing. Thereafter the arsenic lines decrease somewhat, and there is a slight decrease in the lead, tin, and bismuth lines when the globule has practically boiled away (after about 3 minutes' arcing). The increase in sensitivity with the globule method is therefore not due to distillation of impurities from the copper.

MODIFICATIONS TO THE COPPER SPECTRUM.

The copper spectrum obtained from a globule arc is radically different from that given by a solid electrode arc. The spark lines appearing near the poles in the latter are practically suppressed in the former, and many lines absent from or appearing only faintly in the solid electrode arc occur with considerable intensity in the globule arc. The factors, such as temperature and electrical conditions in the arc, which favour the appearance of these lines also enhance the impurity lines. Many of the faint " background " lines are nearly absent from the globule arc; this also assists in the observation of impurity lines. The yellow luminous cone surrounding the arc, as described by W. B. Nottingham,[6] is very pronounced with the globule method.

The state of the globule arc can best be judged from the steady value of the voltage at the time of exposure and from the reversal of the lines Cu 3247·6, 3273·9, 2199·6, and 2293·8 A. and the equality of the lines Cu 2844·2 and 2845·0 A. in the photographed spectrum.

RELATIVE SENSITIVITY OF GLOBULE AND SOLID ELECTRODE ARCS.

The results of observations on sensitivity to impurities made under identical conditions of ampèrage and arc length for the two methods of testing copper are given in Table I. Impurity lines which cannot be detected in the solid electrode arc appear with sufficient intensity to allow of comparison with copper lines in the globule arc. The sensitivity to iron and silver, however, is not greatly increased.

TABLE I.

Element.	Percentage.	Sensitivity in globule arc.	Sensitivity in solid electrode arc.
Bi	0·0002	Bi 3067·7 = Cu 3068·9	not detected
As	0·001	As 2349·8 visible	"
Pb	0·0004	Pb 2833·1 = Cu 2845·0	"
Fe	0·002	Fe 2483·3 < Cu 2479·8	Fe 2483·3 visible
Ni	0·0005	Ni 3134·1 = Cu 3135·2	not detected
Ag	0·001	Ag 3382·9 < Cu 3375·7	Ag 3382·9 < Cu 3375·7
Sb	0·002	Sb 2598·1 > Cu 2570·7	Sb 2598·1 barely visible
Sn	0·0005	Sn 2354·8 = Cu 2363·3	not detected

ESTIMATION OF IMPURITIES.

The tabular data given below in the form of line intensity comparisons are entirely based on chemically analyzed samples. The range of percentage of impurities studied extended into that which can be covered by the solid electrode arc. It was thus found that the globule method is the more reliable for percentages of impurities which approach the limit of detectability of the solid electrode method. The amounts of impurities given, therefore, frequently exceed the description "minute quantity." Breckpot [5] gives intensity data for 1, 0·1, 0·01, and 0·001 per cent. of bismuth, arsenic, lead, silver, and antimony.

Bismuth.

Care should be taken to distinguish the line Bi 3067·7 A. from the line Fe 3067·3 A. when iron is present in quantities greater than 0·01 per cent.

TABLE II.

Bismuth, Per Cent.	Bismuth Line. A.	
	2898·0.	3067·7.
0·0002		= Cu 3068·9
0·0005		> Cu 3068·9 < Cu 3088·0
0·001	< Cu 2905·4	= Cu 3088·0
0·003	= Cu 2905·4	> Cu 3088·0
0·005	> Cu 2905·4 < Cu 2911·0	
0·01	= Cu 2911·0	

Arsenic.

Up to 0·05 per cent. of arsenic the globule method may be advantageously used. For the estimation of arsenic in arsenical coppers containing up to 0·5 per cent. arsenic the globule method is not so suitable as the solid electrode method, owing to the fact that there is a comparatively rapid loss of arsenic due to volatilization with the former method. If, however, some estimation of the arsenic content is required when using the globule method on an arsenical copper, then the exposure should be made during the early stages of arcing.

TABLE III.

Arsenic, Per Cent.	Arsenic Line. A.		
	2349·8.	2780·2.	2860·5.
0·001	b.v.	not detected	
0·003	< Cu 2363·3	b.v.	
0·01	> Cu 2363·3		= Cu 2862·0
0·03			> Cu 2862·0 < Cu 2874·7
0·05			= Cu 2874·7

Lead.

The method used by Hill and Luckey,[4] employing a globule arc, the globule being positive, consisted in noting the time for the lead line 4057·8 A. to disappear from a spectrum observed visually. This indicates that under the conditions they used lead was being removed from the copper, whereas such removal was found not to take place within the range studied here.

TABLE IV.

Lead, Per Cent.	Lead Line. A.		
	2614·2.	2833·1.	2873·3.
0·0004		= Cu 2845·0	
0·001	< Cu 2627·5	> Cu 2845·0	
0·005	> Cu 2627·5 < Cu 2630·0		< Cu 2874·7
0·01	= Cu 2630·0		= Cu 2874·7
0·03	> Cu 2630·0		> Cu 2874·7

Iron.

Great care in the pickling and handling of the samples is essential if distinctions are to be made in amounts of iron of less than 0·01 per cent.

TABLE V.

Iron, Per Cent.	Iron Line. A.	
	2483·3.	2484·2.
0·002	< Cu 2479·8	
0·005	= Cu 2479·8	
0·01	> Cu 2479·8	< Cu 2494·9
0·02		= Cu 2494·9

Nickel.

The most sensitive nickel line is nickel 3415 A., but the full range of analyzed samples can be followed from the comparisons given below.

TABLE VI.

Nickel, Per Cent.	Nickel Line 3134·1 A.
0·0005	b.v. = Cu 3135·2
0·005	< Cu 3131·5
0·01	= Cu 3131·5 < Cu 3120·7
0·02	> Cu 3131·5 = Cu 3120·7
0·03	> Cu 3120·7 < Cu 3140·3
0·06	> Cu 3140·3

Silver.

TABLE VII.

Silver, Per Cent.	Silver Line. A.	
	3280·7.	3382·9.
0·001		< Cu 3375·7
0·002	b.v. < Cu 3266·0	> Cu 3375·7 < Cu 3381·4
0·004	> Cu 3266·0	> Cu 3381·4
0·006	< Cu 3282·7	
0·01	= Cu 3282·7	

Antimony.

At 0·002 per cent., Sb 2598·1 A. $>$ Cu 2570·7 A. $<$ Cu 2577·1 A.

At 0·015 per cent., Sb 2598·1 A. $>$ Cu 2627·5 A. $<$ Cu 2630·0 A.

Tin.

At 0·0005 per cent., Sn 2354·8 A. = Cu 2363·3 A.

At 0·012 per cent., Sn 2421·7 A. = Cu 2479·8 A.

The copper lines used for intensity comparisons all belong to the class which are more intense in the globule than in the normal arc. Many of them are not given in published tables, but their identity has been well established by their constant and regular appearance.

GENERAL REMARKS.

The globule method of arcing is most suited for the examination of relatively pure coppers. Arsenical coppers can be satisfactorily examined for impurities other than arsenic, but an estimation of the arsenic content may tend to be low owing to the rapid loss of arsenic in the globule arc unless the precaution is taken of exposing the plate during the early stages of arcing.

The quantitative results given with coppers deoxidized with phosphorus are not reliable for lead, tin, and iron, although they are satisfactory for bismuth, arsenic, nickel, silver, and antimony.

It is interesting to note that when arcing a copper containing 0·04 per cent. phosphorus by the globule method an original weight of 0·3 grm. metal loses only about half its weight as the result of arcing for 5 minutes, whereas a similar weight of copper free from phosphorus is almost completely volatilized at the end of 3 minutes' arcing, there being insufficient copper left in the globule to sustain a steady arc.

CONCLUSION.

For the detection and estimation of minute quantities of impurities in copper the globule method of arcing is more sensitive than the normally used solid electrode method of arcing. Some precautions are necessary, however, when dealing with arsenical and with phosphorus-deoxidized coppers.

ACKNOWLEDGMENTS.

The author wishes to express his thanks to the Management Board of I.C.I. Metals, Limited, for permission to publish this paper, and to Dr. H. W. Brownsdon for his valuable suggestions and most helpful guidance.

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CORRESPONDENCE.

MR. E. H. S. VAN SOMEREN,* B.Sc. (Member): In qualitative spectrographic analysis by the arc method attempts are made to increase the sensitiveness of the method by increasing the exposure for each spectrum. A point is soon reached where the density of the background obtained on the photographic plate is such that the detection of impurity lines becomes difficult. The use of a contrast photographic plate such as is made for process reproduction work gives a slight advantage over ordinary plates. This continuous background has a fluted structure, and is identical for the copper, zinc, and lead arc spectra, from which I conclude that it is due to the presence in the vapour column of the arc of ions other than those of the metal forming the electrodes. Any change in the electrical condition of the arc which raises the vapour pressure of the metal tends to decrease the relative intensity of this continuous background. Consequently, it is generally best to use the maximum current in the arc which is consistent with stability of the arc and its electrodes; with certain metals a high current arc blows itself out.

Mr. Milbourn is to be congratulated on the painstaking work he has done in the identification and selection of suitable copper lines for comparison with impurity lines in this method of analysis. The value of this paper may be illustrated by Table A, in which the results obtained by two workers independently analyzing the same sample of copper are set out. The first column gives my results, obtained by the courtesy of Messrs. Adam Hilger in their laboratory; the second column gives the figures obtained by Mr. D. M. Smith. The sample of copper was a rod 5 mm. in diameter obtained from Messrs. Hilger.

TABLE A.—*Showing Results Obtained by Two Workers Independently Analyzing the Same Sample of Copper.*

Metal.	E. v. S.	D. M. S.
	Per Cent.	Per Cent.
Bismuth	0·0001	< 0·0002
Arsenic	0·001	0·001–0·002
Lead	0·02–0·03	> 0·02–0·04
Iron	0·002–0·004	0·002
Nickel	0·0005	0·0005
Silver	0·002–0·004	0·005
Antimony . . .	0·001	< 0·002
Tin	0·001–0·004	abt 0·0005

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* London.

The AUTHOR (*in reply*) : Mr. van Someren's interesting remarks on sensitivity can perhaps be expanded by the following observations :

There are a number of factors which affect the rate of vaporization of copper into the arc, and in consequence the vapour density in the arc. These include amperage, size of sample, and thermal conductivity of the copper in a solid electrode arc. It has been observed that, when as a result of these factors, the vapour density in the arc is comparatively low, lines due to minute quantities of impurities, such as bismuth, arsenic, lead, and tin, as well as certain copper lines typified by λ 3088·0 A., are restricted to a region of the spectrum corresponding with that near the negative electrode. As the quantity of impurity present increases, lines due to it increase in length and density; increase in vapour density also causes the above lines to spread across the spectrum until with a globule arc, which has a considerable excess of vapour, they are of practically uniform intensity. Iron lines, and possibly also nickel lines, appear uniform over the major central portion of the width of the spectrum, even with low vapour density.

These observations have been supported by some collateral evidence on the variation of sensitivity with length of arc, and they account, to a large extent, for the increased sensitivity with the globule arc.

Further work is being carried out, extending the above observations and applying them to the analysis of copper and copper-rich alloys.

A "SYNTHETIC SPECTRUM" METHOD OF ANALYSIS AND ITS APPLICATION TO THE QUANTITATIVE ESTIMATION OF SMALL QUANTITIES OF BISMUTH IN COPPER.*

By D. M. SMITH,† A.R.C.S., B.Sc., D.I.C., MEMBER.

SYNOPSIS.

A method has been devised for the production of "synthetic" spectra as standards for comparison, the spectrum of a standard alloy being exactly superimposed on that of the pure metal which forms the main constituent. The total time of the two exposures is equal to the normal time of exposure of a sample which is being analyzed, and a series of spectra is obtained in which the impurity lines show a systematic increase in intensity. While the method was originally applied to the checking of the reliability of standard samples, it can be used for the quantitative determination of impurities in metals, once the standard calibration curve has been obtained. The application to the determination of 0·0001 to 0·004 per cent. of bismuth in copper is described.

INTRODUCTION.

In the standardization of spectrographic methods for the quantitative determination of minor constituents in metals and alloys, samples are adopted as standards when the intensities of the lines due to the constituents under examination exhibit a systematic increase with increasing content. This applies equally to synthetically prepared and chemically analyzed samples. Where it is possible to obtain numerical values for the intensities, deviations are readily detected in a graph showing the relation between the intensity of the line (using as a standard for reference, that of a line of the main constituent) and the percentage content. With methods of the comparison sample and internal standard type, however, purely visual examination and comparison has to be relied on for the detection of discrepancies.

An attempt has been made, therefore, to devise a means of producing a systematic and easily controlled variation of intensity of a line due to an impurity or alloying constituent which would serve as a standard

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

for reference. The time of exposure of a standard alloy appeared to be the most suitable variable, since this can be expressed numerically with a known probable accuracy. Since this method promises to be of general application and, so far as the author is aware, has not been described before, the present paper gives the experimental details and the mode of application in the particular case of the estimation of small quantities of bismuth in copper.

PRINCIPLE OF THE METHOD.

The synthetic spectrum is produced by two exposures, one of an alloy containing an accurately known percentage of the constituent under examination, and the other of the pure metal predominating in the alloy, the two spectra being exactly superimposed. In each case the total time of the two exposures is equal to the normal time of exposure of a sample which is being analyzed. As the time of exposure of the alloy is increased in progressive stages, the time of exposure of the pure metal being correspondingly diminished, the intensity of the line or lines due to the impurity or alloying constituent systematically increases. The spectrum of the pure metal is superimposed on that of the alloy in order to obtain the same intensity of spectrum background and of the lines due to the primary constituent in the synthetic spectrum as in the spectrum of the sample under test.

The effect obtained is similar to that of a series of spectra of graded samples containing increasing proportions of the impurity in question, the lines due to the main constituent remaining constant. Once these spectra have been calibrated by means of intermediate samples of known content, analyses of further samples can be carried out by comparison of their spectra with the synthetic spectra.

SPECTROGRAPHIC DETECTION OF BISMUTH IN COPPER.

With the standard conditions previously adopted for the estimation of the usual impurities in copper,* *viz.* the 3 amp. arc between metallic electrodes, it is difficult to detect 0·001–0·002 per cent. bismuth with certainty on account of the masking of the only bismuth line available, 3067·7 A., by the spectrum background. By increasing the current strength to 7 amp. the intensity of the bismuth line at a given percentage is increased to a greater extent than that of the spectrum background, resulting in greater sensitivity of detection.

The spectra of the various copper samples received were compared with one another, and those showing a systematic increase in intensity of the bismuth line with corresponding increase in percentage content

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* Smith, "Metallurgical Analysis by the Spectrograph," London: 1933, p. 93.

were provisionally adopted as standards. Later samples were then analyzed by means of these standards, the bismuth contents of the provisional standards being either confirmed or modified in accordance with the data thus obtained.

After the examination of numerous spectra, samples containing the following percentages of bismuth were selected as being reliable as standards:

0·0001
0·0006
0·001
0·0025
0·003
0·0035
0·004

A medium-size spectrograph giving a length of spectrum of about 19 cm. for the region 2100–6000 A. provides adequate dispersion in the region of the bismuth line. With the Hilger E.34 spectrograph, as used in the present work, a smaller diaphragm (oval, $\frac{7}{8}$ in. × $\frac{3}{8}$ in.) than that generally used was inserted between the camera lenses in order to obtain improved definition and resolution of the lines. A plate was also photographed on a large E.1 (Littrow) spectrograph in the laboratory of Messrs. Siemens Bros., Woolwich, to whom the author is indebted for the facilities placed at his disposal. The spectra obtained on this plate confirmed the results obtained with the medium-size instrument.

ESTIMATION OF BISMUTH BY THE INTERNAL STANDARD METHOD.

The standardized conditions of analysis adopted for the estimation of 0·0001–0·004 per cent. bismuth in copper, by means of the arc between metallic electrodes, were as follows:

Form of Sample: Two 3 in. length, about $\frac{3}{8}$ in. in diameter, rods or their equivalent, roughly pointed to an angle of about 70°.

Length of Arc: 5 mm. ($\frac{3}{16}$ in.).

Current Strength: 7 amp.

Exposure: After the arc has run for 15 seconds an exposure of 1 minute, of the central part of the discharge, focussed on the slit by means of a spherical lens.

Slit Width: 0·007–0·01 mm.

Photographic Plates: Wellington Antiscreen.

Development: Should be continued until the two faint lines 3069 and 3071 A. are clearly visible on the plate (see Fig. 1, Plate XVII).

The notation in Table I follows the usual conventions,* "bv" indicating that the line is barely visible, the limit of detection having been reached, "<," "=" and ">" indicating that the bismuth

* See H. W. Brownsdon and E. van Someren, *J. Inst. Metals*, 1931, **46**, 106.

Table I.—*Analytical Table for the Estimation of Bismuth in Copper.*

(Arc between metallic electrodes.)

Bismuth, Per Cent.	3067·7 Bi.		
0·0001		by < 3069 *	
0·0006		= and	
0·001	< 3115	> 3071 Cu	
0·0025	=	<	
0·003	> Cu	= 3122	< 3088·5
0·004		> Cu	= Cu

Note.—With high iron and nickel contents there is the possibility of masking or confusion with the lines 3067·3 Fe and 3064·6 Ni.

* These lines are ascribed to copper, since they appear with constant intensity in all the copper spectra examined, including those of high-grade pure copper. (The wave-lengths are only approximate.)

line is respectively weaker than, equal in intensity to, and stronger than, the copper lines used as internal standards.

CALIBRATION OF THE STANDARD SYNTHETIC SPECTRA.

In the particular case studied, the standard alloy selected was of copper with 0·004 per cent. bismuth (referred to subsequently as sample AFT) and the corresponding times of exposure of this sample and of pure copper are given in Table II. The sample of " pure copper " actually used contained 0·00001 per cent. bismuth by chemical analysis. This amount of bismuth, however, was not detected spectrographically, the most sensitive bismuth line 3067·7 A. being absent from spectrum No. 1. For the purposes of this investigation, therefore, the purity was adequate.

The total time of exposure in each case was 2 minutes, as compared with 1 minute as standardized for the internal standard method. In this way greater accuracy was obtained in the times of exposure of the sample AFT. Moreover, any fluctuations in the running of the arc would be of less consequence than might be the case with shorter exposures. The copper lines in the spectra in both cases were quite uniform in strength.

The apparent percentages of bismuth obtained from these composite or " synthetic " spectra were then determined by means of the internal standard data in Table I and confirmed by direct comparison with the spectra of the standard samples. The results are shown graphically in Fig. 2.

The deviation of the only point not on the curve in Fig. 2, is within the limits of experimental error (the curve giving 0·00365 per cent.

TABLE II.—*Times of Exposure for the Synthetic Standard Spectra.*

Spectrum No.	Sample AFT (0·004% Bi).	Pure Copper.
1	0 seconds	120 seconds
2	20 ,,	100 ,,
3	30 ,,	90 ,,
4	35 ,,	85 ,,
5	40 ,,	80 ,,
6	60 ,,	60 ,,
7	90 ,,	30 ,,
8	120 ,,	0 ,,

bismuth, approximately, as compared with the experimental value 0·0035 per cent. bismuth).

It is interesting to note that, so far as the shape of the curve is concerned, Fig. 2 bears some resemblance to the blackening curves of photographic plates (Density ∝ log. Exposure). Plotting the percentage of bismuth against the logarithm of the time of exposure of sample AFT, another curve of similar shape is obtained (Fig. 3). A possible explanation may be offered by regarding Fig. 2 as showing the relation between the time of exposure of the bismuth radiation of wavelength 3067·7 A. (which may be regarded, for exposures of 20 seconds or more, as a reasonably constant source of illumination) and the density of the image on the photographic plate (as represented by the percentage

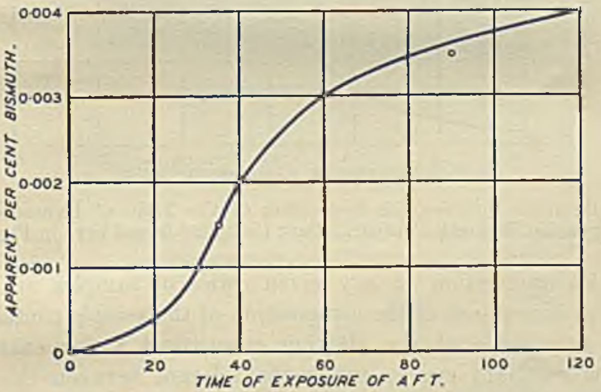

FIG. 2.—Relation Between the Time of Exposure of Sample AFT (Containing 0·004% Bi) and the Apparent Bismuth Content Shown by the Composite Spectrum.

content which would produce it). Until further work is done on this subject it is perhaps premature to arrive at any definite conclusions.

GENERAL APPLICATION OF THE SYNTHETIC SPECTRUM METHOD.

It is believed that the method will prove to be of quite general application. Its value in the case of small quantities of bismuth in copper, using arc spectra, has been demonstrated, and results have since been obtained showing its applicability to the spark spectra of lead with small quantities of cadmium. Other series of alloys are being investigated with a view to establishing the general utility of the method.

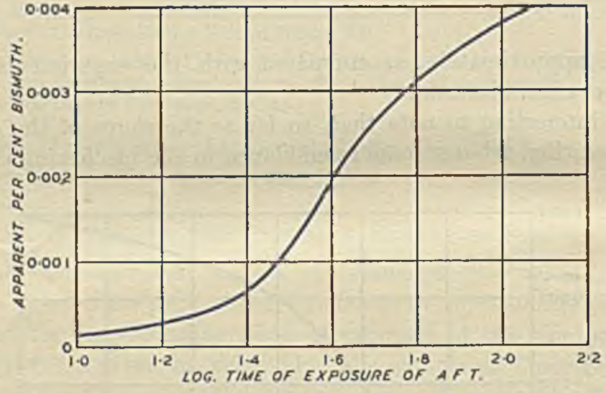

FIG. 3.—Relation Between the Logarithm of the Time of Exposure and the Apparent Bismuth Content. Data Compiled from Curve in Fig. 2.

For its application to any given series of samples an accurate knowledge is required of the composition of the sample containing the highest percentage of the alloying constituent under examination. Once the standard curve, giving the relation between the time of exposure of the alloy and the apparent percentage content given by the synthetic spectrum, has been determined in the manner described, it is available for quantitative determinations.

Comparison would then be made between the spectrum of the sample under test and those obtained by various exposures of the alloy plus the appropriate exposures of the pure metal, *i.e.* the synthetic spectra. From the time of exposure, giving equality of intensity of the impurity line in the two spectra, the corresponding percentage of impurity is then obtained from the graph.

Although no definite tests have yet been made, it is expected that the accuracy of estimation would be of the same order as that obtained by the comparison sample method.

PLATE XVII.

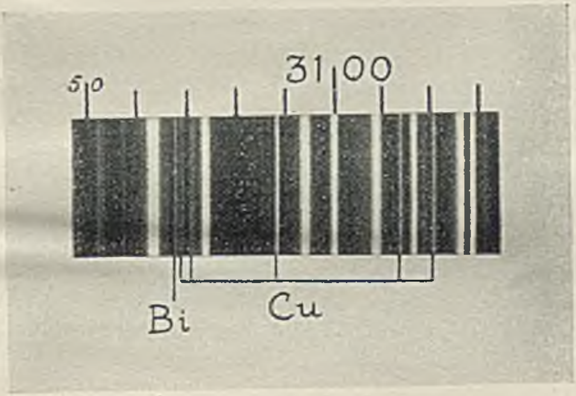

FIG. 1.—Arc Spectrum of Copper Containing 0·001% Bismuth.
(Arc Between Metallic Electrodes.) × 10.

[To face p. 288.

SUMMARY.

The use of "synthetic" standard spectra for the quantitative estimation of impurities in metals is described and illustrated by the particular example of the determination of from 0·0001 to 0·004 per cent. bismuth in copper. Details of the standardization and calibration of the spectra, using the internal standard method of analysis, are given. Further investigations on the application of the principle to both arc and spark spectra are contemplated.

ACKNOWLEDGMENTS.

The author desires to record his indebtedness to the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish this paper, and to Mr. B. Drinkwater, B.Sc., A.R.C.S., A.R.S.M., F.I.C., for valuable collaboration and careful chemical determinations of the bismuth contents of the actual copper samples used.

This work has been greatly assisted by the parallel work in the laboratory of Messrs. British Insulated Cables, Ltd., and the supply of standard samples by Dr. F. J. Brislee, F.I.C., who also suggested the use of a higher current in the arc than normally used for the analysis of copper. Acknowledgment is also made to Mr. L. Reeves who has photographed the spectrograms and assisted in their interpretation.

CORRESPONDENCE.

Mr. M. Milbourn,* B.Sc. (Member): Mr. Smith has evolved a method of producing variations in the intensity of a line due to an impurity, which could well prove of considerable value in certain conditions. It is likely, however, that these conditions will be restricted, since in the analysis of an unknown sample it would be simpler to make a comparison directly with one of the standard samples that must be used for the construction of the curve (Fig. 2), than to use a synthetic spectrum for which two exposures must be made. This double exposure also introduces a further chance of error.

In using the "synthetic spectrum" method, an upper limit is fixed to the quantity of an element that can be estimated. If the range be extended, then accuracy in the lower part is reduced.

I have constructed curves such as Mr. Smith gives in Fig. 2 for the following cases: (1) bismuth in copper up to 0·003 per cent.; (2) lead in brass, up to 0·2 per cent.; (3) zinc in copper-zinc alloys up to 40 per cent. The first gave a curve approximating to that in Fig. 2, but considerably straighter in the lower region. The second gave widely differing results from two experimenters, but the curve approximated to a straight line through scattered points. The third gave a curve similar to that in Fig. 2, but having a longer straight line portion.

In general, the form of the curve may vary with different elements, with

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* Research Physicist, I.C.I. Metals, Ltd., Witton, Birmingham.

different lines of the same element, and with different types of photographic plate. It would be interesting to have some more detailed study of the form of the curve, so that it could be predicted, and analyses carried out without having a series of analyzed samples. The method would then be of considerable practical value.

The Author (*in reply*): I thank Mr. Milbourn for the interest he has shown in this method and for the observations he has made. From results recently obtained, during the investigation of other cases, I can confirm his statement with regard to the reduction of accuracy in the lower part of an extended range.

Investigation of the form of the curve is in progress, with a view to arriving at some general conclusions, but considerable detailed study will be necessary before this end is achieved.

A NOTE ON SOME ANCIENT COPPER-COATED SILVER COINS OF CYPRUS.*

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By STANLEY G. WILLIMOTT,† B.Sc., Ph.D.

SYNOPSIS.

A number of authentic Greek and Roman coins of Cyprus having the appearance of copper or bronze have been found at different times and places. On archæological grounds these coins would have been expected to have been silver, and laboratory investigation proved this to be the case, 92·3 per cent. silver being found in one case and 94 per cent. in another.

The cause of this phenomenon was studied and three possibilities were considered :—(1) galvanic action due to the chance contact of silver coins with a less noble metal, *e.g.* iron, in the presence of water containing copper sulphate as an electrolyte; (2) the electrolytic (cathodic) deposition of copper on silver as a result of contact with an electrolyte charged with copper salts derived from cupriferous pyrites; (3) chemical alteration of the surface of the silver coins by pyro-oxidation of the contained copper as a result of accidental fires.

With regard to cause (1) it was possible to demonstrate this in the laboratory and to coat silver coins with a tenacious film of copper.

AMONGST the many Greek and Roman coins of Cyprus a number of authentic specimens having the appearance of copper have been found at different times and places. On archæological grounds these coins would have been expected to have been of silver. A number of specimens were submitted for laboratory investigation by the Cyprus Museum, Nicosia.

On scraping the surface of the coins, a white metal, suggestive of silver, was in fact revealed, and this supposition was readily confirmed by physical methods of investigation which have the advantage of involving no injury to the object being examined. Such objects, when freshly dug up in excavation, are encrusted with copper salts, and are at first sight suggestive of solid copper or bronze, and, in the absence of other evidence, may be wrongly described and classified. Several such cases, for example, have come to the knowledge of Lucas,‡

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* Manuscript received February 14, 1934. Presented at the Annual Autumn Meeting, Manchester, September 5, 1934.

† Government Analyst, Government Laboratory, Cyprus.

‡ A. Lucas, " Antiques : their Restoration and Preservation," Second Edition. London : 1932.

who found that when the silver is of poor quality and contains a large proportion of copper the corrosion-product may be of a green colour, and the object may look so like corroded bronze or copper that it will often be mistaken for these metals. The coins examined in this investigation, however, had a high content of silver (94 per cent.) and it appeared to be of some interest, therefore, to study the possible conditions in which silver objects, when buried in the soil, may become coated with a deceptive surface layer of copper and its salts.

Three possible causes suggested themselves as being responsible for the phenomena observed :—

(1) galvanic action due to the chance contact of silver coins with a less noble metal, such as iron, in the presence of water containing copper sulphate as an electrolyte.
(2) the electrolytic (cathodic) deposition of copper on silver as a result of contact with an electrolyte charged with copper salts derived from cupriferous pyrites, the ore body acting as anode.
(3) chemical alteration of the surface of the silver coins by pyro-oxidation of the contained copper as a result of accidental fires.

The first and second causes appear to be the most likely explanations of the observed facts, since such conditions may readily exist in ancient tombs in Cyprus. The copper sulphate electrolyte may be derived either from the breakdown of cupriferous pyrites direct, or by dilute sulphuric acid, also arising from the decomposition of pyrites, acting on a mixed lot of copper and silver coins. In the first cause, copper would then be deposited on the silver if in contact with iron, as, for example, in an iron receptacle. As will be seen later, it was possible to demonstrate this in the laboratory, and to coat silver coins with a tenacious film of copper.

The second suggestion presupposes conditions favourable to the setting up of weak external currents between the silver objects and the surrounding ore or rocks, whereby copper is deposited. This possibility, however, is obviously limited to certain areas where silver objects have been in contact with dilute solutions of copper sulphate derived from the decomposition of cupreous ores. As regards the third possibility, this must be limited to accidental fires, which are exceptional, and further, copper oxide, and not metallic copper, is developed on the surface of silver–copper alloys when exposed to high temperatures. The subsequent action of air and moisture would in time produce a deceptive incrustation of green copper salts.

EXPERIMENTAL.

The 32 copper-coated coins examined were of dates from 411–374/3 B.C. to A.D. 180–192. Many of them were current during the Roman occupation, and were probably struck in Cyprus.

No information was available as regards the exact places in which these coins were originally found. The possibility that they might have been plated with copper by intention was regarded as untenable. Examination of the coins showed that the metallic coating was thin but firmly attached, and could not be removed mechanically. The surface layer of greenish copper salts was satisfactorily removed by the well-known treatment with Rochelle salt solution. To determine the composition of such objects without destruction, two methods are available : (*a*) the quantitative spectrographic method of Hartley, and (*b*) the simple qualitative procedure of determination of the specific gravity. No spectrograph being available, recourse was had to the specific gravity method. It was found that the specific gravity varied between 9·8 and 10·2, a value suggestive of alloyed silver. The thin coating of copper was now removed by gentle treatment of the coins with dilute acid, when silver was revealed in each case. This was confirmed by analysis of two different coins, 94 per cent. silver being found in the one case, and 92·3 per cent. in the other; the remainder being copper and impurities.

Having identified the true nature of these coins, experiments were next undertaken to test as far as possible the theories already advanced. The galvanic theory lent itself more readily to experimental verification, and this was first investigated. An acid solution of copper sulphate does not deposit copper on silver immersed in it, since silver is more noble than copper; hence silver objects buried in tombs could not become plated merely by contact with water carrying copper sulphate as electrolyte. It was found, however, that when a silver object, immersed in an acid solution of copper sulphate, is in contact with a less noble metal than copper—as, for example, iron—deposition of copper immediately commences. Rods of clean iron or zinc were conveniently employed for this purpose. This is simply a form of galvanic action in which the copper sulphate, dissolved in the soil water, has been derived either from the breakdown of cupriferous pyrites direct or by the continuous action of dilute sulphuric acid, also derived from the decomposition of pyrite, on a mixed lot of copper and silver coins. The finding of mixed collections of coins is not unusual in the island.*

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* Since the above was written a hoard of several hundred copper-coated Venetian and Turkish silver coins was discovered in March, 1934, during excavations on the ramparts of Nicosia, the capital of Cyprus.

In natural conditions the solutions of copper sulphate would be dilute, and the thickness of the copper film would depend principally on the length of time during which the silver had been exposed to its action.

It is only necessary, then, to suppose that the coins were in an iron receptacle, or simply in contact with an iron object, to have reproduced *in situ* all the conditions necessary for copper to be deposited on the silver coins. Some of the silver coins, which had been freed from copper in the laboratory, were in fact readily replated under these conditions, so as to resemble closely the original specimens after the green incrustation had been removed. The coating of copper was firmly laid on, and could be removed only by chemical treatment. This would seem to be a very probable explanation of the finding of copper-coated coins in Cyprus. Other silver objects may also be found copper-coated; for example, a broken antique bowl, badly encrusted with copper salts, appeared after preliminary cleaning to consist of copper. On investigation it proved to be silver on which had been deposited a definite film of copper and copper salts.

Unfortunately, it was not found possible to investigate experimentally the second suggestion—that the copper-coated coins might be the result of cathodic action between the metallic objects and adjacent ore bodies.

So far as the third cause is concerned—that the copper salts resulted from pyro-oxidation caused by accidental fires—this would seem to be the least likely explanation. In these conditions coins containing about 6 per cent. of copper would develop a film of copper oxide only. Metallic copper would be present only if the coins were subsequently exposed to conditions of reduction.

Experiments showed that gold objects, when exposed to the conditions first considered, also readily take on a deceptive coating of copper. Specimens of copper-coated gold coins have apparently not been found in Cyprus, but some years ago a bowl, found near Athienou, was so corroded with green incrustation as to suggest copper or bronze. When cleaned, the bowl proved to be gold.

ACKNOWLEDGMENTS.

I am indebted to Mr. J. A. Bevan, M.Inst.M.M., and Mr. C. P. Manglis for their interest in this work, and to the Curator of the Cyprus Museum, Nicosia, for information regarding the coins and objects examined.

OBITUARY.

William Bamford died on August 29, 1934. Born at Ashridge, Hertfordshire, he was educated at Berkhamsted School, and on leaving was apprenticed to Messrs. William Cooper & Nephews, chemical manufacturers, with whom he received his early training in their Engineering Department.

At the age of 20 he obtained a position with the R. F. Hall Manufacturing Company, Ltd., patentees of the air valve for cycle tyres, with the production of which Mr. Bamford was connected.

Later he joined the Crown Engine Works, Birmingham, manufacturers of wire-weaving and pin-making machines, and a year later obtained a position as fitter with Messrs. A. Ransome & Company Ltd., of Stanley Works, Chelsea, makers of wood-working machinery. He remained with this firm for four years and towards the end of this period was appointed to the outdoor staff, and was responsible for the erection and running of wood-working plants in various parts of the British Isles and on the Continent.

During this time Mr. Bamford studied under Professor Henry Spooner at the Regent Street Polytechnic, and in March, 1896, joined the firm of Dewrance & Company of London, manufacturers of boiler mountings and steam fittings. In 1905 Mr. Bamford was appointed assistant works manager, and in 1919 became works manager, a position which he held until his death.

As works manager Mr. Bamford was closely connected with the many research activities of Sir John Dewrance, concerning the selection of the most suitable designs and materials to meet the exacting requirements of steam users, necessitated by the steadily increasing pressures and superheats which have been introduced during the last twenty years.

Mr. Bamford took a keen interest in the welfare of the employees. He was chairman of the Sports Committee and Social Club. In his younger days he took an active interest in football, cricket, cross-country running, and rifle shooting; while in his later years he was an enthusiastic golfer. He was an active Freemason, having been initiated in Earl Amherst Lodge, and was a founder and Past-Master of United Engineers Lodge and a member of the Old Boys of Berkhamsted School Lodge. He was a member of the Institution of Mechanical Engineers.

Mr. Bamford was elected a member of the Institute of Metals on May 1, 1923.

William Hastings Bassett, B.S., newly elected President of the American Society for Testing Materials, died at his home in Cheshire, Conn., U.S.A., on July 21, 1934, at the age of 66. A pioneer metallurgist in the non-ferrous metal industry, and directly concerned with many of its technological advances, Mr. Bassett was metallurgical manager of The American Brass Company, Waterbury.

Mr. Bassett's early and sustained work in the American copper and brass industry probably did more than that of any other to place the industry on a scientific and technical basis. He introduced in the United States the use of microscopy in the metallurgy of non-ferrous metals and was among the first to apply the spectroscope to routine work in the non-ferrous industry.

In 1925 he received the James Douglas Medal "for constructive research in copper and brass and other non-ferrous metals and their alloys and for his contributions to the establishment of the high standards of quality."

In June, after serving for two years as Vice-President, he was elected President of the American Society for Testing Materials, with which he had been connected since 1903. As a personal member and the official representative of his company, he participated actively in the work of a number of the Society's committees. He took a leading part in the organization in 1909 of the first two A.S.T.M. standing committees in the non-ferrous field, B–1 on copper wire and B–2 on non-ferrous metals and alloys, and served continuously on these committees until his death. He served as a member of the Society's Executive Committee in 1916–1918. He always took a keen interest in advancing the knowledge of the properties of non-ferrous metals and supported actively a number of research and standardization projects in the Society.

Mr. Bassett received the B.S. degree from Massachusetts Institute of Technology Class of 1891. He was chemist and superintendent of the Popes Island Manufacturing Company, New Bedford, for five years; then chief chemist, Newark Works, New Jersey Zinc Company. After serving as chemist of the Coe Brass Manufacturing Company in 1902, he became chief chemist and metallurgist of The American Brass Company in 1903; technical superintendent and metallurgist in 1912, and in 1930 was appointed to his present office. During the World War he was active on the Committee on Materials for Airplane Construction, in Washington.

He was a Past-President of the American Institute of Mining and Metallurgical Engineers (1930) and a former director of the American Institute of Chemical Engineers. Other societies of which he was a member included the American Chemical Society, the American Society of Mechanical Engineers, the Society of Automotive Engineers, the American Electrochemical Society, the Mining and Metallurgical Society of America, the American Geographical Society, the Franklin Institute, and the Society of Chemical Industry.

Mr. Bassett was elected a member of the Institute of Metals on May 24, 1910.

Arthur Bowker died in Sheffield on July 11, 1934, in his 67th year. He was head of Messrs. Wm. Bowker & Sons, one of the best-known firms of electro-platers and gilders in Sheffield, which was established by his father 45 years ago and which he and his late brother, Mr. Tom Bowker, carried on. Mr. Arthur Bowker was always ready to give assistance to those who needed it, and during the War he did much valuable work for the Belgian refugees in Sheffield. He was a devoted worker for Sheffield Methodism, and was a society steward and trustee of Carver Street Chapel.

In his funeral oration the Rev. E. E. Potts said that if ever there was a full, rich, and complete life, it was that of Mr. Arthur Bowker. He had had to work hard from his earliest days and had applied himself with whole-hearted enthusiasm to his daily task. "Men have spoken to me of his skill as a technical and practical man, and that was so in every part of his life," said Mr. Potts. "He lived in an atmosphere of love and he was a great Methodist and Christian. Perhaps the most compelling thing about his personality was his radiant cheerfulness." That cheerfulness was always in evidence when Mr. Bowker attended meetings of the Sheffield Local Section of the Institute, of which he was a very keen supporter. In addition to his many technical and religious activities, he was a keen Esperantist.

Mr. Bowker was elected a member of the Institute of Metals on March 6, 1923.

Frank Guyver Britton, Director and Manager of the Toyo Babcock Kabushiki Kaisha, who had lived in Yokohama for thirty years died suddenly at his home near Yokohama on June 3, 1934.

Born in Cambridge and educated in England, Mr. Britton went to Japan in 1904 and was appointed manager of the Zemma Iron Works. This firm became in due course the Japanese works of Messrs. Babcock & Wilcox, of London. In 1923 a partnership was formed with the Mitsui interests, when the firm became known as the Toyo Babcock Kabushiki Kaisha. Mr. Britton became general manager and director of this new combination. A member of the Institution of Mechanical Engineers, he was also an active member of the Rotary Club of Yokohama, and as a Mason he was Past-Master of the Yokohama Lodge.

Mr. Britton was highly esteemed by members of the foreign community as well as by the host of Japanese with whom he came into contact during his life in the country of his adoption. He was a modest, unassuming man, somewhat retiring by nature, kindly and generous, and beloved by the members of the staff. The high regard in which he was held by his staff was manifest on the day of his death when 500 of them called at his home to express to the members of his family their sorrow at the loss of one who had not only been their manager but their sincere friend.

Mr. Britton was elected a member of the Institute of Metals on July 4, 1929.

EDWIN LEWIS CROSBY, President, Director, and Founder of Detroit Electric Furnace Company, died on May 5, 1934, at Ludlow, Mass., U.S.A., as a result of injuries received in a motoring accident.

Mr. Crosby was born 53 years ago in Detroit, Mich. After graduating from Plymouth High School, he worked for the Semet Solvay Company in Detroit. Later, he completed successfully a course in electrical engineering and for several years was in charge of electrical operations in the Semet Solvay plant.

In 1905, Mr. Crosby entered the employ of the Detroit Edison Company, where for thirteen years he was chief power salesman. On leaving the Edison Company in May, 1918, he organized the Detroit Electric Furnace Company, of which he became Vice-President and General Manager; in 1920 he was elected to the Presidency of the Company.

Mr. Crosby was an active member of the Electrochemical Society for many years. He was also a member of the Foundrymen's Association and a frequent contributor to foundry and electrical engineering trade journals. His interest in the field of electric melting was communicated to utilities, foundries, and industrial concerns, and his courage and ability in this new industry stamped him as a pioneer in electric melting problems.

Mr. Crosby was elected a member of the Institute of Metals on April 11, 1928.

JOHN HENRY SOAR DICKENSON died suddenly on November 16, 1934, at the age of 52. By his death British metallurgy has lost one of its leading personalities.

Born in 1882 at Ilkeston, Derbyshire, he was educated at the Sheffield Technical School, where he studied metallurgy under Dr. W. Ripper and Professor J. O. Arnold. In 1900, he obtained the Mappin medal and his Associateship at the Sheffield University, in the same year being Honours Prizeman in the City and Guilds of London examination in iron and steel manufacture.

Mr. Dickenson's first industrial experience was in the works of Messrs. Beyer, Peacock & Co., where he gained a wide knowledge of the use of steel for locomotive construction. Subsequently, he went to the Vickers Works, Sheffield, at the request of Mr. Douglas Vickers, to establish a metallurgical investigation department, which has since developed into the research organization of the English Steel Corporation, Ltd. He remained with this firm until his death. Mr. Dickenson was closely in touch with metallurgical practice in Europe (including Russia) and in America, and was a member of the American Society for Testing Materials and the American Society for Metals. He was also a member of the Iron and Steel Institute, was Past-President of the Sheffield Metallurgical Association, and was elected a Fellow of the Institute of Physics in 1922. In the session 1915–1916, the Institution of Automobile Engineers awarded him the Crompton medal in recognition of his services to the advancement of automobile engineering as a result of his researches on the standardization of steels.

In addition to these many activities, Mr. Dickenson found time to serve on many committees being one of the most active members of the British Standards Institution, and Vice-Chairman of the Corrosion Committee and the Heterogeneity Committee of the Iron and Steel Institute. He was also a member of committees dealing with marine, turbine, railway, aero, and electrical engineering and structural work, and when, some five or six years ago, the Admiralty appointed an Advisory Committee to supervise the research work on steel castings, Mr. Dickenson was one of the experts selected. He was also recently elected a member of the Research Council of the Federation of British Iron and Steel Manufacturers.

Mr. Dickenson was the first to investigate the phenomenon of "creep," and his discoveries in this field gave him an international reputation at an early age.

Mr. Dickenson was elected a member of the Institute of Metals on May 2, 1918.

WILLIAM DONNAN died in London on October 20, 1933. He began his career by serving for nine years with Doxford's at Sunderland, first as an apprentice and later as a journeyman. From there he went to William Mills, Ltd., where he held the position of foreman moulder for seven years, in the days when aluminium was first coming into general use and prominence.

From 1906 to 1920 he was head foreman moulder and in charge of the non-ferrous foundry at Sir W. G. Armstrong-Whitworth & Co., Ltd. During the period 1920–1922 he was with the (former) Fulham Bronze Company. In 1922 Mr. Donnan became foundry superintendent at Messrs. Lightalloys, Ltd., which position he held until his death.

Although he held no academic degree, Mr. Donnan was recognized as one having a first-class technical and practical knowledge of foundry working and practice.

He was elected a member of the Institute of Metals on November 7, 1929.

JOHN KARL GWILYM JAMES died in a nursing home in Glasgow on July 14, 1934, after a brief illness.

He was born at Hereford in 1906, and was educated at the Royal Masonic School, Bushey (1916–1923). In October, 1923, he entered Liverpool University, where he graduated B.Eng. in 1926 with first-class honours in metallurgy, having been secretary of the University Metallurgical Society. On leaving the University he entered the employment of the International Electric Company, Ltd., London. In 1928 he joined the staff of the British Aluminium Company, Ltd., at their Research Laboratories at Kinlochleven, Argyll. The following year he was transferred to the managerial staff, and in 1933 to the metallurgical research staff at Kinlochleven.

Mr. James was elected a member of the Institute of Metals in 1925.

DR.-ING. KARL LEO MEISSNER died on July 21, 1934, at the age of 40.

He was born on March 31, 1894, and was educated at the Mommsen Gymnasium in Charlottenburg. He left in 1912 and went to the Technische Hochschule in Berlin to study mechanical engineering but soon took up the study of metallurgy. His work was interrupted by military service, but he graduated in 1921 with a paper entitled "Ternary Alloys of Copper."

Dr. Meissner will always be associated with the discovery of the existence of age-hardenable light metals and with the development of Duralumin. His metallurgical research began in 1924 in the laboratories of Th. Goldschmidt A.G., Essen. From 1924 to 1929 he was assistant at the Stoffabteilung der Deutsche Versuchsanstalt für Luftfahrt, to investigate light metal problems, and his work particularly influenced the age-hardenable light metal alloys. Dr. Meissner contributed appreciably to the elucidation of the age-hardening process and gave much valuable information on the treatment and application of the technically important light metal alloys.

In 1926, Dr. Meissner became a lecturer at the Technische Hochschule, Berlin, in the department engaged in the study of light metals in machine construction, especially aircraft construction.

In 1928, Dr. Beck, Director of the Dürener Metallwerke A.G., Düren, where Duralumin was first developed, approached Dr. Meissner, whose knowledge of the patent situation of light metals was as extensive as his scientific knowledge, to become Director of the Research Department of the Dürener Metallwerke.

Metallurgy has lost in him a light metal expert whose knowledge and experimental skill has added much to our knowledge. The Dürener Metallwerke mourns a colleague beloved by all, and numerous members of the Institute of Metals will hold him in affectionate remembrance.

Dr. Meissner was elected a member of the Institute of Metals on March 8, 1926, and contributed several papers to the Institute's *Journal*.

LUDWIG VOGELSTEIN died on September 23, 1934.

He was originally employed by the firm of Aron, Hirsch, & Sohn, of Halburstadt, and was sent to New York about 1895 to establish a branch firm there under the name L. Vogelstein & Company. Before very long he became a naturalized American citizen, and, under his guidance, the business expanded with the growth of the American metal trade up to the outbreak of the War. The entry of America into the War involved the separation of the German interests and these were handed over to the custodian of enemy property. At the same time, the American interests in the Metallgesellschaft subsidiary, the American Metal Company, were cut off from the parent organization and, at the conclusion of the War, a fusion was effected between the two American concerns under the name "The American Metal Company." Mr. Berthold Hochschild was the first chairman, and at his death Mr. Vogelstein succeeded to this position. The expansion of the company was largely due to Mr. Vogelstein's personality and business ability.

Mr. Vogelstein was elected a member of the Institute of Metals on July 20, 1925.

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